

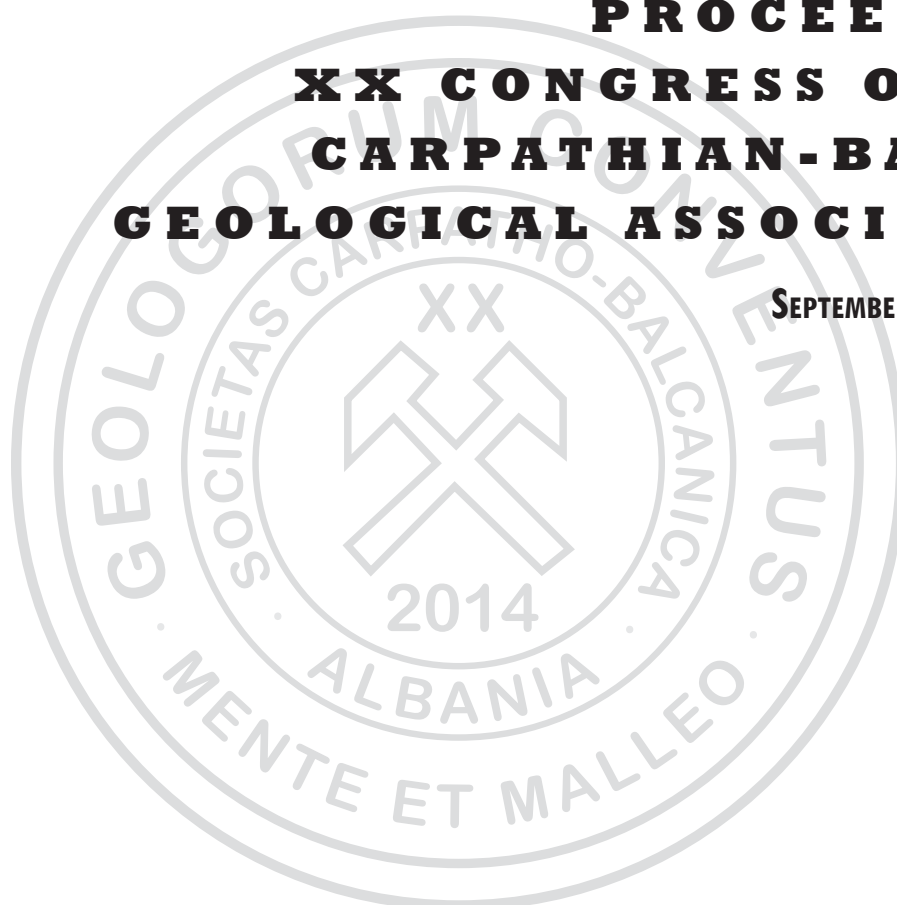


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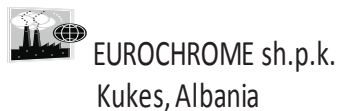
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## STRUCTURAL ARCHITECTURE OF THE BOUNDARY BETWEEN THE PERI-ADRIATIC DEPRESSION AND THE IONIAN FOLD-THRUST BELT IN SOUTHERN ALBANIA

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### Abstract

The Albanides in the Balkan Peninsula are part of the Alpine orogenic belt and host one of the most significant oil fields in SE Europe. The Late Mesozoic-Cenozoic evolution of the Albanides has been strongly controlled by the relative movements of Adria or Apulia, a microcontinent with a West Gondwana affinity. In northeastern Albania, the Internal Albanides consists of Paleozoic - Jurassic basement rocks, which involved rift-drift, seafloor spreading and subduction zone tectonics of the Pindis-Mirdita ocean basin. The External Albanides, on the other hand, represent a fold-and-thrust belt with deformation in a broad zone of convergence. This tectonic domain is divided, from east to west, into five major structural zones: the Krasta-Cukali Zone, the Kruja Zone, the Peri-Adriatic Depression, the Ionian Zone, and the Sazani Zone, which involves the Apulian platform in the lower plate. The External Albanides are dissected by NE-SW striking Vlorë-Elbasan Transfer Zone, which substantially affects the geodynamic evolution of the Albanides. The fault zone that is tectonically active from Triassic to recent have some diapirs structures along itself.

During the Triassic to Early Jurassic, the Albanides experienced the stage of continental rifting that caused the breaking up of Pangaea and formation of carbonate platforms and pelagic basins such as Krasta and Cukali Basins. As continental rifting proceeds, the Alpine Tethys occurred and the Mirdita oceanic basin was formed as a response of the opening of the ocean in the Middle Jurassic. The Apulian platform was broken up into the Ionian Basin and the Kruja platform under extensional tectonic regime. In the Late Jurassic, the Mirdita oceanic basin was completely closed and the folding played a dominant role in the area. Though the end of the Late Cretaceous, Mirdita oceanic basin was considerably folded and the Krasta Basin began to subduct beneath the Mirdita frontal thrust. In the Late Eocene, the Krasta Basin was closed and subsequently folded, whereas the Kruja platform commenced to subduct

beneath the Krasta frontal thrust and the Mirdita ophiolites overlaid the Krasta Zone. At the end of the Oligocene, the Kruja and internal Ionian zones were folded while the external Ionian Zone subducted beneath the internal Ionian one and was folded at the Middle Miocene. At the same time, the Sazani platform started to subduct beneath the external Ionian frontal thrust.

The structural architecture of the External Albanides is characterized by NW-SE-running and SW-verging thrust fault systems that involve a thick series of Mesozoic – Tertiary passive margin carbonates, unconformably overlain by Oligocene clastic units. The northern Ionian Zone has been prolific for oil and gas production, whereas the more intensely deformed southern Ionian Zone has been less explored. The southern Ionian Zone comprises a series of anticline and syncline structure shaping the recent topography of Albania. The Peri-Adriatic Depression west of the Sazani Zone has been recently identified as a major gas prospect. It is characterized by Oligocene flysch and Miocene-Pliocene molasses series.

**Keywords:** *Ionian Zone, Peri-Adriatic Depression, fold-and-thrust belt, Vlorë-Elbasan Transfer Zone*



## MODELING THE PRESENT DAY STRESS FIELD OF THE PANNONIAN BASIN FROM NEOTECTONIC MAPS

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### Abstract

A synthesis of recent geodynamics in the Pannonian Basin has been made by Horváth et al. in 2006. They compiled ten maps (scale 1:1 500 000) covering the area of the Carpathian Region from the Dolomites on the West, to the Outer Eastern Carpathians on the East, and from the Dinarides on the South, to the Molasse Foredeep of the Outer Western Carpathians on the North. Their modeling method based on measurements (borehole-, focal mechanism- and geodesic data) and the result is a possible structural pattern of the region. Our study is based on their compiled map of neotectonic (active) structures.

Our analysis is aimed to project a possible 2D stress field over the already mapped/known/compiled lineament pattern to reproduce the main characteristics of the measured stress field. Our primary intention was to test a method which is aimed to reconstruct paleo-stress fields. The method includes a component-wise interpolation of the tensors, which is based on the generated irregular point cloud in the puffer zone of the mapped lineaments. The interpolated values appears on contour and tensor maps, and shows the relative stress field of the area. At first, the structural lines on the map were classified according to their geodynamic parameters (i.e. normal, reverse, right- and left lateral strike-slip faults, etc.) and stored in a geo-referenced mapping database. This database contains the polyline sections of the structures as vectors (i.e. line sections), and the directions of the stress field as attributes of these vectors. The directions of the dip-parallel-, strike-parallel- and vertical stress-vectors are calculated from the geodynamical parameters of the line section. Each point in the point cloud inherits the stress property of the line section, from which it was derived.

The reproduced stress-field model is the result of several point-cloud generating- and interpolation methods which was mainly implemented by a program code. The analysis of the interpolated tensor fields revealed that the model was able to reproduce a geodynamic synthesis of the Pannonian Basin, which can be correlated with the synthesis of the original map.

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## CONTROL OF ROCK RHEOLOGY ON DEFORMATION – A CASE STUDY FROM BOTEV VRAH THRUST, CENTRAL BALKANIDES, BULGARIA

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### Abstract

The Late Alpine Botev Vrah Thrust is a structure of regional importance covering a great part of Central Stara Planina Mountain (Fig. 1). It is one of the most impressive examples of thick-skinned tectonics in the Balkanides. The thrusting occurred at shallow crustal levels at temperatures not higher than 220–250 °C. The allochthon consists of various crystalline rocks of pre-Permian age, most of which of granitoid composition. They are thrust northward over variegated by age and lithology rock formations – Paleozoic granitoids and low-grade metasediments, Permian volcanics, Triassic dolomites, etc. The youngest rocks below the thrust surface are Late Cretaceous-Paleocene carbonate to clayey-carbonate sediments.

Documentation and detailed mapping of the thrust zone are carried out in order to estimate the deformation and emplacement mechanisms of the allochthon. Thrust-related deformation within both hanging wall and footwall is studied in meso- and micro-scale. A characteristic feature of the thrust zone is its asymmetry and complex nature according to the lithological features of rocks involved in the process of thrusting.

The thrust zone that juxtaposes the crystalline rocks over granitoids, low-grade metasediments, volcanics or dolomites represents narrow discrete surfaces of localized non-penetrative brittle deformation. The fault core is built of brittle fault rocks (ultracataclasite, cataclasite and tectonic breccias, and rarely gouge – Fig. 2 a, b) with thickness of several mm to some cm (rarely to 30–40 cm). The damage zones are not clearly presented and their thickness is small (up to 2–3 m). Planar structures are rarely formed, only cataclastic foliation is observed in some domains. The most common microstructures are cracks, discrete shears, dark ultracataclastic bands (Fig. 2 c, d). Thus indicates the dominated deformation mechanism has been the cataclastic flow. At some places structures as gouge intrusions in the fault core, rotation and folding of some inclusions

within the fault zone and foliation formation (mainly in gouge) give evidence for presence of processes of mesoscopic ductile flow as well. All brittle deformation structures in these rocks are irregularly and locally distributed within the thrust zone.

Deformation of the Upper Cretaceous-Paleocene carbonate to clayey-carbonate rocks and some schists of the metasedimentary succession that built the thrust footwall is brittle-ductile to ductile. The contacts where these lithological varieties are observed, represent a wide (up to tens of metres) zone of penetrative deformation that affected only the authochthon. Several types of mega-meso- and micro-scale isoclinal to open folds are documented. Penetrative foliation as well as mineral and stretching lineations is well-presented. Other structures as injections, imbrications, sigma clasts of more competent layers and Riedel shears also occur (Fig. 2 e, f). Microstructural observations confirm the brittle-ductile style of deformation. Characteristic structures are pressure solution seams of clay minerals and Fe oxides, calcite twinnings, veins oriented parallel to foliation (Fig. 2 g, h). The dominant deformation mechanisms of these rocks have been the diffusive mass transfer (pressure solution) new mineral growth, grain boundary sliding and rarely re-crystallization. The fragmentation and fracturing of some grains and the presence of local zones of brecciation in micro-scale shows that cataclastic flow has also played role for deformation.

The carried out meso- and microstructural investigations of tectonites within the Botev Vrah thrust zone demonstrate that rheology of the rock varieties from both hanging wall and footwall is the main factor that has controlled the type of deformation structures presented. The weak carbonate and clayey carbonate rocks in the thrust footwall accommodated thrust-related deformation and facilitates the allochthon movement to the north.

**Keywords:** *deformation, rheology, thrust tectonics, Central Balkanides*

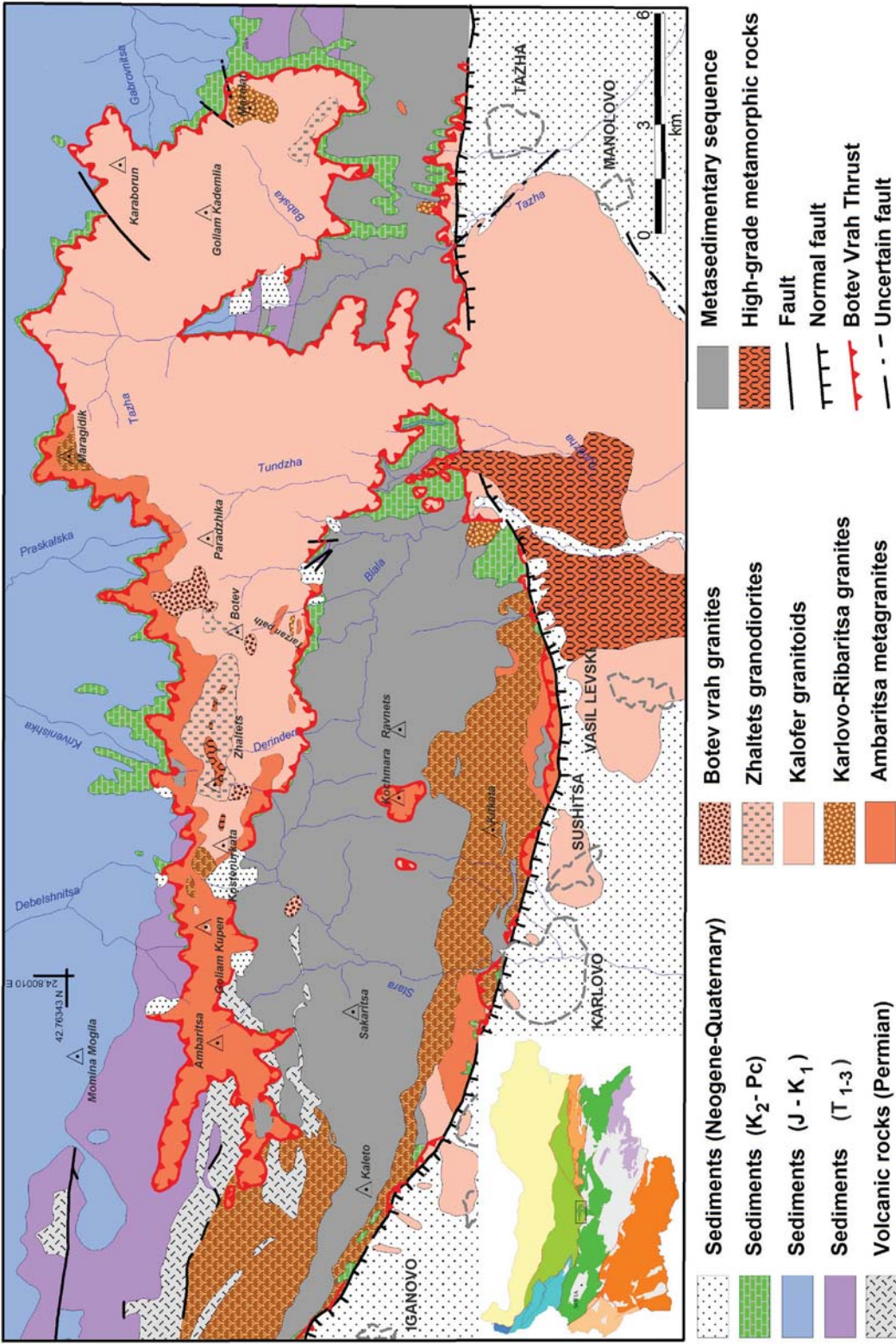
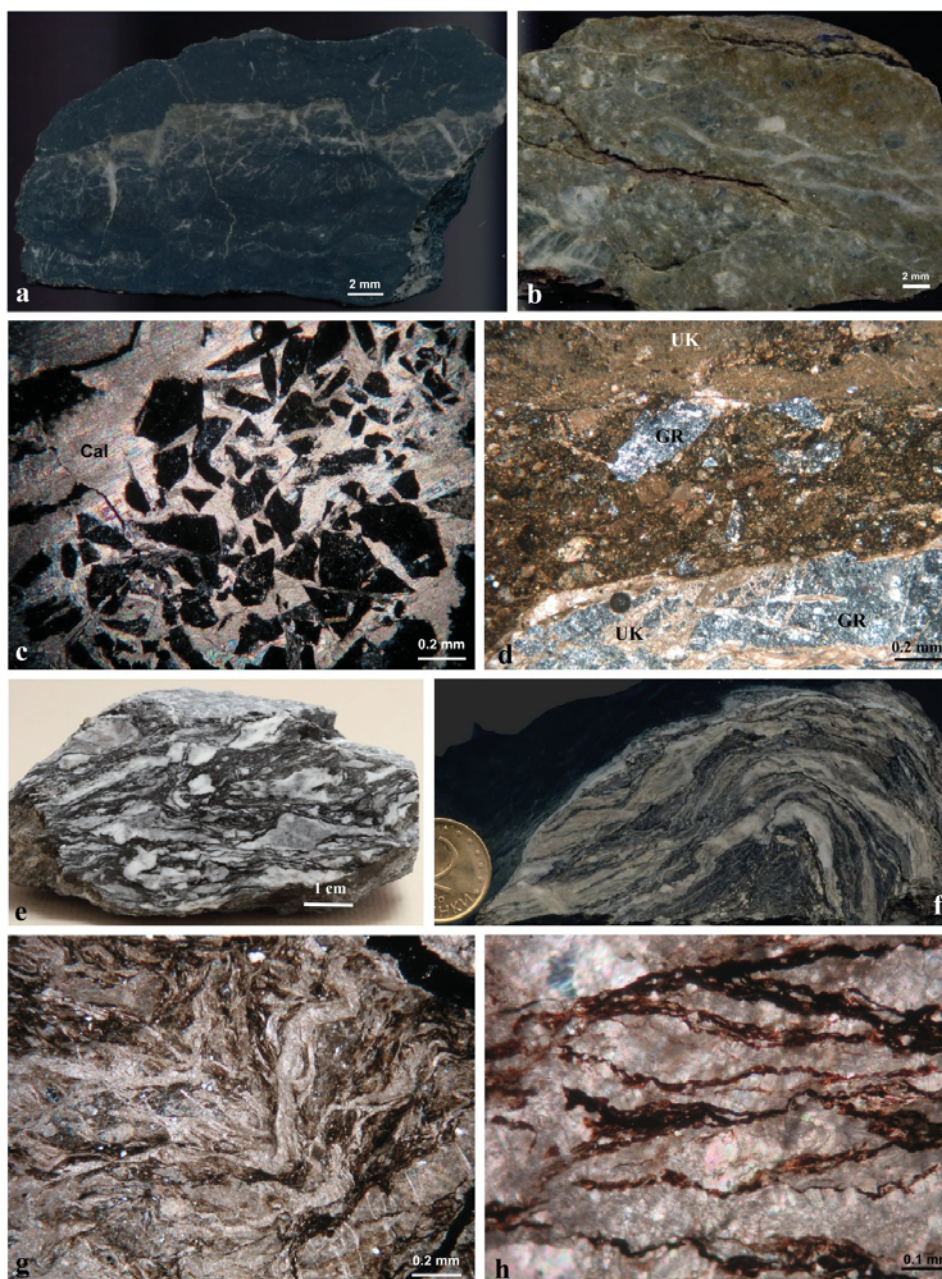


Figure 1. Geological sketch map of Central Stara Planina Mountain and its position in the Balkanides. Tectonic zones within the Balkanides are given in the inset after Ivanov (1983).





**Figure 2.** Photos of polished hand samples and thin sections of tectonites from Botev Vrah thrust zone: a) ultracataclasite of granitic origin; b) breccia-ultracataclasite of granitic origin, calcite veins have been injected during deformation; c) tectonic microbreccia of granite; d) sharp contact between cataclastic granite (GR) and ultracataclasite (UK) – the ultracataclasite contains granitic clasts and within the granite injections of ultracataclasite can be observed; e) and f) folded foliation, sigma-like competent clasts and segregation of dark clay and white carbonate material in mylonitic carbonate rocks; g) folded calcite veins and pressure solution seams in mylonitic limestone; h) pressure solution seams parallel to foliation built of clay minerals and Fe oxides in mylonitic limestone.

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## TECTONIC ASPECTS RELATED TO BADENIAN SALT FROM TRANSYLVANIAN BASIN (ROMANIA) – IMPLICATIONS FOR GAS ACCUMULATIONS

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### Abstract

Transylvanian Basin is the great province concerning the gas accumulation from Central and South-East Europe where the main geological structures for entrapment of the gas are located in the unfaulted and faulted Upper Miocene-Pliocene domes. Most of these structures are generated by the tectonic activity of the salt layer. The domes and diapir structures from the Transylvanian Basin are in connection with the Badenian salt, manifestation related to the tectonics movement of the adjacent blocks (tectonokinetic mechanisms in combination with the halokinetic processes). Following this idea, were assessed five stratigraphic levels of the Upper Miocene which make up the “Gas-bearing Formation”. The geological interpretation was based, mostly on the seismic lines beside to the rest of the published and unpublished geological data. Regarding the Mio-Pliocene tectonic activity of the basin, should be concluded that the most of the faults or system faults described here have affected all the Upper Miocene and Pliocene formations with implication in the appearance and development of gas fields.

**Keywords:** *Transylvanian Basin, seismic interpretation, Upper Miocene, salt tectonic, diapiric structures*

### Introduction

Transylvanian Basin is the one of the main gas producer from Central and South-East Europe. Gas fields are located in the Upper Badenian - Early Pliocene (“Gas-bearing formation”). The Transylvanian Basin is a post-tectonic, a typically back-arc basin (Săndulescu 1988) and is located in the eastern part of the European Alpine System Orogen. It resulted from the Austrian tectonic collision of the Foreapulian and Getic blocks (Hosy 1999) and is developed on a basement which was formed at the beginning of Late Albian. Therefore, this basin comprises Carpathian deformed units (including Tethyan Suture Zone, known as the

Vardar-Mureș unit) and Upper Cretaceous - Middle Miocene post-tectogenetic sedimentary cover (Săndulescu 1994). The scope of this work is the reassessment of the Upper Miocene deposits concerning the formation and development of gaseous diapiric domes.

### Short overview of the geotectonic evolution

The Tethyan extensional phase (simple shear) in the Transylvanian domain (Wernicke 1981; fide Bădescu 1998a; Ciulavu et al. 2000) is well evidenced by the disposition of normal fault systems (Jurassic), oriented approximately on N-S direction, found mostly in the central area and at a lesser extent in the northern part. The Early Cretaceous compressional event is clearly evidenced in the Transylvanian Basin by the N-S trending overthrusts with eastern vergency. Also, this tectonic event is known as the overthrust of the Jurassic ophiolites upon the Lower Cretaceous deposits. Upper Cretaceous Laramian compressions led to new deformations (reversal of the Senonian rift systems with N-S orientation in the northern part) followed by the major phase of erosion. The next summarized events with implication in the Transylvanian domain are: latest Cretaceous to Early Paleogene uplift and erosion (Ciulavu 1998); Middle Eocene subsidence and Laramian thrusts reactivation (Laramian reactivation phase) and Puini basin final inversion (Ciulavu et al. 2000), restricted Lower Miocene foreland basin (Ciulavu 1998) in front of the Piennides (Burdigalian Hida molasse foreland deposit). Also, it should be mentioned the push to the north and clockwise rotating with 70°-90° of the Tisza-Dacia block during the Early Miocene (Pătrașcu et al. 1994).

The basin reached its present shape at the end of the Old Styrian tectogenesis. The effects of the new Styrian deformations have led to the intense subsidence followed by the regional sedimentation started in the upper part of Lower Badenian (Dej Tuff Complex) and deposition of the hypersaline



type sedimentation (Salt Formation) during Middle Badenian (Ciupagea et al. 1970). The latest tectonic events (The Wallachian phase) recorded in the Transylvanian Basin had led to the tilting and uplifting of the entire basin toward W-SW and determined the deposition of the clastic sediments in the distal zone. Note that sediments were affected by the diapiric processes which were reactivated in the Late Sarmatian. Pannonian deposits are syn-tectonic to Carpathian nappes emplacement. Subsequent uplift and erosion at the end of Pannonian mark the end of basinal sedimentation in Transylvania. Most of the unconformities are linked to adjacent Carpathians Miocene tectonic movements (Kr  zek et al. 2010).

### Data and methods

Based on the seismic lines, wells and geological data, the following Upper Miocene successions were reinterpreted and correlated at the regional scale: Lower, Middle and Upper Badenian, Lower Sarmatian and Sarmatian ss. These stratigraphic intervals together with the Latest Miocene and Pliocene deposits are named “the Gas-bearing formation” in the Transylvanian Basin. For seismic interpretation, we used the software package from Schlumberger Company (Charisma GeoFrame). As concerning the Badenian deposits, it should be mentioned that this age was divided (Ciupagea et al. 1970) to the lower (Dej Tuff complex), middle (Salt Formation) and upper level (Upper Badenian).

#### Lower Badenian (Dej Tuff Complex)

This horizon overlays the pre-Badenian deposits and had covered the structural shapes inherited; it should be mentioned that the Miocene formations which are sunken from edge towards centre of the basin can be observed (Fig. 1). Moreover, it

reveals the depocentre that played a role in the further evolution of the above salt layer. There were observed small anticlines, where, sometimes, the Lower Badenian is missing due to failure to file or because slip on the fault plane generated by the flanks of this structures. The identified fault at the top of the deposits are propagated from the pre-Badenian basement. Thus, the recorded faults are in connection with the tectonic activity of the Pre-neogene evolution of the Transylvanian Basin.

#### Middle Badenian (so-called Salt Formation).

The Salt Formation played a major role in the formation of the favourable geological structures (non-faulted and faulted anticlines) for gas accumulations. The Middle Badenian evaporite depositional system has a characteristic chaotic to transparent seismic facies. At the top of the salt layer there are contoured about 33 salt domes (Coltoi 2011, 2013) and are recorded many types of faults which conducted to the appearance of the domes structures for gas entrapment (Fig. 2). The faults can be grouped by their position relative to the margins of the Transylvanian basin (Coltoi 2011, 2013) in the western, central and northern groups. Most of the new identified faults are generated by the salt layers activity, but there are, also, faults propagated from the pre-Badenian basement (either faults existing before the deposition of salt, or subsequently reactivated).

**Upper Badenian.** The existing morphology combined with activity of the salt layer has controlled the tectonic and sedimentological evolution of this geological horizon. Besides the existence of faults recorded in the Lower Badenian or oldest, appear new faults, generally, the reverse faults. Also, it is mentioned the reactivation of existing Middle Badenian faults, evidenced by the ascending the salty layer which reached the outcrop stage. The faults grouping recorded to the top of

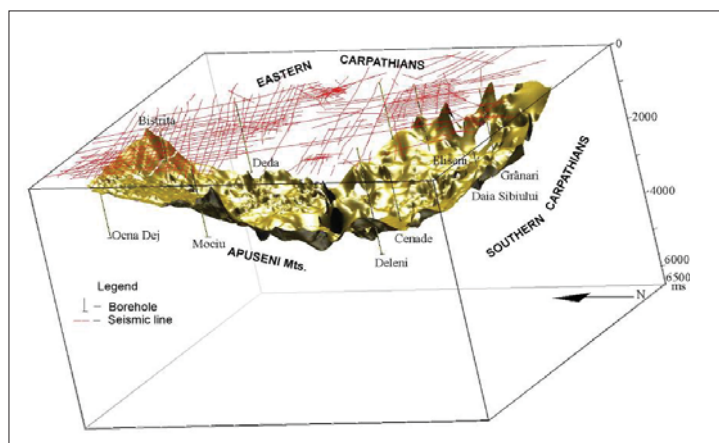


Figure 1. 3D view of the top of Lower Badenian

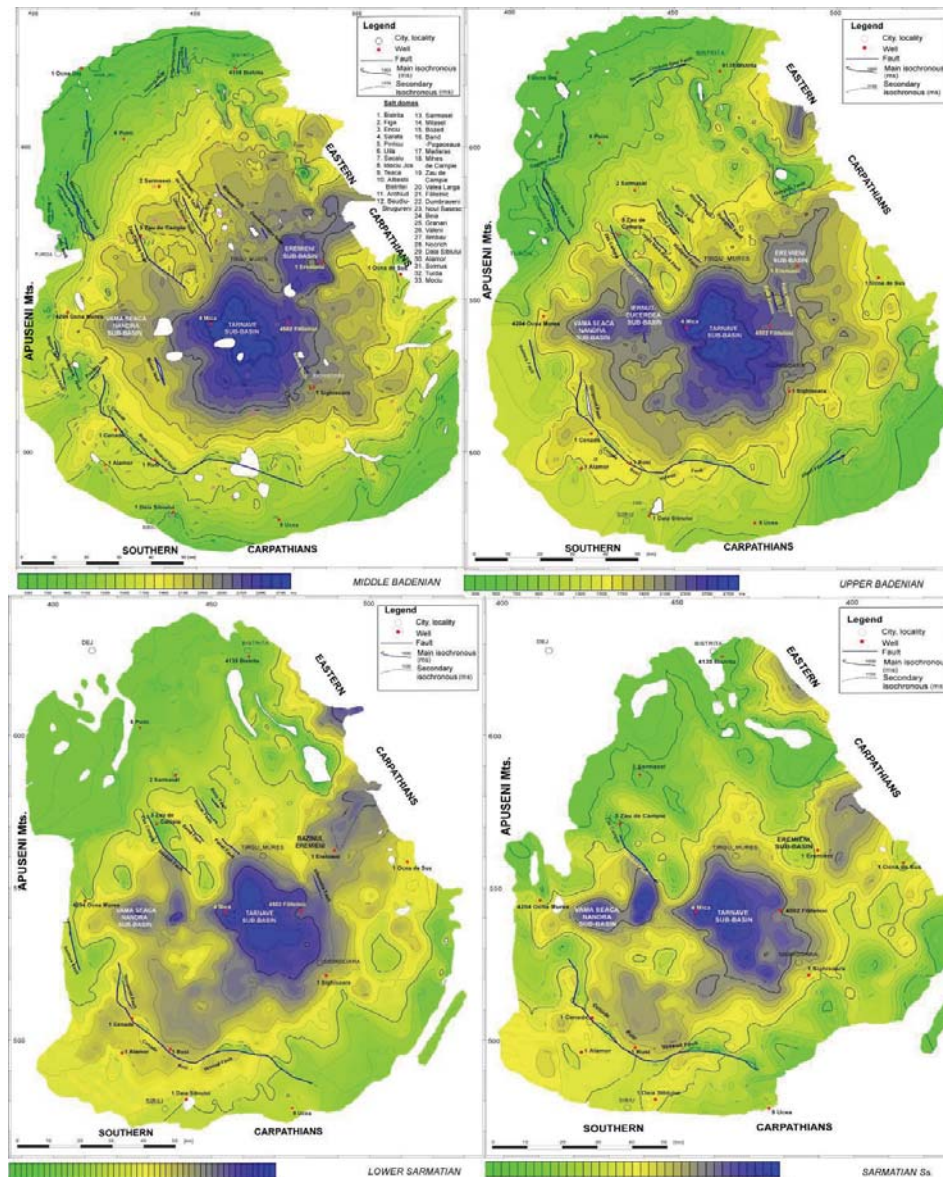


Figure 2. Structural maps with isochronous (ms TWT) – top of the Upper Miocene levels

Salt Formation is keep but must be mentioned that some of them have changed their genetic character (e.g. normal faults have become reverse faults) or have stopped inside the Upper Badenian. This situation (stopping their activity that should be named the stopped of the diapiric activity) is valid for faults from the northern group. As a conclusion it shows that this zone had escaped the influence of the tectonic regime for a period of time, the only recorded activity being the halokinetic gliding of the salt layer. Another situation is linked by the change in the vergence of the faults and decrease of the diapiric amplitude, recorded, especially, to the central group.

**Lower Sarmatian and Sarmatian ss.** From structural point of view, the main characteristic is

represented by the movement along the diapiric faults (fault-propagation-fold structures). In the Sarmatian is observed reduction of the number of faults, diapiric activity being offset by recent tectonic movements in neighboring areas. Stopping the activity may be related to the intensity of the diapiric processes along the eastern diapiric alignment who consumed probably some of the energy propagation of faults, together with a short period of tectonic calm in the Eastern Carpathians. Also, it can be seen that the diapiric amplitude from the eastern part of the basin is high and can be explained by the absence of stratigraphic interval portions quite large due to erosion or salt slippage from the center toward the eastern edge.

## Conclusions

The Upper Miocene formations are affected by normal and reverse faults and fault systems propagated either by the Pre-Badenian basement deposits or generated by diapiric activity of the Salt Formation (Middle Badenian). At the top of the Salt Formation level are identified and contoured about 33 salt domes and many types of grouped faults (western, central and northern groups). These domes have played a major role in the gas accumulation. The diapiric salt is the combined result of tectonokinetic - halokinetic processes, tectonics having a more important role compared to halokinetics mechanism. Also, another characteristic recorded in the Miocene deposits is represented by the movement along the diapiric faults (fault-propagation-fold structures).

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## NEW INTERPRETATIONS ON GEOLOGICAL AND TECTONIC CONSTRUCTION OF SOUTHERN PART OF KRUJA ZONE

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### Abstract

Last studies carried in the southern part of the Kruja zone based on recent biostratigraphical and tectonic data offer new interpretations in the context of the geological framework.

**A-Biostratigraphy:** The oldest deposits formed in Kruja zone are those of Lower Cretaceous which outcrop in Tomorr, Kulmak and Qeshibesh structures. It was distinguished the CsB1 shallow benthic zone with *Sellialveolina vialli* and were identified planktonic foraminifera as *Hedbergella* and *Ticinella*.

Taking into consideration the shallow water benthic zonations, two important shallow water facies in the eastern sub-zone structures and a mix one in Tomorri subzone (excepting Melesini anticline) were separated within the carbonate deposits.

In the Tomorri, Kulmake, Qeshibeshi and Kerpice structures, the CsB2-7 shallow benthic zones typical for Middle Cenomanian - Late Maastrichtian (correlated with those of Fleury J.J 1980), as well as planktonic zones with *A. mayeroensis* - *G. gansseri*, *R. fornicata*-*G. stuartiformis* were identified within the deposits of Upper Cretaceous.

In the eastern chain structures only benthic microfauna was identified. The Paleocene deposits of these structures are typical for shallow water environments where SBZ 1-3 shallow benthic zones are typical for Danian-Thanetian. In the western chain structures, along the shallow benthic zones were identified the following planktonic zones with *Morozovella pseudobulloides* - *M. angulata*, *M. pseudomenardii* and *M. velascoensi*.

It is confirmed the gap of Upper Eocene deposits that has different stratigraphic levels within different structures. In the deposits of the eastern structures and in the horsts of Kulmaka and Qeshibeshi, SBZ 18-19 and 20 shallow benthic zones typical for Barthonian-Priabonian were

distinguished.

In Melesini anticline, microfauna is the same with that of Ionian zone.

Flysch deposits have a successive extension, except the horsts that are transgressive over the Cretaceous and Eocene carbonates.

**B. Tectonic and paleogeography:** The study area is a large block with longitudinal and cross faults. From tectonical point of view two sub zones are distinguished:

1. Dajti subzone (including anticline chains of Kozan - Galigat and Letani - Tervolli)
2. Tomorri subzone (includes anticline chain of Sarandoporo - Melesin - Lengatic - Çorovodë - Tomorr) and eastern chain (Qeshibeshi - Kulmaka - Kerpice horsts etc.).

Qeshibeshi, Kulmaka and Kerpica carbonates were interpreted as horsts. Facial changes within the carbonate deposits can be explained by the presence of cross faults formed during the rifting process and subsequently reactivated.

Based on the prolongation of Kruja zone towards south (Gavrovo zone in Greece) and towards north (Dalmate zone in Montenegro) and also on paleotectonic development of the region, the eastern prolongation of Kruja zone under the Krasta - Cukali zone is accepted.

The relationship with the Ionian zone is of overthrusting regime.

The tectonic zone of Krasta - Cukali is accepted as carriage over structures of Kruja zone, covering at least one structural chain.

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## JURASSIC TO EARLY CRETACEOUS BASIN EVOLUTION OF THE NORTHERN TRANS-DANUBIAN RANGE: STRUCTURAL INFLUENCES OF TWO OCEANS DATING

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### Abstract

The northern Transdanubian Range (TR), in Hungary, occupied a paleogeographical position between the Neotethys and Alpine Tethys during the Late Jurassic and Early Cretaceous. Structural events in the two oceanic domains strongly controlled the basin evolution. We used field structural measurements, mapping, sedimentological and stratigraphical analysis to date the succession, reconstruct the basin geometry and structural evolution. To place structural data in Alpine frame, an 80–50 counterclockwise Cenozoic rotation should be considered.

Jurassic basin evolution started with differentiation of the Triassic carbonate platform in the Sinemurian. Syn-sedimentary dykes and faults prove the extensional deformation related to early rifting events of the Alpine Tethys. The direction of extension was NNE–SSW at present position. Different Jurassic successions indicate map-scale faults: WNW–ESE trending normal, and N–S striking transfer faults with oblique-slip. As the revival of Early Jurassic faulting, nodular “Ammonitico rosso” and Bositra limestones deposited in syn-sedimentary half-grabens.

In geodynamic models, Late Middle to Late Jurassic times were marked by the subduction of the Neotethys Ocean. For the TR, such models would mean N–S to NE–SW directed compression. However, direct structural observations indicate extensional or transtensional deformation. Observations can be consistent with a model that Late Jurassic extension could form on the bended part of the slab subducting to N or NE. The obducting Neotethyan oceanic crust and related nappes thrust over this downbended slab.

Long-lasting carbonate sedimentation ceased in the Late Berriasian. The following Valanginian to Aptian basin evolution was dominated by clastic input from the approaching Alpine–Carpathian–

Dinaridic nappe pile containing Neotethyan ophiolite and accreted passive margin rocks. The subsidence of the basin was caused by the increasing load of the emerging orogenic wedge. The TR remained on the southern side of this flexural basin during the Valanginian–Hauterivian. The instable slope was deformed by large slides with northern or north-eastern vergency. The more southerly located forebulge was marked by strongly reduced carbonate sequence.

In the Barremian to Aptian, the coarse clastic sedimentation has dominated over the marl deposits. Sedimentation took place in form of submarine fans. The orogenic wedge approached but still did not reach the TR clastic basin. After sedimentation ceased, the northern TR was gently folded and faulted by N–S or NE–SW compression in the earliest Albian.

As a major change, the whole TR was deformed by NW–SE compression. Large-scale NE-trending folds and thrust faults were completed from Albian to Coniacian (113–86 Ma). As part of this phase, the TR thrust over different Alpine nappe units and integrated to the Austroalpine system.

This structural evolution suggests that the TR changed completely its structural position: it was on the lower plate in the Jurassic–Early Cretaceous and became the highest unit in the “Mid-Cretaceous” phase. This needs a major reorganisation of the subducting and overriding plates. We follow earlier suggestions that a major strike-slip fault operated during this time. The large shift placed the TR and its Neotethys-related foreland-type Early Cretaceous basin in the rear of the subduction, in the highest position.

## GEOLOGICAL STRUCTURE, TECTONIC AND PALEOGEOGRAPHIC MOMENTS OF MOGLICA OSTROVICA REGION INCLUDING THE AREA SOUTH OF IT.

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### Abstract

In this work, the author discusses geological data collected during a period of 50 years.

On the basis of these data was implemented the concept of geological structure. The author makes paleogeographic and tectonic interpretations that are different from previous interpretations; he makes a more objective assessment of the tectonic overlap and disjunctions. South of the horst-syncline Ostrovica, the conditions allow to imagine the existence of a deep transverse fault, which changed the paleontography south of this region. This new idea contrasts with the old ideas as well as that of some ideas of some present authors who consider this area as belonging to Mirdita zone reached by thrusting the region of Leskovik until the Ionian tectonic zone. Considering southern Ostrovica as

an area of deep transverse fault, it was shown a different story of geological development. The region has been a pelagic trough, wherein, during the Cretaceous came in form of huge olistromes and olistolites changing the bottom of the trough (with mountains rising near to the water surface of the sea) and deep precipices.

Therefore, along with the carbonate sedimentation, planktonic microfauna is represented by *Globotruncanidae*. On the ridges have been sedimented shallow water deposits with benthic microfauna represented by *Orbitoides*, etc.

It is noted that the carbonate and terrigenous deposits of Gramos region do not constitute a particular zone or subzone; they form an area represented by typically Cretaceous-Paleogene deposits of Krasta zone.



## **BASIN MODELLING: APPLICATION OF SURPAC BY USING BOREHOLE DATA. A CASE STUDY: SOMA BASIN, WESTERN ANATOLIA**

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### **Abstract**

Surpac is a geology and mining planning software, supporting open pit and underground operations and exploration projects. It is used to determine the physical characteristics of a deposit, even when the information available to them is limited. It is possible to provide correlation between buried stratigraphic units and drawing 3D cross section with the software. It can be view and output sections using boreholes and existing topographic or pre-modelled data.

Western Anatolia is part of the Aegean Extensional Province, which is a region of extensional deformation driven by the complicated convergence of the African and Eurasian plates. Late Cenozoic tectonics in Western Anatolia Extensional Province can be grouped into two main generalised classes: a continuum of N–S extensional tectonics of western Turkey and successively alternating stress systems. The study area, Soma Basin, is located in Western Anatolia and is an extensional basin filled with Neogene–Quaternary sediments lying unconformably on Mesozoic limestones and greywackes. The NE–SW Bakırçay, E–W Soma and NW–SE Kırkağaç Grabens control the morphology of the area. Çamlıca High, bounded by these grabens, includes the NW–SE Kırakdere Graben. To understand the tectonics of the region, first of all, the outcrop studies were carried out. The boundary faults of the grabens are high-angle normal faults and strike-slip faults with normal components.

Then, palaeostress analyses of the fault-slip data were used in the study area. According to stress

analyses, the region was deformed by N–S, NE–SW, dominantly and NW–SE oriented extensional regimes since the latest Miocene.

Soma Graben has many similarities with the other western Anatolia grabens. Almost all of the grabens involve observable amounts coal-bearing layers in marginal lacustrine deposits. Subsurface correlation is important because it displays sedimentary fill from the margin to the centre of the basin. In the region 339, exploration wells have been drilled by various enterprises until now. These boreholes penetrated the Neogene sediments and the basement rocks, 283 boreholes having coal-bearing layers. The highest and the lowest value of the Miocene units were measured and correlated by the program. With the help of all that information, the basin geometry was created and it was drawn 3D geological cross section in different directions where the faults which cut the Miocene units were determined. The basin geometry shows that the southwest margin of the basin which is bounded by Karadere fault, is deeper than the other margins. According to analyses, the fault could be active during Miocene. Some faults cut only Early Miocene deposits. This data gives important information about the age and the origin of the faults. Small scaled, NW–SE oriented normal faults and N–S transfer faults between them exist in the basin fill, most of them being buried faults. Consequently, the syn-sedimentary structures have been formed simultaneously during the recent tectonic regime. The development of the strike-slip active faults which control the basins is related to İzmir-Balıkesir Transfer Zone.

## SOURCE AND TECTONIC IMPLICATION OF THE INTERMEDIATE TO ACIDIC VOLCANIC CLASTS FROM JURASSIC NEOTETHYAN MELANGES ON THE BASIS OF GEOCHEMISTRY AND RADIOMETRIC AGE DATING

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### Abstract

Volcanic olistolithes were examined from the Middle to Late Jurassic low-grade metasedimentary complex of the Meliata and Mónosbél nappes (NE Hungary, SE Slovakia). These nappes consist of thin tectonic slices derived from subduction-related trenches of the Neotethys Ocean. During its closure, the Meliata nappe thrust over the northern, imbricated West Carpathian margin. In contrast, the Mónosbél nappe is situated under the obducted Dinaridic ophiolite sheet which thrust over the southern Neotethyan margin, represented by the Bükk “para-autochthon”.

Geochemical characteristics of cm to 100 m in size rhyolite and andesite clasts of these two melange nappes were investigated. The REE patterns of all the volcanics are very similar. They show 60-200 fold enrichment in light REE relative to CI chondrites (Anders and Grevesse 1989). However, the enrichment in heavy rare-earth elements is only 10-20 fold. Thus the light and heavy REEs are relatively well fractionated ( $La_N/Lu_N = 2.32-7.69$ ). The most remarkable feature of the normalized REE pattern is the pronounced negative Eu anomaly ( $Eu_N/Sm_N = 0.58-0.98$ ), indicating plagioclase crystallization prior to the genesis of the melts. Trace-element patterns of the different occurrences are also very similar. In general, CI chondrite normalized values show significant enrichment in LILE and lower enrichment in HFSE (20-50 fold). Among the LILE elements Cs, Rb, Ba along with U shows great variability due to their high mobility. U fractionation may refer to later migration of  $U^{6+}$  in well-oxygenated  $H_2O$  rich fluids. In contrast with them, the normalized Th values are almost identical, showing 470-720 fold enrichment. Y/Nb, Yb/Ta, Nb+Y/Rb and Ta+Yb/Rb discrimination diagrams indicates volcanic arc environment (Pearce et al. 1984), while Ta/Yb vs. Th/Yb diagram refers to active continental margin setting (Gorton & Schandal 2000).

U-Pb isotope analyses were performed on zircon crystals by LA-ICP-MS. The results are

culminating around two ages: 220 Ma and 206 Ma. Both of them indicate volcanic activity in the Late Triassic, which can correspond to two more or less distinct episodes within a long magmatic activity.

Geochemical analysis of several potential Middle to Late Triassic rhyolites and andesites, were performed in order to find the original source of the redeposited clasts. As a result, Middle Triassic tuffs and acidic to intermediate volcanics deriving from the Bükk (Dinaridic margin) and the Transdanubian Range (Upper Austroalpine) have almost identical geochemical pattern. No significant volcanic activity has been proven on the northern margin of the Neotethys Ocean at this period.

Geodynamic implications: 1) The observed geochemical signature indicates Mid- to Late Triassic active margin setting or volcanic island arc. According to our present-day knowledge the subduction of the Neotethys Ocean had not started till that time. It raises the possibility that it is an inherited geochemical signal, indicating geochemical memories of the Paleotethyan subduction.

2) While the melange nappes thrust over the different margins (N and S), their clast composition is similar, thus the clasts at least partly have common source, from the Dinaridic and/or Austroalpine margins. While the ophiolite obduction onto the southern margin is proved to be Late Jurassic, the only Cretaceous nappe contacts have been documented on the northern (Inner Western Carpathian) margin, although subduction also started in the Middle Jurassic. It can be interpreted in two ways: either the latest Jurassic to Early Cretaceous nappe emplacement dismembered the unique (similar) Jurassic trenches into nappe sheets with different tectonic transport directions, emplaced onto different margins or alternatively the first accreted Dinaridic melange nappes were partly thrust on top of the northern margin, via back-thrusting, during the Cretaceous deformation.

## KINK BANDS AND CHEVRON FOLDS CHARACTERISTICS OF THE SARANDA ANTICLINE. ESTIMATION OF THE “MELO GEOLOGIST’S MOSAIC”, SOUTH-WESTERN ALBANIA.

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### Abstract

The purpose of this study is to make the qualitative and quantitative analysis of the kink bands from an outcrop situated in southern Albania, nearby the city of Saranda, to place this particular deformation feature into its local and regional context, to discuss the structural and tectonic significance of kinking and to explain the tectonic conditions in which it occurs in the study area. Observations of events leading to development of kink bands, their origin and changes in their morphology are recorded during the deformation in the “MELO Geologist’s mosaic” in southern Albania. Kinking in natural deformed limestone strata has been investigated to determinate the complete history of this deformation during the Paleocene. A model is presented to show in general terms the characteristics of these types of folds and also to explain the origin of observed kink. Kink bands are among the most common of folds. One thing that makes them so domesticated is their fracture-like or fault-like character. Like a fracture, the width of a kink band is typically many times smaller than the length of the kink band. Like a fold, the layering is bent, tilted and even crimped sometimes into its characteristic zigzag shape. Kink bands generally only occur in strongly foliated anisotropic rock (i.e. they are often second or a later generation structure developed after a first penetrative cleavage has been formed) and may occur in single or in conjugate pairs. If the later occurs, they may then be used to determine palaeostress orientations. A lot of research has been done on these structures, especially by Borg & Handin (1966) who defined a kink in minerals as subparallel boundaries, kink band boundaries (KBBs).

**Key words:** *Ionian Zone, Paleocene, Kink Bands, Chevron Folds, “MELO Geologist’s mosaic”*

### Morphological and geological characteristics of the Saranda anticline.

The Saranda anticline is part of the Ionian Zone, mostly consisting of deep marine carbonates with

cherty intercalations, dating from Jurassic to Eocene (Fig. 1/a). Later, these formations are covered by terrigene flysch deposits of Oligocene - Aquitanian age. This deep sedimentary carbonate basin was preceded by lagoon to platform depositional settings during Permian - Triassic with deposition of evaporites (gypsum, anhydrites) followed later on by dolomitic strata of Upper Triassic age. These evaporite deposits form decollement levels in the surface, near the thrust planes. The structure of Saranda is situated in the southwestern part of Albania and is about 20 km long, starting from the south, in Butrinti, continuing along the coast of the Ionian Sea and ending in Lukove (Fig. 1/b).

From Saranda and more further to the north, along the coast, uncovered in the beginning, the center and the beginning of the western flank of the structure with gentle dip, and more further into the North, to Bay of Kakome, uncovered also the external part of the western flank with dipping till 70° - 80°.

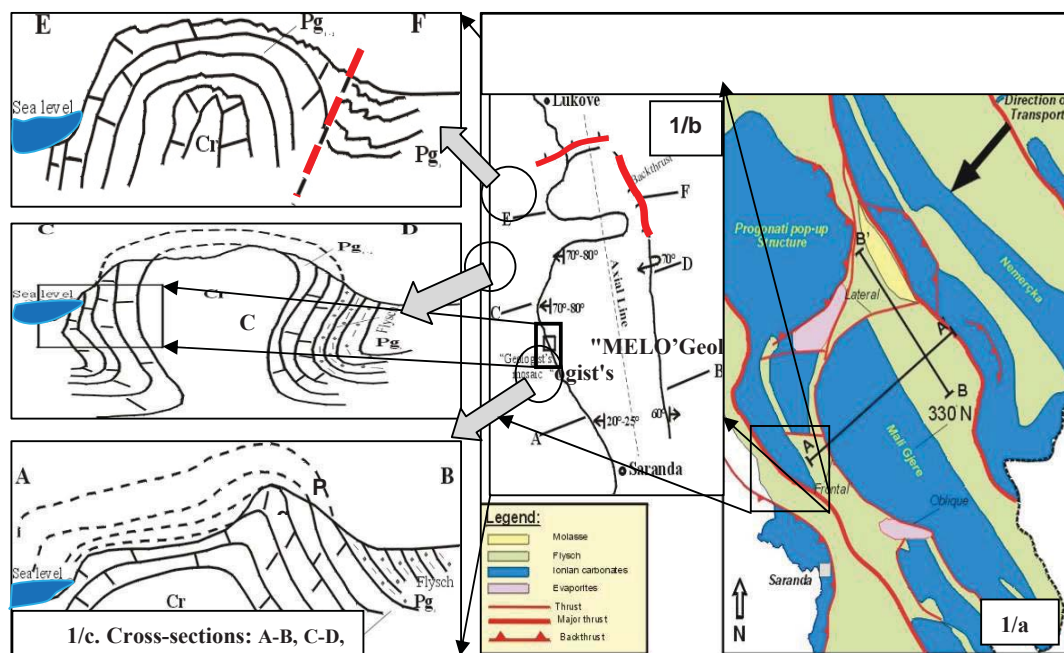
In both sides of the Kakome Bay’s the flanks and center of anticline are exposed. The center of the anticline is not as wide as in Saranda, but the flanks of anticline have a bigger dipping, in both western and eastern side (overturned to the east; Fig. 1/b & 1/c). Along the coast of the Ionian Sea, north and south of the Kakome Bay, only the western flank of the Saranda’s anticline is exposed. This flank has a high dipping (70° - 80°) to west - southwest into the Ionian Sea.

Alternation of the thick carbonate strata (mostly limestone) or turbidite horizons with thin strata gives along the coast an impression of intrusion and extrusion according to their dipping.

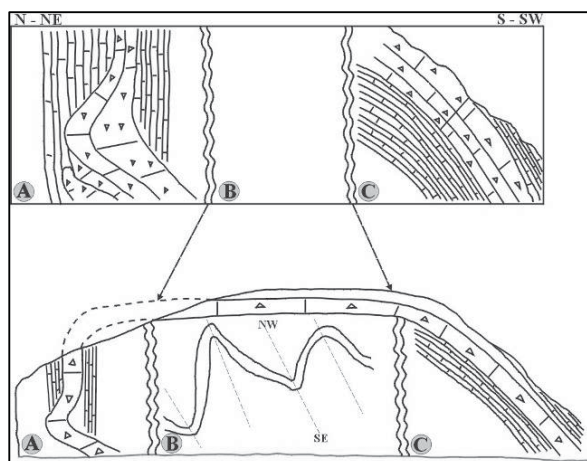
### “Melo Geologist’s Mosaic”

In geological aspect and interpretation, this “MO-SAIC” represents a complication dome-brachyanticline in the western flank of the Saranda anticline. This section is viewed as an asymmetric anticline. The southeastern flank has a gentle dipping (about 25° - 30°), while the northwestern flank has the





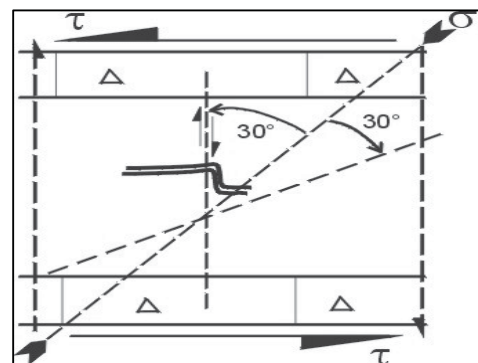
**Figure 1.** Schematic tectonic map of Saranda anticline, Mali Gjere (modified after Bega et al. 2001).



**Figure 2.** General schematic view of the "MELO 'GEOLOGIST'S MOSAIC".

steepness bigger than that (almost vertical, Fig. 2). In terms of geological setting, this section is of Paleocene age. Mostly, the center of the structure is covered as a "roof" from a thick turbidite horizon, which is uncovered in the southwestern flank of the mosaic. The carbonate strata are represented by thin-bedded limestones with reddish and/or greenish cherty intercalations few centimeters thick and by very thin clay-siliceous-carbonate beds.

The opinion for the section is: more than a layering of the anticline is also complicated because of the undulation of the crest line in shape of culmination, which have been created the section that is well exposed in the mosaic. The difference in thickness between turbiditic limestone strata which have been repeated in the section and



**Figure 3.** Schematic view of the maximal and tangential stress that is acted in the kink bands (Melo, 1991/b)

which has a thickness of 1-2 meters, and thin limestone (0.4 meters) strata with cherty intercalations which are also dominant in the section, have been created a mosaic kink bands and chevron folds inside this section with different shapes and with a ratio  $n \approx 3$  ( $n = d_2/d_1$ ). These kink bands and chevron folds are not characteristic for the turbidite limestone strata, which has been as boundaries inside of which have been developed the disharmonic microfolds. Geometric characteristics of the microfolds are very different, they change in the southeastern flank of the mosaic, in the core, northwestern flank as from the top to the bottom of the mosaic.

The southeastern flank of the mosaic is less affected by the microfolds. This flank which has a gentle dipping and could have been affected by the tectonic press or even extension, that caused non-development of the typical microfolds, but just

some flexural slips and some kink bands. If it we supposed that both of the turbidite horizons where thin carbonate strata are attached, will move up and down, the stress (Fig. 3) creates an orientation when the shear stress ( $\tau$ ) acted as a band and creates the kink bands. All these folds are linked with the stress tectonic regime which has been occurred later, with the force orientation in oblique manner or along the layering of the hole anticline structure of Saranda with normal stress oriented from southeast - northwest which in the framework of structuration of the Ionian zone, create also the structure of Saranda.

### Conclusions

The most important folding phase is after the Burdigalian and just before the Serravalian Tortonian. During this phase, we have the creation of the Saranda's structure layering northwest southeast; in the south asymmetric or overturned, in the southwest contoured by the thrust, in the north overturned, while in the eastern flank complicated with backthrust. In this phase were also formed the chevron folds in the "MELO Geologist's mosaic". Based in the layering northwest of the structure which is of the same corresponds with all the other structures of the Ionian zone, as well in the dipping of the axial plane to the northeast, the stress fields have been in compression regarding to the maximal stress ( $\sigma_1$ ) almost horizontal with the orientation northeast - southwest and minimal stress ( $\sigma_3$ ), vertical. The average stress ( $\sigma_2$ ) has been positioned in the same direction as the crest line (northwest - southeast), perpendicular to the plane of the  $\sigma_1$  and  $\sigma_3$ .

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# PLATE I



## CENOZOIC BRITTLE TECTONIC HISTORY OF THE KOPAONIK AREA (INTERNAL DINARIDES, SERBIA)

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### Abstract

The Internal Dinarides represent a part of the complex Dinaric orogen, situated in the central part of the Balkan Peninsula. The immediate research area, i.e. the Kopaonik mountain, is situated in the suture zone of the Vardar ocean. Its tectonic setting is conditioned by the tectonic evolution of this complex suture zone. Tectonic evolution of this area started with the Late Cretaceous subduction of the Western Vardar Unit, and was followed by post-collisional and neotectonic phases. While the older, ductile tectonic evolution of the research area is very well documented, younger, brittle tectonic phases, remained almost completely unknown. In this research we performed a calculation of the tectonic stress tensors in order to determine brittle tectonic regimes acting in the Kopaonik area, as well as their relative chronology.

Fault slip data were collected from different geological units, including Triassic limestones, Jurassic serpentinitised peridotites, Cretaceous limestones and sandstones. Determination of the slip sense on the fault planes was done using slip criteria marked as Young Geological Data of the World Stress Map project. The most common slip indicators observed on fault planes were calcite and magnesite fibers, cataclastic lineation, gouging-grain grooves and “carrot-shaped” markings. The relative chronology of brittle structures was determined using criteria of cross-cutting relationships of faults and striations, fracture mineralization and structural features of the brittle overprint of rocks.

Four deformation phases were distinguished. Phase D1 is characterized by E – W contraction, most possibly related to the westward propagation of thrusting of the Dinaric orogenic wedge over the Adriatic platform. N – S to NE – SW compression indicated by thrust faulting of NE- and NW-trending faults represent phase D2. This phase is a result of Oligocene to earliest Miocene shortening of the Dinaric orogenic wedge and is most likely correlated with Oligocene post-collisional magmatism of this area. Deformation phase D3 is regarded as extensional phase. Based on our field observations of overprinting striations, two subphases were clearly distinguished, both belonging to the same extensional event. Subphase D3a is characterized by E - W extension, comprising early Miocene opening of the Dinaridic intra-mountain basins, and also represents a prominent early to middle Miocene extensional phase of the Pannonian basin. In the immediate research area, this subphase is responsible for exhumation of the Kopaonik granitoids. Subphase D3b is represented by NW - SE (orogen parallel) extension, and is most likely a result of Middle Miocene to early Late Miocene lake sedimentary cycle in Dinarides and basaltic volcanism. The youngest strike-slip deformation phase D4 is indicated by sinistral faulting along generally E-trending faults and dextral faulting along N-trending faults. This deformation phase is characterized by N – S oriented compressional and E – W extensional axes.



## TRANSGRESSION OF THE LOWER MIOCENE ON CARBONATE ANTICLINE OF TERVOLLI, GRAMSHI-ELBASAN (CENTRAL-SOUTHERN ALBANIA)

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### Abstract

The anticline structure of Tervolli is located at east of Gramshi town, in central-southern Albania. It has a NE-SE orientation, same as that of the Albanides Complex and is a part of Kruja tectonic zone (the equivalent of Gavrovo tectonic zone in Greece).

On the slopes of this anticline structure and on its upper section are exposed carbonate deposits of Upper Cretaceous age, while on its flanks was settled a carbonate formation belonging to Upper Cretaceous-Upper Eocene characterized by a continuous sedimentation and followed by flysch deposits of Lower-Middle Oligocene. In the southwestern slope of the anticline structure, some isolated molassic deposits of about 150-200 m thick, transgressively placed on the Upper Cretaceous-Upper Eocene limestones occur.

The Lower Miocene transgression on the carbonate deposits of Kruja zone represents an atypical event in the geological setting of Albanides. These transgressive deposits consist of alternations of the sandstones, silts, clays associated with bioclastic limestones. The macrofauna is represented by different gastropods, bivalves and red algae as *Lithothamnium*.

The origin of the bitumen present in the sandstones from the bottom of the transgressive sequence was also highlighted in this work. The age of this transgressive sequence was dated by microfauna associations.

The micropaleontological studies show that the planktonic foraminifera are completely absent, while species belonging to *Lepidocyclina*-*Miogypsina* zone were studied in thin sections and from washed soft material and confirm that the molassic deposits have a Lower Miocene age (Upper Aquitanian-Lower Burdigalian).

These cavities hosted in the top of the Upper Cretaceous - Upper Eocene carbonate structure are filled with material ranging from gravels to different detrital rocks testifying the transgressive character of the mollase present in the anticline structure of Tervolli. These deposits were formed in the coastal part of a shallow sea (littoral zone) at depths of 0-50m. Paleogeographic interpretations and their correlation with other areas show similar deposits of same ages.

**Key words:** *Miocene, transgression, Lower Miocene, anticline, Tervolli*



## TERTIARY VOLCANISM THROUGH MERDARE AND TUPALLE FAULTS

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### Abstract

From the general point of view, during the Tertiary time, in Kosovo were developed two volcanic belts: Trepça and Artana. In the case of Artana volcanic belt, the volcanic activity had started in Upper Oligocene and ended during Upper Pliocene. The products of this activity are represented by tuffs, breccias and sediments of Upper Oligocene which crop out in the Strezovci area.

The Trepça volcanic belt is supposed to be formed in two phases: the first phase - I) started in the Lower Miocene and is represented by pyroclastic rocks, amphibolites, andesites and dacites and a second phase - II) of Middle Miocene age, placed above the first phase formations, which is represented by dyke intrusions and pyroclastites. This volcanic activity is supposed to cease at the end of Middle Miocene.

The aim of this work is to compare our data to other previous works from different authors in order to give our opinion regarding the age of Merdare and Tupalle faults, their relationships with other tectonic activities recorded in the region, the spreading centre volcanism occurred through these faults and the relationships of this volcanism with the hydrothermal polymetallic sulphide deposits.

About the Artana volcanic belt, we gave our opinion regarding the possible spreading centre volcanism, even if due to erosion phenomena, almost all tracks of volcanic calderas were lost.

**Keywords:** *Tertiary volcanism, volcanic belt, longitudinal faults*

## SOME ARGUMENTS ABOUT THE DIVIDING IN THE TECTONIC ZONES OF ALBANIA

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### Abstract

The Albanides are part of the Mediterranean periferic chain, constituting a certain cross body inside of it. The tectonic–structural evolution of this body is part of all Mediterranean chain. After different authors within this chain were separated some big tectono–structural units, based on the relationships between them and on the lithofacial content. The strain regime, the longitudinal and crossing tectonic fractures as direct consequences integrated in the context of the whole story of this geological evolution, obviously has played a very important role in the aspect of the formation of these tectono–facial regional units and later, of their tectonic and structural evolution.

We think that Albanides can be separated in two tectonical huge units: in the Adriatic Platform unit (Adria) or Apulian and the Albanian Orogenic unit. Both units are characterized by lithofacial and tectonic features totally different from the each others. The Adriatic Platform characterized by shallow water facies, absolutely allochthonous, is now subject to a continuous tectonic dipping regime under Apenine overthrust from one side and the Albanides Orogenic, from the other side. The nature of contact displays features typical for a collision zone representing the collision between two continental plates, Africa and Eurasia. It is characterised by shallow water facies and a distensive tectonic regime associated with many major faults and few secondary faults and as result, they have a weak structure.

Concerning the Albanian Orogenic Units, we consider that they are separated in three tectonic complexes: Outer Albanides, Central Albanides and Internal Albanides. All these three big facial–structural units are dominated by a compressive regime and consequently they are subject to rising, moves and continual overfaults to western direction. More the units occupy an easternmost position, more bigger is the scale of the overfaults.

In the Outer Albanides are included Ionian and Kruja zones. These tectonic facial units have approximately common features with each other. It is clearly observed their linearity, the north–western orientation of the structural elements, their continual overfaults in south–western direction, their lithofacial represented by the evaporite formation of the basement followed by the carbonate formation and closed by the flysch formation. The contact which limits on west the Ionian zone is while and the overfault front of the Albanide Orogenic Unit, which is characterised from a comprehensive tectonic regime dominated by fault and thrust fault associated with new structures.

Part of the Central Albanides, are the tectono–facial units of Albanian Alps, Krasta–Cukali and overthrust Cretaceous unit of Poda–Pashtrik. The first two have a central position along the geological structure of the Albanides and are characterised by a diversity of the structural and litho–facial features, making possible the fragmentation of these tectonic units in transversal and longitudinal direction in some smaller tectono–facial units, which we consider to be relatively autochthonous. The Cretaceous nested unit of Poda–Pashtrik is situated in a lateral position, as a lowland or as transgressive tongue, placed in discordance above the Internal Albanides, which according to their position we consider that they are absolutely allochthonous. Beside its formational diversity, the Central Albanian tectonic complex is characterised by lithofacial uniting elements, making them as differently as correlated to each other. In these conditions, as part of the Central Albanides we consider Krasta–Cukali–Alpe tectonic zone, which has been separated in Krasta, Sheldie, Cukali and Alpes tectonic subzones, together with the nested unit of Poda–Pashtrik. Seen from a regional perspective, it means that the High Carst Unit in Dinarides and those of Tripoliza and Parnasse zones in Hellenides must be the northwestern and southern continuity of the Krasta–Cukali–Alpes tectonic zone. The

characteristic of this tectonic zone is obviously overfault above the Kruja zone, the discontinuity from some cross fractures, the big width up to 65 km, its outcrops as tectonic windows in the Internal Albanides depth and the function of this geological territory in the conditions of a strain regime in compression.

Based on the nature of the relationships between the lithofacial formations, the we separated the Internal Albanides into four tectonic nappes: Jurassic–Cretaceous Flysch Nappe, Schist-Granite Nappe, Triassic-Jurassic Carbonate Nappe and Ophiolitic

Nappe. In the whole territory, this tectonic nappes complex, keeps a same placing order in relation with each other. It is characterized by complete allochthonism of rock formations and by the strain regime that performed as a pasive tectonic unit. The Jurassic–Cretaceous Flysch Nappe, although it is most recent in terms of geological age, constructs the floor of this overthrusting complex. Above is placed Shisch–Granite Nappe, followed by the Triassic–Jurassic Nappe and, the all succesion being covered by the Ophiolitic Nappe.

## OLIGOCENE–MIOCENE TECTONIC EVOLUTION OF THE CENTRAL PART OF THE MID-HUNGARIAN SHEAR ZONE

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### Abstract

This industrial seismic based study aims at the detailed tectonic evaluation of Oligocene and Miocene structures in the central part of the Mid-Hungarian Shear Zone in the Pannonian Basin, between Jászberény and Adony. Four partly overlapping 3D seismic surveys provided the base of the project and were supplemented by 2D seismic sections. Seismic interpretation results were corroborated by section restoration.

The Mid-Hungarian Shear Zone, lying between the Balaton Line in the northwest and the Mid-Hungarian Line in the southeast, was a narrow northeast-southwest striking convergent fold and thrust belt in the Late Oligocene to Early Miocene, characterised by thin-skinned thrust ridges and synsedimentary synclines, also regarded as ramp basins. The intensity of shortening increased southwestwards, related to vertical axis rotational events within the shear zone. The thrust belt started to built up around Jászberény in the northeast. The Tóalmás and Monor Areas (in the central part of the study area) were only mildly deformed, while the Bugyi and Adony Areas (in the southwest) suffered intense shortening, uplift and related erosion in several phases.

A first clockwise rotation occurred during the Egerian, and resulted in increased shortening of the southwestern parts, most likely even a thrust nappe in the Adony area. This was followed by a second clockwise rotation (most likely) in the Ottományian.

Being in the convergence and translation zone between the oppositely rotating ALCAPA and Tisza terranes, the Mid-Hungarian Shear Zone is regarded a pure shear dominated transpressional orogen in the Late Oligocene to Early Miocene, with strain partitioning and internal rotations being important factors in the deformation history of the zone.

The Bugyi High is a Sarmatian–earliest Pannonian age sinistral pop-up structure superposed on an earlier thrust, related to a counterclockwise rotation event within the shear zone. During the Pannonian (or slightly earlier), sinistral strike-slip movements initiated in a wide zone, with localised deformation being mainly along the Tóalmás Zone. This resulted in the spindle-shaped Mende-Sülysáp pull-apart basin and related structures. The strike-slip zone, being essentially superposed on the Balaton Line, crosscut earlier thrusts and basins at acute angles, thus resulting in complex geometries.

The Adony Basin is an early Pannonian pull-apart basin of the Tóalmás Zone superposed on a Late Oligocene to Middle Miocene ramp basin. Strike-slip faulting was partly detached from the basement on local salt of Badenian age. The margins of the basin coincided with the fronts of earlier thrusts. In the basin, gravity sliding on the steep margins resulted in salt welds and detachment folds.

## STRUCTURAL COMPLEXITIES AT AND AROUND THE TRIASSIC–JURASSIC GSSP AT KUHJOCH, NORTHERN CALCAREOUS ALPS, AUSTRIA

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### Abstract

The Global Stratotype Section and Point (GSSP) for the Triassic–Jurassic system boundary was defined in the Lechtal nappe of the Northern Calcareous Alps, on the overturned limb of the Karwendel syncline, in two subparallel artificial trenches on both sides of Kuhjoch pass (Kuhjoch West and East). The system boundary was drawn at the first occurrence of *Psiloceras spelae*, regarded as the oldest Jurassic ammonite species, in the clays of the Tiefengraben Member of the Kendlbach Formation. To supplement the great amount of existing stratigraphical, paleontological and geochemical data by constructing a geological profile across the GSSP, describing the deformation history and conditions in the area and clarifying structural geological phenomena at the site, the authors carried out field work at the site in August 2012.

In the homogeneous clays of the GSSP, two intersecting surface sets were identified, with the steeper set tentatively established as bedding, the flatter one as axial planar foliation of the large scale overturned fold.

The contact between the Triassic Kössen Limestone and the stratigraphically overlying clays of the Tiefengraben Member is tectonic in both trenches: a steep, roughly east-west trending fault separates the two formations. Fault striations and slickenfibres indicate a reverse setting. Based on the outcrop pattern, the minimal offset on the fault is 6–8 metres. In the footwall, a continuous sequence from the Kössen Limestone to the basalmost Tiefengraben Member could be excavated. In the hanging wall, only the Tiefengraben Member and underlying younger formations were identified, the Kössen Formation being eroded. Thus there is no complete and continuous stratigraphic section across the Tiefengraben Member in the Kuhjoch trenches.

The trace of the fault is shifted between the eastern and western trenches by ~5 metres: a north-south trending fault with apparent dextral offset separates the two sections.

Based on our transect across the Karwendel syncline, the steep, overturned, almost isoclinal fold was deformed in a semiductile manner. This is indicated by outcrop scale asymmetric, mainly upright, isoclinal folds in many places in the vicinity of the GSSP, and disjunctive axial planar foliation in the marl and clay intervals.

Brittle deformational features are also abundant. The majority of observed faults clearly postdates folding/tilting. The geometry of some of them, however, becomes kinematically more valid if the structures were rotated back to bedding being horizontal. This means that these faults are more likely to be pre-tilt (i.e. pre-folding) structures. This scenario is also thought to be valid for the fault at the GSSP: the steep reverse fault would become a simple normal fault if the now overturned bedding was rotated to the pre-folding geometry.

Based on these findings, the Kuhjoch GSSP does not fulfil the requirement for a GSSP to be free of tectonic disturbances near boundary level.



## MESO-ALPIDIC EVOLUTION OF THE KLIPPEN BELT AREA (WESTERN CARPATHIANS, SLOVAKIA): TECTONIC CONTROLS OVER THE COUPLED FOREDEEP-WIDGETOP BASIN SYSTEM

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### Abstract

The Pieniny Klippen Belt (PKB) and neighbouring zones of the Western Carpathians represent an ancient accretionary wedge that evolved along the outer edge of the Austroalpine units of the Central Western Carpathians during the latest Cretaceous and Early Paleogene. The synorogenic sedimentary record of these zones is interpreted as a foreland basin system in a convergence setting that included the lower plate trench-foredeep and upper plate wedgetop-piggyback depozones. The peripheral foredeep basins of the Oravic tectonic system are characterized by clastic fans and aprons with a coarsening-upward trend. The coarse-grained and immature clastic material of mass-flow breccias was derived from the leading edges of overriding thrust sheets, including the “exotic” pebbles recycled from mid-Cretaceous conglomerates of the Austroalpine Klappe Unit. The foredeep basins developed sequentially in the PKB Oravic units, first in the Pieniny Unit (Coniacian - Campanian), then in the Subpieniny Unit (Maastrichtian) and finally in the Šariš Unit (Paleocene - Ypresian). In contrast, the wedgetop, Gosau-type basins are superimposed on frontal elements of the Austroalpine thrust wedge. These contain, in addition to the material derived from the underlying wedge, also considerable amount of bioclastic material, including disintegrated reef bodies. The successive transgression-regression depositional cycles and corresponding deformation stages are interpreted in terms of accretionary wedge dynamics maintaining the critical taper only transiently. The supercritical taper states are recorded by regression, shallowing and erosion in the wedgetop area, while the trench was supplied by large amounts of clastics and olistostromes. On the other hand, the collapse stages tending to subcritical wedge taper are indicated by widespread marine transgressions or ingressions and deepening up to bathyal conditions generally. As a result, evolution of the entire foredeep-wedgetop basin system was principally controlled by a complex interplay among the regional tectonic

evolution of the Alpine-Carpathian orogenic system, local wedge dynamics and eustatic sea-level fluctuations.

**Key words:** *Western Carpathians, Oravic units, Gosau Supergroup, synorogenic sediments, tectonic evolution*

### Introduction

The Pieniny Klippen belt (PKB) is a narrow, compositionally and structurally complex zone that separates the Cretaceous basement-cover nappe stack of the Central Western Carpathians (CWC) from the Tertiary accretionary wedge of the External Carpathians (EWC, Flysch Belt). The PKB unites various units of two different palaeogeographic provenances – the Oravic cover units detached from a continental fragment in the intra-Penninic position, and frontal elements of the Austroalpine (CWC) cover nappe systems, particularly of the Fatric (Križna) Superunit (Manín, Klappe, Drietoma and Haligovce units, cf. Plašienka 2012). Being composed exclusively of non-metamorphic sediments, the PKB shows complex structural relationships between the “klippen” composed of rigid Middle Jurassic and Lower Cretaceous limestones and the “klippen mantle” consisting of soft synrift Lower Jurassic and synorogenic Upper Cretaceous to Paleogene shales, marls and flysch deposits (e.g. Andrusov 1974; Birkenmajer 1977, 1986). During the meso-Alpidic epoch (i.e. Senonian through Middle Eocene), the Western Carpathian zones along the PKB experienced a polystage tectonic evolution as they were gradually shifted from the front of the CWC thrust system to the rear of the developing EWC accretionary wedge. Finally, during the Early–Middle Miocene, the PKB and adjacent units were welded to the backstop CWC block, being separated from the Flysch Belt by steep reverse oblique to strike-slip faults. In this short contribution, it is argued that various synorogenic sediments of the “klippen mantle” originated in different, but mutually related parts of the foreland basin system, the evolution of which

was principally controlled by the local wedge dynamics.

### **Evolution of Oravic peripheral foredeep basins**

Three large-scale thrust units are presently distinguished within the PKB (Oravicum): the Šariš, Subpieniny and Pieniny nappes from bottom to top that include several local subunits and/or successions. The innermost Pieniny nappe was derived from a basinal area with deep-water pelagic successions terminated by Turonian–Santonian sandy turbidites and conglomerates composed of partly “exotic” material (Snežnica and Sromowce Fms, Birkenmajer 1977). This coarsening-upward synorogenic sequence developed in foreground of the Fatric Klape nappe which provided majority of the clastic material, including the “exotic” one, which was most probably resedimented from the mid-Cretaceous, Upohlav-type conglomerates (Plašienka 1995, 2012). The Senonian strata of the Subpieniny Unit (Czorsztyn and related transitional successions) are predominantly composed of red pelagic marlstones of the couches rouges facies, known as the “Púchov marls” in the PKB (Jaworki Fm. after Birkenmajer 1977) topped by the Jarmuta Fm. The Maastrichtian sequence of calcareous flysch terminated by the Gregorianka Breccia Member (Nemčok et al. 1989) composed of material derived exclusively from the overriding Pieniny nappe. The outer- and lowermost Oravic element of the PKB is the Šariš Unit (Plašienka and Mikuš 2010; Plašienka 2012) that includes more-or-less continuous, but strongly condensed and dismembered Jurassic to Cretaceous deep-water pelagic succession grading into the Maastrichtian?–Paleocene–Lower/Middle Eocene Proč Fm. (Leško 1960). This represents a coarsening-upward, synorogenic calcareous turbiditic sequence containing huge slide bodies (sedimentary klippen-olistolites) and mass-flow breccias (Milpoš Breccia Mb.) composed of material that principally originated from the overriding Subpieniny nappe.

### **Development of Western Carpathian Gosau basins**

Seven Senonian through Paleogene sedimentary sequences can be distinguished atop the frontal elements of the CWC cover nappe systems (for their detailed lithostratigraphy see e.g. Salaj and

Priečhodská 1987; Salaj 1994): (1) Coniacian–Campanian transgressive deposits include basal polymict or carbonate-dominated conglomerates (Rašov and Valchov Fms) and sandstones with littoral fauna and reef bodies; followed by (2) a deepening and fining-upward sequence of calcareous sandstones and variegated marlstones of the couches rouges facies (Púchov Fm.); (3) Upper Campanian to Maastrichtian regressive sequence is represented by shallow-water bioclastic limestones, tempestites, calcareous sandstones and conglomerates with blocks of rudists-bearing bioherms (Ihřište and Bradlo Fms); (4) Thanetian–Ypresian strata are dominantly composed of shallow water bioclastic and sandy limestones with conglomerates and reef olistoliths (Kambühel Fm.); (5) partly transgressive coarse-grained carbonate breccias and conglomerates with blocks of reef limestones of the Lower to Middle Eocene Súľov Fm. are followed by calcareous turbiditic sandstones and bathyal variegated claystones (Lower–Middle Lutetian Domaniža Fm.); (6) after the Upper Lutetian gap, a new Bartonian–Rupelian sequence forms a fill of the extensive Central Carpathian Paleogene Basin, which ultimately covered most of the CWC area during the Late Oligocene (7). It is inferred that these sequences represent undulating transgression-regression cycles controlled by cumulative effects of the local compressive-distensile tectonic pulses in concurrence with the global sea-level oscillations.

### **Discussion – the tectonic model**

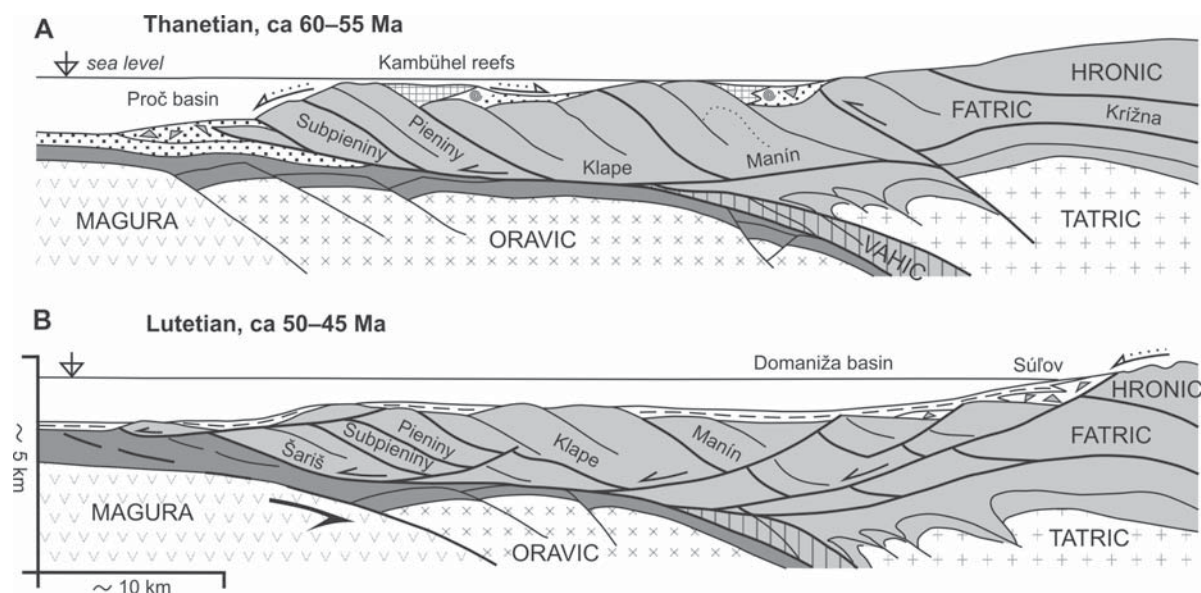
Synorogenic deposits of the Oravic units with coarsening-upward trends that were fed by material derived from the prograding fronts of overriding nappes are interpreted as the foredeep-trench basins. Progressive outward younging of the terminal synorogenic formations indicates sequential thrusting, therefore ages of these sediments are considered as indicative for timing of the thrusting events and their propagation within the Oravic nappe stack of the later PKB.

Many characteristics of the Gosau basins that developed at the toe of the Western Carpathian orogenic wedge can be explained by the critical taper theory (e.g. Dahlen 1990). In view of that, the two phases of the regressive-transgressive sedimentary cycles would represent: a) regression and inversion of piggy-back basins and ultimately surface uplift, potential emersion and local erosion were generated by build-up of compressive

stresses within a wedge, its internal shortening and ensuing thickening up to the supercritical wedge taper; b) transgression and rapid subsidence of the wedge-top basins occurred after the overthickened wedge had surpassed the critical taper and internal strength limits and underwent an extensional collapse.

Based on combination of data from the foredeep and wedgetop basins, the following tectonic scenario is proposed for evolution of the synorogenic basins that are differentiated according to the above discerned depositional stages: (1) After foregoing Upper Turonian emplacement of the CWC nappe systems and onset of subduction of the South Penninic-Vahic ocean, the peripheral foredeep Snežnica-Sromowce (later Pieniny Unit of the PKB) and the wedge-top Rašov-Valchov basins were established during the Coniacian–Santonian. (2) During the Lower–Middle Campanian, the sea level rose and the wedge collapsed gravitationally to the subcritical taper state, therefore connection between the foredeep and wedge-top basinal areas was enabled. This resulted in unified sedimentation of pelagic variegated marls and shales in the widespread Púchov basin; (3) In the latest Cretaceous times, the clastics-dominated foredeep relocated outwards to the later Subpieniny Unit (Jarmuta basin), whilst the wedgetop area was gradually uplifted due to the wedge compression

and thickening, as recorded by regressive formations of the piggyback Bradlo-Ihršte basins. After closure of the Váh Ocean, the wedge stayed in a compressional regime generated by collision of the CWC with the Oravic continental fragment. (4) The peripheral foredeep was shifted to its northern margin facing the Magura Ocean and was filled with coarse clastics with huge olistostromatic bodies (Proč basin of the later PKB Šariš Unit) during the Lower Paleogene. The wedge area was compressed, uplifted, emerged and partly eroded, as evidenced by frequent gaps in the sedimentary record. During the Thanetian–Ypresian sea-level rise, the still contracted wedgetop-piggyback basins were influenced by shallow-marine bioclastic input and abundant reef olistoliths (Fig. 1A); (5) For the period of Lutetian, the wedge collapsed and subsided to bathyal depths again. The large and deep Súľov-Domaniža basin originated, which communicated also with the EWC basins with similar sedimentary conditions (Fig. 1B). Its inner CWC margin was bounded by normal faults, which supplied the adjacent peripheries by vast masses of unsorted carbonate scarp breccias (Súľov Fm.), whilst the backstop CWC zones were still contractionally uplifted; (6) The Late Lutetian – Early Bartonian episode of compressional basin inversion was followed by widespread Bartonian–Priabonian transgression



**Figure 1.** Tentative palaeotectonic sections of the foredeep-piggyback basin system selected for two Paleogene stages to illustrate the critical-supercritical wedge taper state (A) and the subcritical taper situation (B). Basement complexes are hachured grey, lower plate sediments are shown dark grey, upper plate sediments are light grey, synorogenic sediments contemporaneous to the particular stage are hachured black, seawater is shown blank. A – Stage (4), gradual underthrusting of the Oravic domain below the CWC thrust stack with supercritical wedge taper, Proč foredeep and shallow wedge-top basins with Kambüchel bioherms; B – Stage (5), commencement of subduction of the Magura oceanic lithosphere, wedge collapse to subcritical taper, Domaniža wedge-top pelagic basin with marginal Súľov carbonate clastic aprons.



of the CCPB related to the renewed sea-level rise and following (7) Upper Oligocene extensional collapse of the CWC area.

## Conclusions

The PKB Oravic units were located in the lower-plate position and their synorogenic sediments, typically with a coarsening and thickening-upward trend and with terrigenous clastic material predominantly derived from the overriding thrust sheets, were deposited in the peripheral foredeep-trench type furrows. On the other hand, the coeval wedgetop-piggyback Gosau-type basins developed atop the accretionary wedge of the upper plate tip, exhibit strong influences imposed by structural development of the underlying wedge. As a result, the tectonic evolution of both basin types was mutually influenced and jointly conditioned by the wedge dynamics. Stages with critical to supercritical wedge taper situations are characterized by event deposition of coarse clastic mass-flows and aprons in the peripheral foredeeps of the Oravic units, and by regression and ephemeral reef build-ups in the piggyback Gosau basins. Accelerated forward movements of the wedge tip were related to the wedge collapse stages in particular. The subsequent subcritical wedge taper states are indicated by rapid deepening, decrease in clastic supply and unifying of sedimentary conditions in both the foredeep and wedgetop basins. The transgression-regression events within the wedgetop area occasionally might have or might have not corresponded to the global sea-level changes.

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## IMPLICATIONS FOR THE TECTONO-MAGMATIC EVOLUTION OF THE SERBO-MACEDONIAN MASSIF FROM A GEOLOGICAL MAPPING OF THE AMMOULIANI ISLAND (NORTHERN GREECE).

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### Abstract

Ammouliani Island is a small island in Northern Greece with its exposed rocks belonging to the Serbo-Macedonian Massif (SMM) of the Hellenic hinterland. Its geology is of great importance since in this island, the NW-SE orogenic fabric of the Hellenic hinterland appears to have changed to ENE-WSW and this change is a striking feature of the Hellenic hinterland. Our effort was to understand better these facts, and for this purpose, is presented a geological map at scale 1:10,000 upon detailed fieldwork and with the interpretation of satellite imagery. In addition, a special interest has been given on the recording and processing the tectonic elements of the mapping units.

The SMM has been divided long ago into two units. The lower Kerdilion Unit, which consists of fine- to medium-grained biotite gneisses, biotite-hornblende gneisses, amphibolites and marbles and the upper Vertiskos unit which mainly consists of two-mica gneisses, muscovite gneisses, muscovite-garnet gneisses, staurolite- kyanite-garnet gneisses and augen gneisses.

The separation of the SMM in units and the nature of the contacts between these units have recently been important research subjects. More recent views for the area of the SMM, made a different or new grouping for several rocks of the region covered by the SMM or even more, they tried to correlate several of these rocks with those of the Rhodope Massif. As a result, the contact between Kerdilion and Vertiskos Unit which had previously been considered as a conformable stratigraphic contact but after more recent studies is considered as a tectonic contact.

Based on our geological mapping, the constructed geological cross sections and stratigraphic columns as well as information of previous published maps, we mapped the exposed rocks of the Ammoliani Island into three different map units. The lower map unit that mainly consists of amphibolites, biotite gneisses and marbles is considered

part of the Kerdilion Unit, the age of which is considered Paleozoic. Although, in other parts of the Chalkidiki peninsula, the Kerdilion Unit also includes migmatitic gneisses indicating some of migmatization processes, in the Ammoliani Island this migmatization has hardly been observed. The exposed rocks of the Kerdilion Unit are tectonically overlain by rocks characterized by a strong migmatization and shearing such as quartzofeldspathic gneisses and anatexites-granitic gneisses. Due to this intense migmatization and shearing, the latter rocks were grouped in a new unit called Ammoliani Unit. In fact, the Ammoliani Unit is dominated by leucocratic rocks (or leucosomes) in comparison to the underlying melanocratic rocks of the Kerdilion Unit. Above the rocks of the Ammoliani Unit, monotonous dark brown gneissic rocks without showing in the field clues of migmatization processes are placed tectonically and they have been mapped as part of the Vertiskos Unit. Finally, we have Mesozoic(?) acid intrusions metamorphosed in plagioclase-microcline gneisses and Tertiary granites intruded into the previous mapping units but without presenting analogous intense deformation.

Also, in the field were recorded structural elements. As a result, three main folding events (F1, F2 and F3) have been defined in the exposed rocks of the island with the F1 to be related with the intense migmatization and shearing, whereas the last two (F2 & F3) are progressive to each other and they are related to the Mesozoic orogenic processes. In addition, NE-ENE-striking shear zones were observed and the Ouranopolis granitoid is placed parallel with them. The bending of the orogenic fabric from NW-SE to ENE-WSW is younger than the F2 and F3 folding events and it is related with the Tertiary orogenic (tectono-magmatic) processes due to the convergence between Apulia and Eurasia plates.

## ALBANIDES FOLD-AND-THRUST BELTS OVERTHRUST ONTO THE APULIA FORELAND

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### Abstract

Many geological, geophysical and drilled wells data, as well as regional integrated syntheses depict the Albanides as a segment of the whole Alpine chain located between Dinarides in the northwest and Hellenides in the southeast. The Dinarides, Albanides and Hellenides are folded and overthrust south westward in form of tectonic nappes owing to the collision between the Apulia Foreland and the Euro-Asiatic one. Thus the whole Albanides tectonic setting comprises partly the Apulia Foreland named Sazani zone, Orogenic fold-and-thrust belts nappes, Periadriatic Foredeep named Durresi Depression and two intermountain or piggy back depressions.

Apulia Foreland (Sazani zone) has a restricted outcrop along the south-western edge of Albanides onshore, while at depth it is detected throughout the Albanian offshore of Adriatic and Ionian Sea and in few onshore seismic lines. Outcropped sections and the drilled wells ones confirm that the Apulia Foreland comprises a thick carbonate platform of Upper Triassic to Oligocene age, followed upward by transgressive premolassic and molassic sequences. Meanwhile, evaporitic deposits of considerable thickness Upper Triassic to Lower Cretaceous age lie under the base of the carbonate section of the Apulia Foreland and the Ionian-Kruja tectonic nappe.

The Albanides Orogeny comprises several tectonic nappes, which are divided into Internal and External tectonic zones based on the presence of the ophiolitic rocks. The tectonic nappes of the Albanides orogeny overthrust onto each other south-westward and onto the Apulia-Sazani-Paxos Foreland beginning with the Ionian-Kruja-Gavrovo nappe, which wholly is the youngest in age. Meanwhile going north eastward across the External Albanides outcrop nappes of the Krasta-Pindus, marly flysch, volcanic sedimentary-mélange, ophiolitic rocks, etc. The overthrust

front of the Albanides orogeny onto the Apulia-Sazani Foreland outcrop obviously in Llogara pass in southwestern Albania, whereas its northwest and southeast continuity is completely masked by Periadriatic Foredeep deposits. Nevertheless reliable 2D seismic lines data have enabled following of the overthrust front location under the Durresi Depression deposits from north of the Llogara Pass to west of Durresi anticline gas discovery.

Periadriatic Foredeep consists of premolassic, molassic and late molassic deposits of Miocene to Pliocene-Quaternary age, which transgressively cover most of the Apulia-Sazani-Paxos Foreland and partly the Ionian-Kruja-Gavrovo orogenic nappe.

From the hydrocarbon potential point of view, the most prolific units are Durresi Depression, Ionian-Kruja nappe and the Apulia Foreland carbonates. These units comprise several types of hydrocarbon accumulation traps and many depicted prospects in the targets of the Cretaceous-Paleogene limestone and the Neogene sandstone. But, the depicted prospects need further attention to prepare for their final check and evaluation by drilling. In other words it is required a constant search to review the exploration philosophy and improve seismic acquisition and processing technology, as the most effective way to discover new hydrocarbon reserves.

## QUATERNARY DEPOSITS (VALLACHIAN BASIN) FORM THE EXTERNAL REGIONAL OF THE CARPATHIAN OROGENE (ROMANIA)

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### Abstract

This work refers to stratigraphic, tectonic and paleogeographic aspects of the Quaternary deposits located in the junction area of the Carpathian Orogene and Romanian Foreland that led to several results: definition of the Valah Nappe (generated by the Vrancea Valah Tectogenetic Phase at 2.58 My.); definition of the Focșani Pasaden Tectogenetic Phase at 1.0 My.; definition of the Valah Basin represented by the deposits of the Valah Cycle (Pleistocene, ~2.58 -0.01 My.); overall shape of the assembly deposition and ambient of the Valah Basin; proposal of the Quaternary stratigraphy scale of the Valah Basin valid for the entire Paratethys Domain.

**Keywords:** *Valah Basin, Valah Nappe, Valah Cycle, Pleistocene, Buridavian, Ordessensian*

### Introduction

The summary of current information (Săndulescu 1984; Mațenco and Bertotti 2000; Badescu 2005) highlights (Stănoiu 2012-2013, 2013) that the four major tectogenetic phases (Old Styrian, New Styrian, Moldavian and Vrancea Valah) which distorted the Cenozoic deposits of the external region of the Carpathian Orogene caused the formation of four significant block overthrust tectonic megastructures: Old Styrian Nappe, New Styrian Nappe, Moldavian Nappe (Subcarpathian Nappe, Săndulescu 1984) and Valah Nappe defined by Stănoiu (2012-2013, 2013) in the Vrancea Bending of the Carpathian Orogene between Trotuș Valley and Teleajen Valley. Following the four structured units mentioned here, four paleogeographic units, well-defined tectonically and lithostratigraphically (Old Styrian Basin, New Styrian Basin, Moldavian Basin and Valah Basin), corresponding to four tecto-stratigraphic cycles, were formed; Valah Cycle being represented by Pleistocene deposits (~2.58-0.01 My.) of the Valah Basin, the external and the newest of the four

mentioned basins. Vrancea Valah Tectogenetic Phase was specified (Stănoiu, 2012-2013, 2013) at ~2.58 My, at the boundary between Romanian and Buridavian within the lithostratigraphic “unit” of the Căndești Beds, at the boundary between the gravels of Motru - Vâlsan Member (Romanian) and the gravels of Magura Odobești Member (Buridavian).

### Methods and results

This approach aims to present a new stratigraphic scale (Figs. 1-4) valid (Stănoiu 2012-2013, 2013) for the entire Paratethys Domain based on lithostratigraphic, tectonic (Figs. 1-4) and climatic (Fig. 4) criteria, supplemented by biostratigraphic (Andreescu et al. 2011) and infra-red stimulated luminescence criteria (Shalkoplias 1983, etc). Within the Valah Basin's evolution was assessed (Stănoiu 2012-2013, 2013) that there are several main ambiances: 1) Dacic Ambiance, low alluvial plain type, represented by unconsolidated ground, very palud, drained by Dacic River Network (braided-anastomosed-meandering valleys, without terraces); 2) Odobești Ambiance characterized by a moderate palud terrain, poorly consolidated, represented especially by alluvial fans consisting predominantly of Carpathian and Subcarpathian origin gravels, drained by Odobești River Network, mostly torrential, without terraces; 3) Frătești Ambiance characterized by poorly consolidated ground, more marshy than that of Odobești Ambiance, drained by braided-anastomosed-meandering valleys of Frătești River Network, without terraces; 4) Valah Ambiance defined as consolidated (firmly) dry ground, drained by right valleys of the Valah River Network, with terraces evident from ~0.8My.

Depositional ensemble of the Valah Basin highlights (Stănoiu 2012-2013, 2013; Figs. 1-4) two major units: 1) central depositional unit, dominated by Dacic Ambiance, placed inside the Slatina-Titu-Măicănești-Focșani Perimeter (highly subsiding), represented by thick and with no discordances sandy-clay deposits

(Slatina-Titu-Măicănești Formation: Slatina-Titu and Titu-Măicănești Members); 2) marginal depositional unit, represented mainly by gravels (Odohești-Frătești Group) at ~2.58 My with lower thickness and two major discordances

(controlled by Vrancea Valah Tectogenetic Phase) and at ~1.0My (controlled by Focșani Pasaden Tectogenetic Phase) specified by Stănoiu (2012-2013, 2013). In the marginal depositional unit are separated two important subunits: 1)

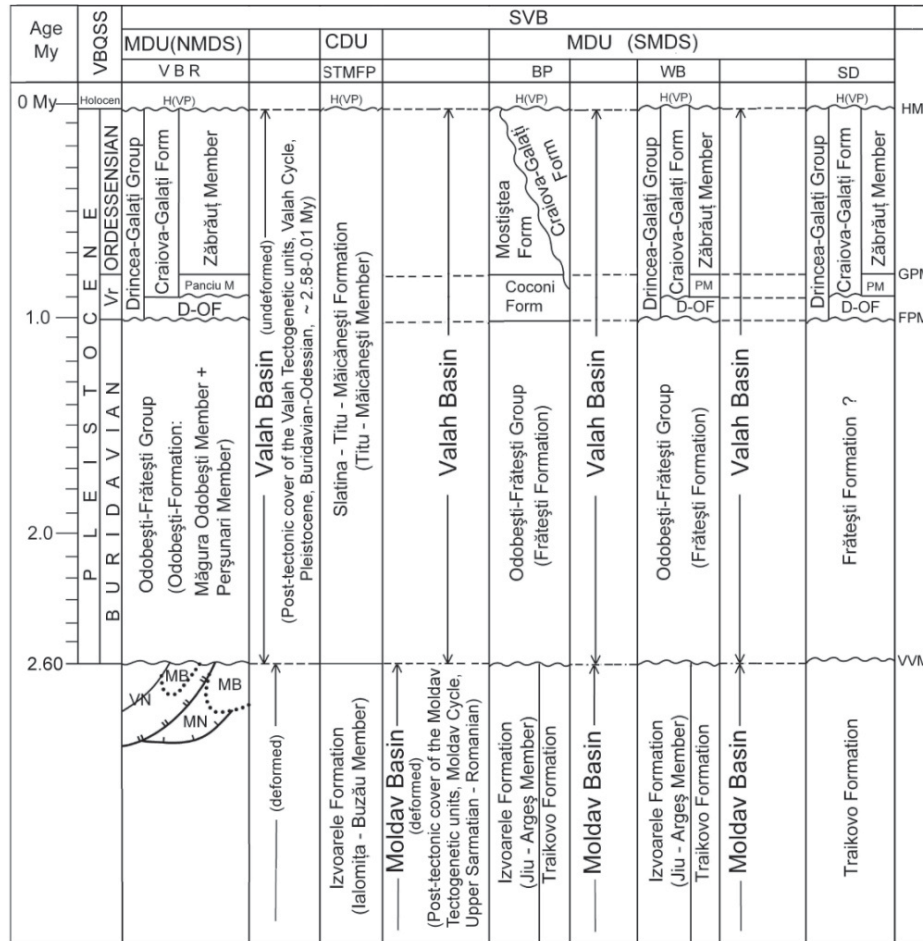


Figure 1.

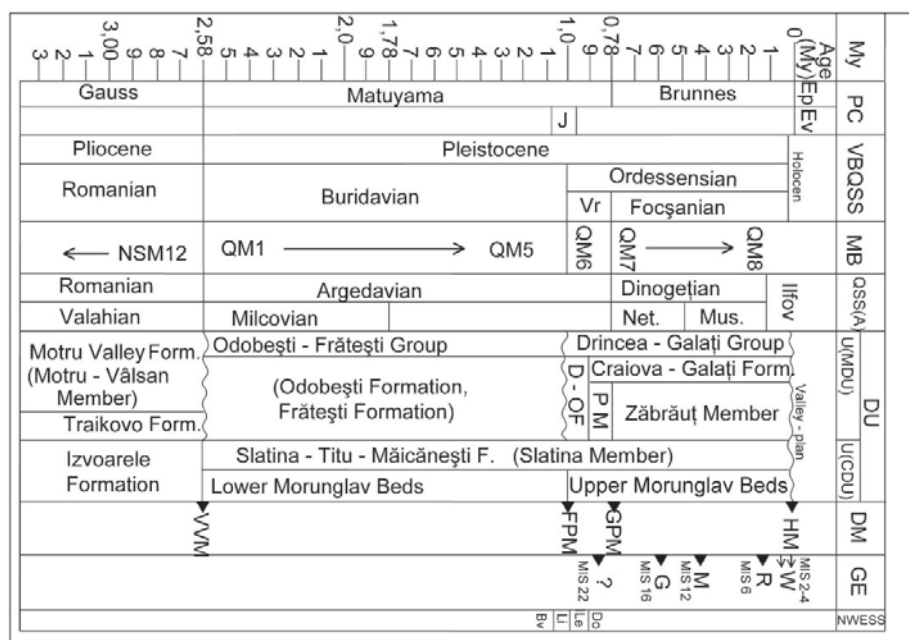


Figure 2.



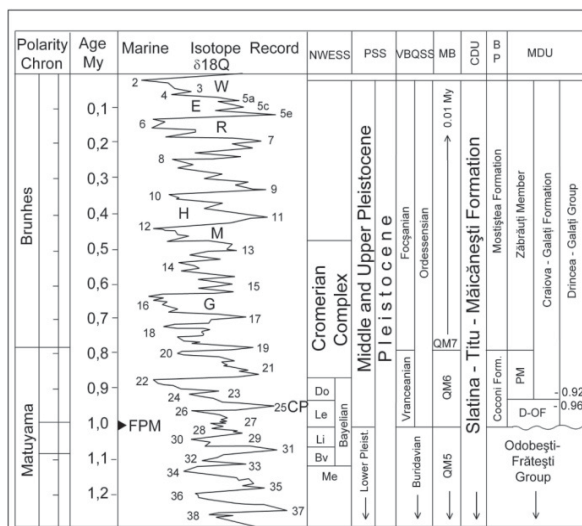


Figure 3.

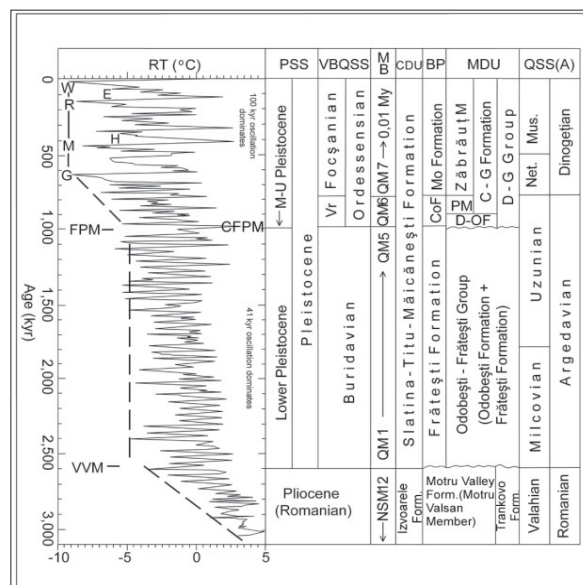


Figure 4.

Figure 1-4. Correlation in the Valah Basin - Explications (after Stanoiu, 2012-2013, 2013)

SVB – Stratigraphy of the Valah Basin; NWESS – North West European Stratigraphic Stages (Do – Dorst, Le – Leerdan, Li – Linge, Bv – Bavel, Me – Menopian – after Kolsoten and Gibard, 1996); PSS – Pliocene Stratigraphic Scale (after Steininger and Rogl, 1984); VBQSS – Valah Basin Quaternary Stratigraphic Scale (after Stanoiu 2012, 2013); H (VP) – Holocene (Valley-Plan); Vr – Vranceanian; MDU – Marginal Depositional Unit; NMDS – North Marginal Depositional Subunits; SMDS – South Marginal Depositional Subunits; CDU – Central Depositional Unit; VBR – Vrancea Bend Region; STMFP – Slatina-Titu-Maicănești-Focsani Perimeter; BP – Bucharest Perimeter; WB – West Bucharest; SD – South Danube; PC – Polarity Chron; RT (°C) – Relative Temperature (after Muller and MacDonald, 2008); GE – Glacial and Interglacial Events (G – Gunz, M – Mindel, H – Holsteinian, R – Riss, E – Emian, W – Wurm, after Husen and Reitner, 2011); DM – Discontinuity Moments (VVM – Vrancea Valah Moment, FPM – Focsani Pasaden Moment, GPM – Getic Pasaden Moment, H – Hierosus Moment – after Stanoiu 2012, 2013); QSS(A) – Quaternary Stratigraphic Scale (after Andreescu et al. 2011); MA(A) – Moluscs Biozones (after Andreescu et al. 2011); DOF – Drincea – Olt Formation; PM – Panciu Member; VN – Valah Nappe; MN – Moldav Nappe; MB – Moldav Basin; 0.92 and 0.96 My. (after Shalkopliias, 1983).

northern edge depositional subunit (Carpathian - Mateescu 1927; Stanoiu 2012-2013, 2013), dominated by Odobești Ambiance represented by Odobești Formation (Magura Odobești Member, Perșunari Member, Tetoiu Member), clearly discordant, of Buridavian age; 2) southern edge depositional subunit (Balkan - Liteanu 1952; Andreescu et al. 2011), dominated by Frătești Ambiance, represented by discordant Frătești Formation of Buridavian age. In Ordessensian (~1.0-0.01 My) marginal depositional subunit dominated by Valah Ambiance is represented by discordant Drincea-Galați Group (as a result of Focșani Pasaden Tectogenetic Phase), composed of discordant Drincea-Olt Formation (discordant red clay, corresponding to Leerdan Interglacial Event and Focșani Pasaden Climatic Moment) and periglacial Craiova-Galați Formation (loess – paleosol alternance), which began with Dorst Glacier Event and highlights a lower heterochrone limit and is predominantly discordant.

At the end of Buridavian, central depositional unit

expanded outward across Bucharest Perimeter as a result of Focșani Pasaden Tectogenetic Phase (~1.0My). The result was a predominantly clayey (Coconi Formation) and sandy-clay (Mostiștea Formation) deposits from Coconi - Mostiștea Group.

The depositional assembly of the Valah Basin is also valid for the Moldavian Basin (Dacic Basin: Saulea et al. 1969; Jipa and Morariu 2009).

## Conclusions

Quaternary (Pleistocene) from the external region of the Carpathian Orogene (integrated in Moldavides or Foreland Basin) belongs to Valah Basin (after the forming of the Valah Nappe, generated by the Vrancea Valah Tectogenetic Phase at 2.58 My.) corresponding to the Valah Cycle (Buridavian-Ordessensian, ~2.58-0.01 My), represented by undeformed and discordant continental deposits over to deformed Romanian

deposits which belong to Moldav Basin (Dacic Basin).

In the depositional complex of the Valah Basin are distinguished two major units: the central depositional unit, controlled by Dacic Ambiance, represented by thick sandy-clay deposits, without discordance, and the marginal depositional unit controlled by the Odobești-Frătești Ambiance. This is characterized mainly by gravels (in Buridavian age) and by existing two major discordances, controlled by Vrancea Valah Tectogenetic Phase (2.58 My.) and Focșani Pasaden Tectogenetic Phase (1.0 My)

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## ASSEMBLY AND CUMULATIVE ASSOCIATION OF THE BIG BIVALVES WITH THICK TESTS (MEGALODONTIDS) IN LIASSIC CARBONATES OF THE EXTERNAL TELL (OUARSENIS, ALGERIA)

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### Abstract

In the external Tell (alpine field) of Ouarsenis (Algeria), the Liassic carbonates are characterized by an assemblage of bivalves with thick tests enfeoff to proximal platforms. The analysis of this Megalodontids allowed to highlight several associations largely dominated by *Lithiotis*. Qualitative and quantitative evolution of Megalodontids depends closely on the dislocation of the initial carbonate platform, which, during Carixian period, the Lower and Middle Liassic occupied large areas within the Tethyan domain. This poses problems and blocking of the ecological exchange, and favore the appearance of the provincialism. These facts provide new complementary elements to previous knowledge on the behavior of foraminifera and their sensitivity to environmental conditions as well as physiographic and ecological changes that control their spatial and temporal distribution (spatio - temporal *Continium*). Although morphological and tratologic differentiation may reflect the isolation of certain groups in various environments of the same platform or makes difficult the communication with the open areas.

The evolution of marine populations within different environments is the consquence of the extensional tilted blocks that affected the initial carbonate platform architecture.

The strategy adopted by Megalodontids meets the constraints imposed by the complexity of the extensional tilted blocks. This has simultaneously conditioned some aspects of Liassic sedimentation and induced a very contrasted paleogeography..

In the higher areas, there are only small *Lithiotis* within the sedimentary fill of channels. The *Opisoma* are deposited on the banks and the rest of Megalodontids associated with gastropods are accumulated in disorder, forming bioaccumulation and/or in the umbilicus.

The platform limestones include various associations of these specialized forms: *Lithiotis* and *Lithioperla* (frequent; assemblage 1); large *Cochlearites* (rare; assemblage 2) and *Protodicerias*, *Opisoma* (common; assemblage 3). Always, these facies characterize shallow water deposits sometimes exposed to tidal conditions (1). They can form either accumulations within the filling of tidal channels, small bioconstructions (1 and 2) or layers (3). They can also be dispersed and dissociated by tidal current and storms (1).

**Keywords:** *Megalodontids, Association, Environment, Lias, Ouarsenis, Algeria*

## FORAMINIFERAL BIOSTRATIGRAPHY AND PALEOENVIRONMENTS IN THE NORTHERN PART OF THE EASTERN CARPATHIANS (TARCĂU NAPPE, ROMANIA)

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### Abstract

The studied Upper Cretaceous to Eocene formations are part of the northern Tarcău Nappe (Eastern Carpathians) and are represented by a turbiditic succession. Sixty-one samples were studied for biostratigraphic and paleoenvironmental purposes from the Putna Valley section.

Five types of foraminiferal assemblages were separated based on relative abundances of agglutinated taxa: *Nothia* assemblage (Late Cretaceous), *Karrerulina* assemblage (Early Paleocene), *Recurvoides* assemblage (Late Paleocene), *Glomospira* assemblage (Early Eocene) and *Reophax pilulifer* assemblage (Middle Eocene).

Five biozones of agglutinated foraminifera were separated based on acmes or stratigraphic ranges:

1. *Caudammina ovulum gigantea* Zone – defined by the first and last occurrence of the diagnostic taxon. It characterizes the Hangu Formation (Upper Maastrichtian).
2. *Rzehakina fissistomata* Zone – defined by the first and last occurrence of the diagnostic taxon. It is typical for the Izvor Formation (Paleocene).
3. *Glomospira* Zone – defined by the acme of the *Glomospira charoides* and *G. gordialis*. This bioevent is characteristic for the Early Eocene of the Straja Formation.
4. *Reophax pilulifer* Zone – defined by the acme of the diagnostic taxon. It is characteristic for the Middle Eocene Scorbura Formation.

Additional biostratigraphical data for the Late Cretaceous were given by *Heterohelix* species.

The distribution of agglutinated foraminifera morphogroups and the diversity values provide information on the evolution of the sedimentary basin during the Late Cretaceous to Middle Eocene. The settings were upper/middle bathyal during the Late Cretaceous, with low content of organic matter flux (tubular agglutinated

foraminifera are dominant). The Paleocene was defined by a deepening of the substrate (middle/lower bathyal to abyssal) as suggested by the dominance of coarse grained agglutinated foraminifera. The beginning of the Eocene was characterized by unstable middle bathyal settings with low sedimentary input (the *Glomospira* event is typically associated to this type of settings). The settings were upper bathyal during the Middle and Late Eocene (*Reophax pilulifer* acme suggests shallower settings).

The agglutinated foraminifera morphogroups (consisting mainly of coarsely agglutinated taxa like *Nothia*, *Rhabdammina*, *Rizammina*, *Hyperammina*) and the diversity analyses demonstrate that all foraminifera populations belong to the “flysch type” biofacies, typical for deep-water environments (Kaminski & Gradstein, 2005).

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## MOLASSES BASIN ANALYSES IN THE ADRIATIC FOREDEEP THE SEQUENCE STRATIGRAPHY

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### Abstract

The purpose of this work is to illustrate the principles of seismic facies analysis used in the interpretation of siliciclastic sedimentary rocks, especially in Molassic deposits. The recognition and definition of a seismic facies and the analysis of its vertical evolution (facies associations) lead to an environmental interpretation which can give useful information on both sedimentary facies and reservoir characteristics. With this aim, the major depositional systems ranging from continental to deep marine environments and the depositional elements in which they can be subdivided, will be briefly overviewed in terms of extension, geometry, continuity and lateral variations. For each of these systems, the major physical active processes during the deposition, the resulting sedimentary structures and their vertical and lateral evolution have been pointed out. The comparison between the environmental interpretation derived from bottom cores, well - logs and that derived from the current depositional models is used to predict the nature and distribution of reservoir and seal sealing rocks. All indicators data of multidisciplines (seismic, palaeontology, sedimentology, etc.) have been integrated. Based on the deep processing seismic lines, by interpreting the reflection terminations such as downlap, onlapp, toplap, erosional truncation, apparent truncation etc., is attained to identify:

- The sequence boundary of basal surface type (Sb<sub>1</sub> or Sb<sub>2</sub>)
- The boundary surfaces such as downlap, transgression and flooding surfaces
- System tracts and seismic facies within siliciclastic sequences

In each sequence is analysed the eustasy (sea level changes), the reflection configuration, such as sheet, hummocky, oblique, sigmoid, parallel to sub parallel, divergent, etc., the main facies and paleoenvironments. Due to base lap + toplap/ reflection configuration ratio, a certain numbers of seismic facies maps have been compiled. The correlation of depositional units is based on the combination of seismic stratigraphy data with biostratigraphic data. In local correlations, the well - logs are used as well. In a regional context, the microfacies and biozones, seismic facies and reflection terminations have been used as criteria in the evaluation of sequence boundaries, downlap surfaces, transgressive surfaces and maximum flooding surfaces. By means of seismic facies parameters, it is attained to individualize the genetic units, such as depositional sequences and system tracts. In Molassic formations, ten sequences of third and fourth orders are individualized, which correspond to the base of stages or respectively to the biozones bases. It happens to be more than two or three sequences in one stage, as in Tortonian, Lower Pliocene and Quaternary. Based on numerous seismic data and many well - logs, these sequences compound the most recognizable ones.

## INTRASPECIFIC VARIABILITY OF *BARBATODON TRANSYLVANICUS* (MAMMALIA: MULTITUBERCULATA) FROM THE HAȚEG BASIN (ROMANIA)

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### Abstract

Latest Cretaceous (Maastrichtian) multituberculate remains are scarce in Europe. The so-called “Hațeg Island” (Romania) is until now the only area where such fossils were found. Two genera are reported from this region: *Kogaionon* and *Barbatodon*, both belonging to the endemic family Kogaionidae. A single species of the genus *Kogaionon*, *K. ungureanui* (RĂDULESCU & SAMSON, 1996) is reported to date, while two species of the genus *Barbatodon*, *B. transylvanicus* (RĂDULESCU & SAMSON, 1986) and *B. oardaensis* (CODREA, SOLOMON, VENCZEL & SMITH, 2014) are known until now.

Herein, new *Barbatodon* remains from the Pui locality (Hațeg Basin) are reported, including the most complete dentaries with all cheek teeth rows found to date. The material was recovered from the red beds which are exposed in the riverbed of Bărbat River. *B. transylvanicus* is the single mammal reported from Pui.

The Hațeg Basin, located in the Southern Carpathians is already notorious for the terrestrial Maastrichtian deposits bearing peculiar vertebrates, dominated by dwarf dinosaurs. Francisc Nopcsa, at the end of the 19<sup>th</sup> century was the first paleontologist that brought on this peculiar fauna. The basin started to evolve hard upon the latest Cretaceous tectogenesis (“Laramian”).

Pui is the south-easternmost locality where Maastrichtian continental deposits dominated by red beds are exposed. The fluvial origin of these deposits was already pointed out by Nopcsa's first studies. The Pui commune is located about 20 km southeast from the town of Hațeg, in Hunedoara County. The locality is crossed by the Bărbat River. In the riverbed, the red beds can be observed due to river stream erosion.

The age of these deposits is Early Maastrichtian, as documented by pollen or microvertebrates, but also by paleomagnetic studies (beginning of the C32n.1n - end of the C31n Chrones).

The new material from Pui provides new data concerning the dentition, and also about the dentary morphology of *B. transylvanicus*. It opens new opportunities for comparisons with *Kogaionon*. Intraspecific variability is reported in *B. transylvanicus* dentition such as the different cusp formula of m1 (3-4:3), M1 (3-4:4:2), M2 (2:3-4), p4 (10-11 serrations) based on the new remains. Also differences are reported herein, in the general shape and length of the dentary. The size variability of the teeth allows estimations of teeth size variability for this species. All these differences are here interpreted as intraspecific variability.

The origin of kogaionids is still under debate. Due to the lack of other multituberculates from the latest Cretaceous of Europe it is difficult to assume which are the ancestors of this peculiar group. It is possible that the island acted as a refuge for these endemic mammals and as a result, a high local diversification of the group could occur. There is a similarity with the Hațeg dinosaurs, which also bear primitive characters.

Despite the fact that the origin of kogaionids is still unclear, we may notice a Westward direction of their dispersal in Cenozoic. After the K/T boundary, kogaionids are reported so far from the earliest Paleocene of Spain, the Middle Paleocene of Belgium and the Late Paleocene of France and Romania.

## THE PERMIAN AND TRIASSIC IN THE ALBANIAN ALPS

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### Abstract

The Albanian Alps are formed by a succession of stacked thrust sheets overriding the Cukali Zone. The lowermost thrust sheet contains Permian to Middle Triassic rocks, whilst the second contains Lower Triassic to Jurassic rocks. We describe the part of the sedimentary succession of Permian to Middle Triassic, and we consider it as a part of the Adria passive margin.

A carbonate ramp deepening towards NE, developed during the Middle Permian, was intersected by a significant block faulting with carbonate breccia deposition. The Lower Triassic and the Lower Anisian were characterized by huge terrigenous deposit with cobble conglomerate levels up to 80 m-thick, linking this area with the equivalent area in southern Montenegro. We recognize here for the first time a fan with very coarse detritus. Gradually, the clastic sedimentation has ceased during the Pelsonian and a wide calcarenitic ramp was formed in the area, with small local build up. Basin-ward, the red nodular limestone

of the Han Bulog Formation, were interbedded with the calcarenitic layers coming from the ramp. The drowning to more open conditions occurred towards the end of the Pelsonian in the basinal area and later on the more internal parts. Subsequently, cherty limestone and tuffitic layers are spread on the whole area. Towards the end of the Ladinian, with the end of the volcanic activity, red pelagic limestone occurred for a short interval. By the latest Ladinian or earliest Carnian, the area returned in shallow water conditions, with peritidal carbonate platform. In the Theth area, an internal lagoon with black organic rich dolostone and limestone was developed and it seems to be unique in that part of the Adria passive margin.

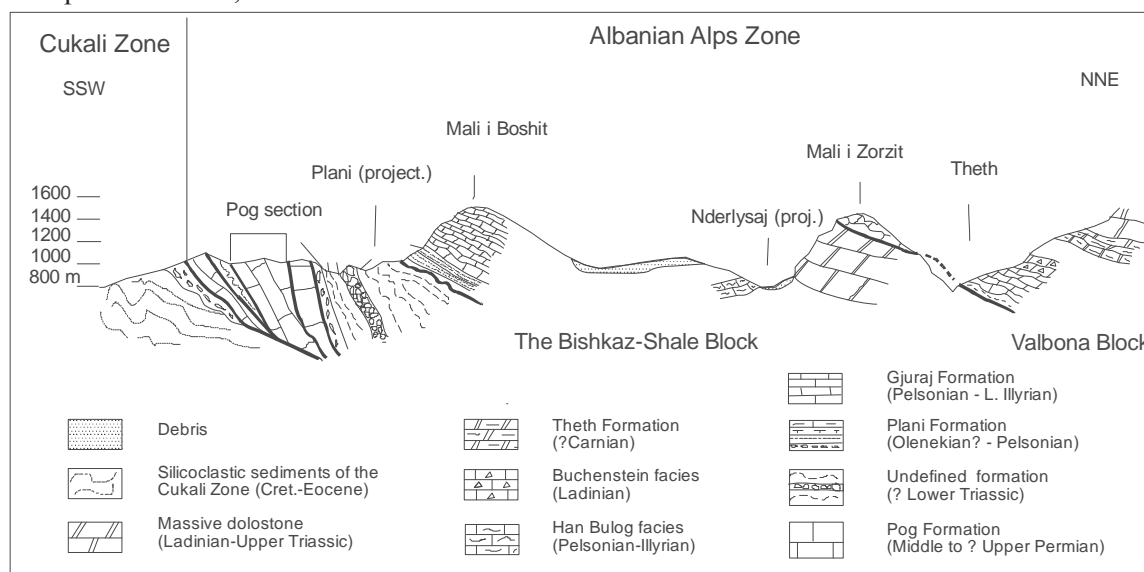


Figure 1. Cross-section through the lower part of the Albanian Alps edifice.

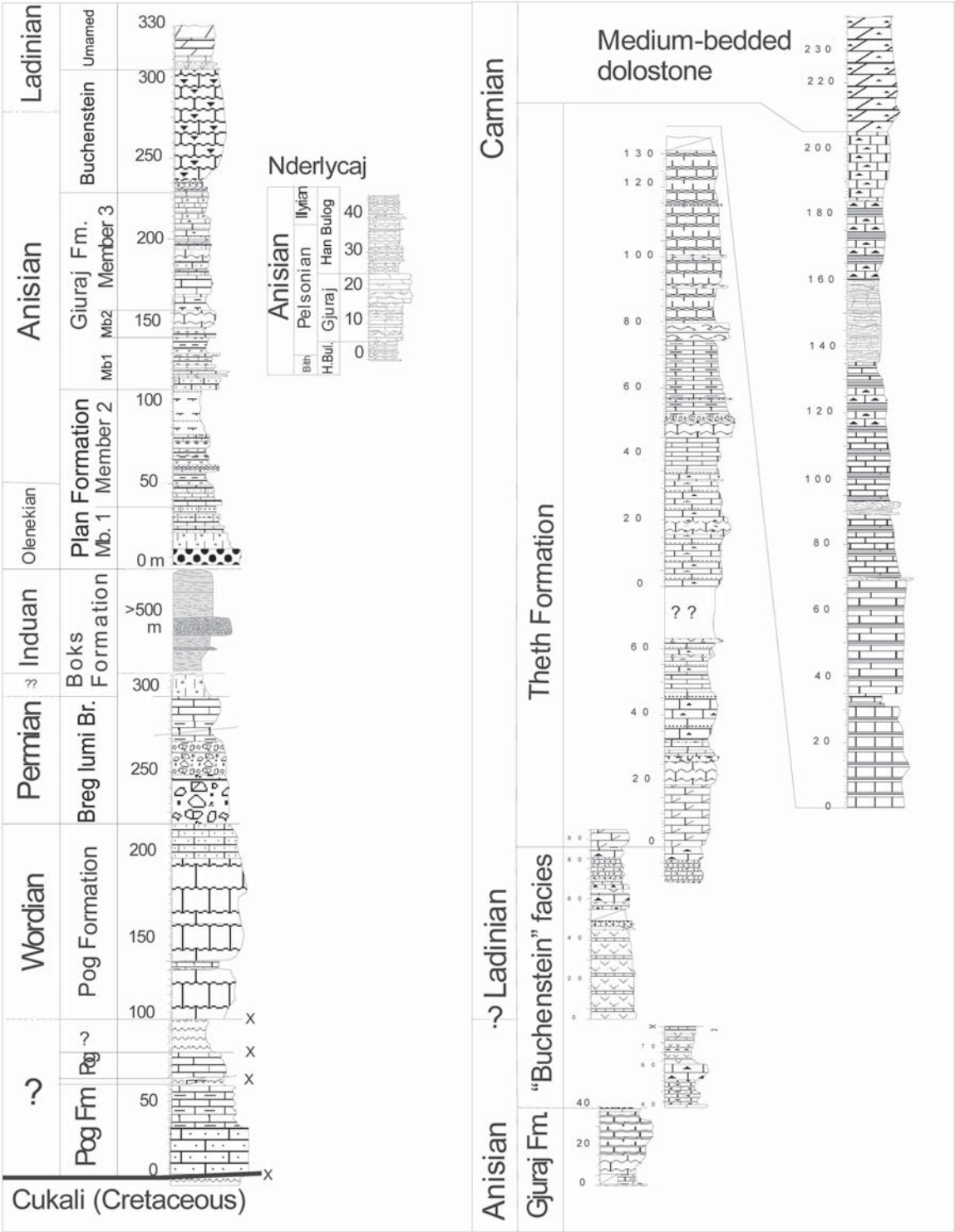


Figure 2. To the left, the synthetic log of the Bishkaz Shala Block and to the right the synthetic log of the Valbona Block.



## LATE GLACIAL AND HOLOCENE ENVIRONMENTAL DYNAMICS IN THE SOUTH-EASTERN FOOTHILLS OF THE UKRAINIAN CARPATHIANS: PALAEOONTOLOGICAL AND LITHOLOGICAL DATA FROM THE SUKHY CHAMBER OF BUKOVYNKA CAVE

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### Abstract

Results of a palynological and lithological study of clastic sediments in the Bukovynka Cave, supported by mammal remains, show vegetational and climatic changes during the Late Glacial and Holocene, in the south-eastern part of the Ukrainian Carpathians. Boreal birch-pine forests existed during the Allerød and Young Dryas and habitats for *Ursus arctos* (<sup>14</sup>C 10730 ±60 BP). The spread of wet-loving conifers during the Allerød indicates a humid climate. The increase in the NAP, *Pinus cembra* pollen and spores of arcto-boreal species of Lycopodiaceae give evidence of a drier and colder climate during the Young Dryas. The few pollen of broad-leaved taxa in the Late Glacial deposits indicate the presence of refugia with such species in the Southern Carpathians. The first half of the Mid-Holocene is marked by the spread of diverse broad-leaved taxa and an increase in clay weathering indices (indicating a mild climate). At the end of Mid-Holocene and the Mid-Subboreal, the diversity of broad-leaved trees and mesophytic herbs strongly decreased. The climate became drier, which is also confirmed by the presence of bones of steppe rodent, *Marmota bobak*. The Subatlantic (after a palaeomagnetic marker at 2800 BP) is represented in the Sukhy Chamber by a cool and wet phase at the beginning, a warm phase between 2000 and 1000 yr BP, the Little Ice Age and the modern warm phase. The beginning of agriculture is marked by the appearance of cereal pollen immediately before 2800 BP (the Late Bronze Age).

**Keywords:** *palynology, palaeontology, cave sediments, palaeoclimate*

### Introduction

The Bukovynka Cave is located in the village of Stal'nivtsi (Chernivtsi region), on the IV terrace of the River Prut. The present-day vegetation is

meadow-steppe surrounded by *Carpinus-Quercus* forest. This artesian cave, formed in the Miocene gypsum strata, has a Quaternary clastic infilling. The study of the deposits and mammal taphonomy in the cave (in the Trapezny Chamber) has been carried out by Vremir et al. (2000), Ridush (2004), whereas palaeomagnetic research and its palaeoenvironmental implication (in the Sukhy Chamber) has been provided by Ridush and Bondar (2011). This paper gives results of pollen, mammal and grain-size studies in the Sukhy Chamber deposits. In the section studied, the <sup>14</sup>C-date 10 730 BP corresponds to the Younger Dryas and the palaeomagnetic date 2 800 BP marks the end of the Subboreal (see Fig.1). In the Chernivtsi region, pollen study of the Holocene has been previously performed on flood-plain deposits of the River Prut: the Onut site without 'absolute' dates (Artyushenko et al. 1982). The Last Glacial palynology is studied for the first time.

### Material and Methods

20 samples from clastic cave sediments (2.35 m thick) have been subjected to pollen and grain-size analyses, the latter using the 'pipette' technique of Kachinsky (1965). In order to get pollen from clastic sediments, the following technique has been applied: treatment with 10% HCl, 10% KOH, cold treatment with HF, disintegration in a solution of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and separation in heavy liquid (CdI<sub>2</sub> and KI) with a specific gravity 2.2. The abundance and good preservation of pollen give show that the cave chamber turned periodically into a sedimentation trap. Re-deposited pollen occurs very rarely. Mammal bones are mostly well preserved. The uppermost sample of the sediments shows a much larger proportion of *Pinus* pollen than in the surface samples from the cave entrance. The high proportion of *Pinus sylvestris* pollen in the surface soil samples (30-40%) also does not correspond to the limited role that pine has in the modern vegetation. Thus, our interpretation

is that pine pollen is over-represented because of its ability to travel farther on the wind than other pollen and its better preservation in rocks.

## Results and Discussion

**The Late Glacial.** At the bottom of the Sukhy Chamber section (2.35-1.95 m), there are sediments of fluvial origin (81-91% of fine sand, small admixtures of clay, silt, and coarse sand). Arboreal pollen (AP) of a rather diverse composition prevails. Despite boreal trees (*Pinus sylvestris*, *P. cembra*, *Picea*, *Abies*, *Alnus*, *Betula*) being strongly dominant, a few pollen grains of broad-leaved taxa (*Ulmus*, *Acer*, *Corylus*) also occur. Pollen of wet-loving coniferous trees (*Picea*, *Abies*, *P. cembra*) indicates that the climate was rather humid. This is confirmed by the pollen diversity of mesophytic herbs. The predominance of Cichoriaceae in the non-arboreal pollen (NAP) was evidently controlled by the strong disturbance of soils around the cave. The simultaneous presence of pollen of cold-loving *Pinus cembra* and broad-leaved species shows that the vegetation was of an interstadial type. The deposits were formed during the Alleröd, as shown by  $^{14}\text{C}$ -date obtained from the *Ursus arctos* bones in the overlying layer. The climate was cooler and wetter than nowadays. Pollen of *Pinus cembra* and *Corylus* also occur in Alleröd deposits in the central Ukrainian Carpathians (Chumak 2012). The early appearance of broad-leaved taxa might indicate their refugia in the Southern Carpathians. Light loams with a high content of large silt ('loess') particles (76-79%) are present in the interval 1.95-1.65 m. Their formation occurred through the strong input of aeolian dust during the Younger Dryas ( $^{14}\text{C}$  10 730 $\pm$ 60 BP). Pollen of wet-loving *Abies*, *Picea* and warmth-loving broad-leaved trees disappear or occur rarely, whereas the pollen frequency of *Pinus cembra*, shrubs (*Juniperus*, Malaceae, Rhamnaceae) and NAP increases. Arcto-boreal forms of Lycopodiaceae indicate that the climate of the Young Dryas was cold and dry. Birch-pine forest still existed, as is also confirmed by presence of *Ursus arctos* bones.

**The Holocene.** Holocene sedimentation started with formation of a layer of fluvial origin (1.65 -1.50 m), which contains 90% of sand particles. The appearance of the pollen of diverse broad-leaved taxa (*Carpinus*, *Quercus*, *Ulmus*, *Fraxinus*) indicates the Mid-Holocene age of these deposits. Obviously, Early Holocene sediments were

removed by erosion. Judging from the further increase in pollen diversity of warmth-loving taxa (*Fagus*, *Tilia* and *Cornus* appear), the reddish-brown loam (1.50 -1.35 m) also belongs to the Mid-Holocene. High humidity is indicated by re-appearance of pollen of *Abies* and *Alnus*, and an increase in Ericaceae and Polypodiaceae. The climate was warmer than nowadays. Modern human impact might be the reason for the smaller proportion of broad-leaved tree pollen in the surface soil sample, as compared to the Mid-Holocene spectra. The next phase is represented by dark-brown loam (1.35-1.15 m) with dominance of large silt particles (77-79%), fragmented bones and coprolites. The pollen diversity of broad-leaved trees decreases (*Ulmus* prevails), as do the frequencies of wet-loving Ericaceae and Polypodiaceae. Asteraceae and Cichoriaceae pollen prevailed over mesophytic herbs. This indicates an increase in aridity, which is also confirmed by presence of undisturbed bones of the stepperodent *Marmota bobak*. Dry phases occurred in Ukraine during the end of Late Atlantic and in the Middle Subboreal (Gerasimenko 1997). Areas of open-steppe landscapes existed around the site. The succeeding phase is also represented by dark, coarse silt loam (1.15 - 0.90 m) which is separated from the underlying unit by a thin sand bed. The distinctive palaeomagnetic event recorded at this level is correlated with the 2800 BP excursion of the Ukrainian Holocene magnetostratigraphic framework (Ridush, Bondar 2011), i.e. with the Late Subboreal. The climate of this time was humid (Artyushenko et al. 1982; Gerasimenko 1997). In the Sukhy Chamber, the increase in precipitation is marked by the appearance of *Picea*, *Abies*, Ericaceae, Polypodiaceae and the increase of pollen of mesophytic herbs and broad-leaved taxa (*Carpinus*, *Quercus*, *Tilia* and *Corylus*). In the Central Ukrainian Carpathians an *Abies* peak also occurred in the Late Subboreal (Chumak 2012). The appearance of cereal pollen indicates the beginning of intense agricultural activity during the Late Bronze Age.

A further increase in pollen diversity of wet-loving plants (*Abies*, *Picea*, *Pinus cembra*, *Alnus*, *Fagus*, *Carpinus* and Cyperaceae) occurs in the sandy loams (19-20% sand particles, 62-69% coarse silt) at 0.90-0.68 m. This indicates a rise in precipitation and decline in temperature. The next phase, in dark-brown loams (0.68-0.35 m), is marked by the maximum pollen frequencies of broad-leaved

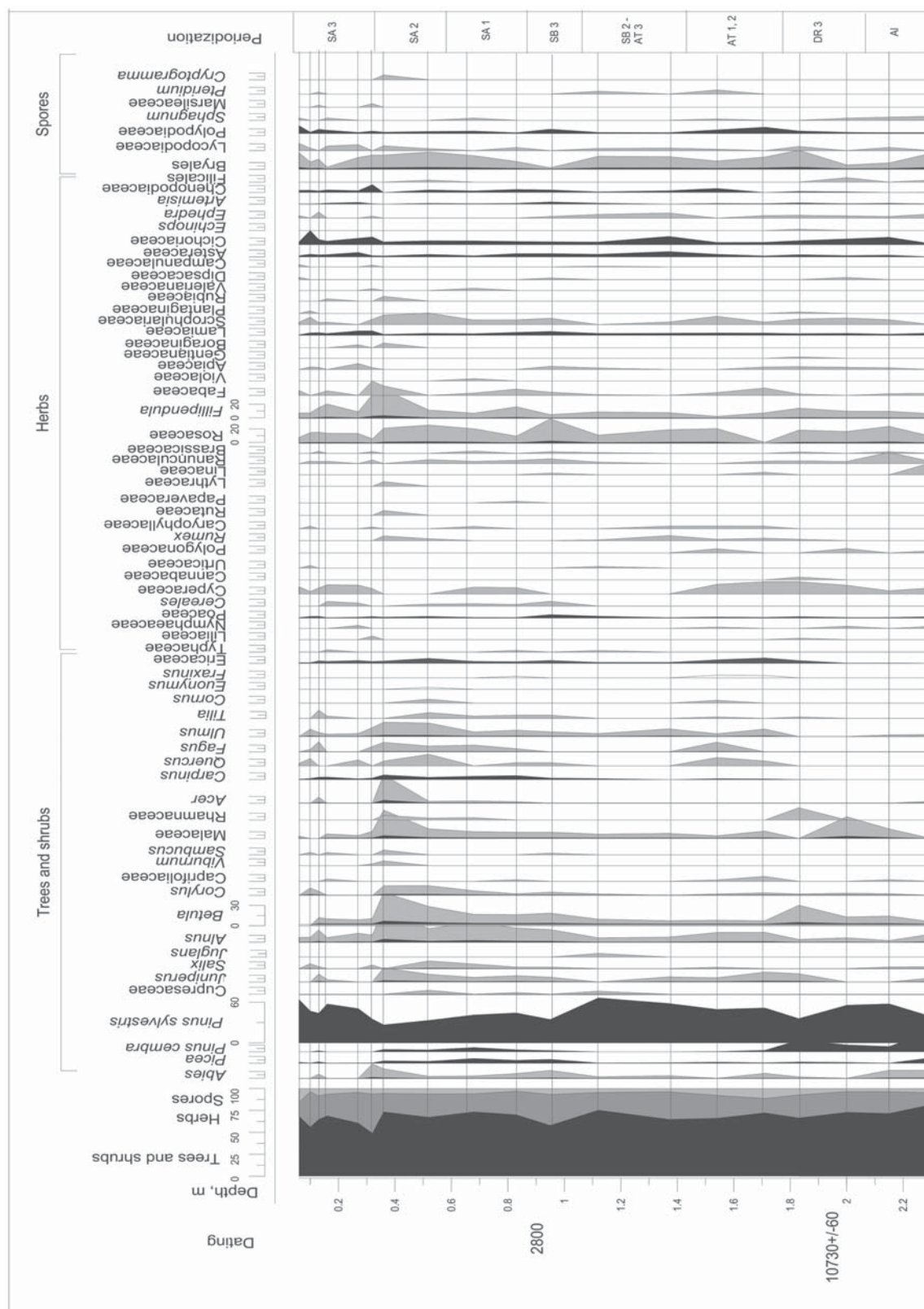


Figure 1. Pollen diagram of the Bukovynka site (The Sukhy Chamber)

trees and bushes, as well as an increase in coarse silt particles (73-81%). As both units are located above the 2800 yr BP marker, they are correlated with the Early and Mid Subatlantic. In Ukraine, the beginning of the Early Subatlantic (2600-2300 BP) was cool and wet, whereas two very warm phases occurred at the end of Early Subatlantic and in the Middle Subatlantic, between 2000 and 1000 yr BP (Gerasimenko 1997). Between 0.35 and 0.16 m, the light-coloured loam also contains a large proportion of coarse silt (76-85%), but the pollen composition is quite different. Pollen of wet-loving plants disappears (with the exception of hydrophytes), and the NAP (particularly of *Chenopodiaceae*, *Asteraceae* and *Cichoriaceae*) reaches its maximum. This dry and cool phase corresponds to the Little Ice Age (700-200 yr BP). Above is a dark-brown loam (0.16-0.10 m) with coarse silt (68-77%), which is separated from the underlying unit by a thin bed with 75% of sand grains. Based on pollen, frequencies and diversity of broad-leaved trees (including wet-loving ones) increased at this time, possibly during warming after the Little Ice Age. The last unit is a thinly laminated loam with a large content of sand particles (20%). The increase in NAP and wind-blown pine pollen seen in the upper units obviously corresponds to intense forest clearance in the area.

## Conclusions

The study of the sedimentary archive in the Bukovynka Cave provides important data on the biota and climatic development of the south-eastern foothills of the Ukrainian Carpathians during the Late Glacial and Holocene. The results of parallel pollen and grain size analyses corroborate one another in their palaeoenvironmental implications and show the following vegetational and climate changes: boreal forest during the Alleröd; forest-steppe under a colder and drier climate during the Young Dryas; temperate forest in the humid Mid Holocene; forest-steppe under the drier climate at the end of Mid Holocene and Mid Subboreal; broad-leaved forest under a wet warm climate in the Late Subboreal; mesophytic forest in a wet cool climate at the beginning of the Subatlantic (after 2800 BP); mesophytic broad-leaved forest in the mild climate between 2000 and 1000 yr BP; the decrease in number and diversity of broad-leaved trees during the Little Ice Age, and, finally, the modern warm phase with the forest-steppe, affected by intense forest clearance.

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## VEGETATION AND CLIMATIC CHANGES IN THE EASTERN FOOTHILLS OF THE CARPATHIANS BASED ON POLLEN DATA FROM THE UPPER PALEOLITHIC SITE DOROSHIIVTSI III (UKRAINE)

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### Abstract

Pollen, lithostratigraphy, palaeontology and archaeology of the Upper Pleniglacial deposits (12 m thick) in the Doroshivtsi III section (Chernivtsi region) have been studied in detail, and they show multiple environmental fluctuations in the Middle Dniester valley during the second half of the Late Pleniglacial. Prior the LGM, periglacial tundra-steppe on loams alternated with subperiglacial forest-tundra-steppe and boreal forest-steppe on humic soils (<sup>14</sup>C 22 330 BP). During the LGM, the periglacial climate got wetter, but colder (cryophytes spread more extensively): tundra with steppe vegetation elements on gleyed loams (<sup>14</sup>C 20 976 BP) alternated with forest-tundra and forest-tundra-steppe on gley soils (<sup>14</sup>C 20 504 BP). After the LGM, north-boreal forest-steppe on incipient soil was replaced by tundra-steppe on loess. Seven Upper Paleolithic layers (the Gravettian culture) occur within the described deposits, and most of them are connected with warmer phases. The fauna of all cultural layers is dominated by *Mammuthus primigenius* and *Rangifer tarandus*. Dofinivka times (18-15 kyr BP) were marked by alternation of interstadials (boreal forest-steppe on humic soils df<sub>1</sub> and df<sub>2</sub> and subperiglacial forest-steppe on incipient soils df<sub>3</sub>) and stadials (subperiglacial and periglacial steppe on loesses). During Early Prychernomorsk times (15-13 kyr BP), periglacial tundra-steppe re-appeared on loesses. A few pollen of broad-leaved trees occur in the df<sub>1</sub> and df<sub>2</sub> palaeosols, whereas they are absent in the plain part of the Middle Dniester valley. This enables to suggest that small refugia for broad-leaved trees could have existed in the Eastern Carpathians during the Pleniglacial.

**Keywords:** Late Pleniglacial, palynology, stratigraphy, palaeoclimate

### Introduction

The Upper Paleolithic site Doroshivtsi III is the most complete section of Late Pleniglacial deposits in the eastern foothills of the Ukrainian Carpathians. It is located on the II terrace of the right bank of the River Dniester in Doroshivtsi village (Chernivtsi region). The lithostratigraphy and <sup>14</sup>C-chronology of the section were first described by P. Haesaerts (Kulakovska et al. 2011; Haesaerts et al. 2013). The section (12 m thick) represents a cyclic alternation of palaeosols and pedosediments with non-soil deposits. The lower part of the section (12m-6m) consists of sandy loams and tundra gleys, and the upper part includes loess-like loams and thin humic soils. <sup>14</sup>C-dates from the lower part of the section (22 330, 20 976, 20 740 BP) give evidence that it was formed during the LGM. According to the Quaternary stratigraphical framework of Ukraine, this corresponds to the cold Bug unit. Seven Upper Paleolithic layers occur in this unit, and the layers 3, 4 and 6 (see Fig. 1) are particularly rich in the Gravettian artefacts. The fauna of all cultural layers is dominated by *Mammuthus primigenius* Blumenbach and *Rangifer tarandus* L., and only few bones of *Alopex lagopus*, *Canus lupus* and *Equus* sp. have been found.

### Material and Method

34 samples from palaeosol and non-soil units in the depth interval 2.5-8.0 m have been palynologically analyzed. In order to get pollen from clastic sediments, the following technique has been applied: treatment with 10% HCl, 10% KOH, cold treatment with HF, disintegration in a solution of sodium pyrophosphate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>), and separation in heavy liquid (CdI<sub>2</sub> and KI) of specific

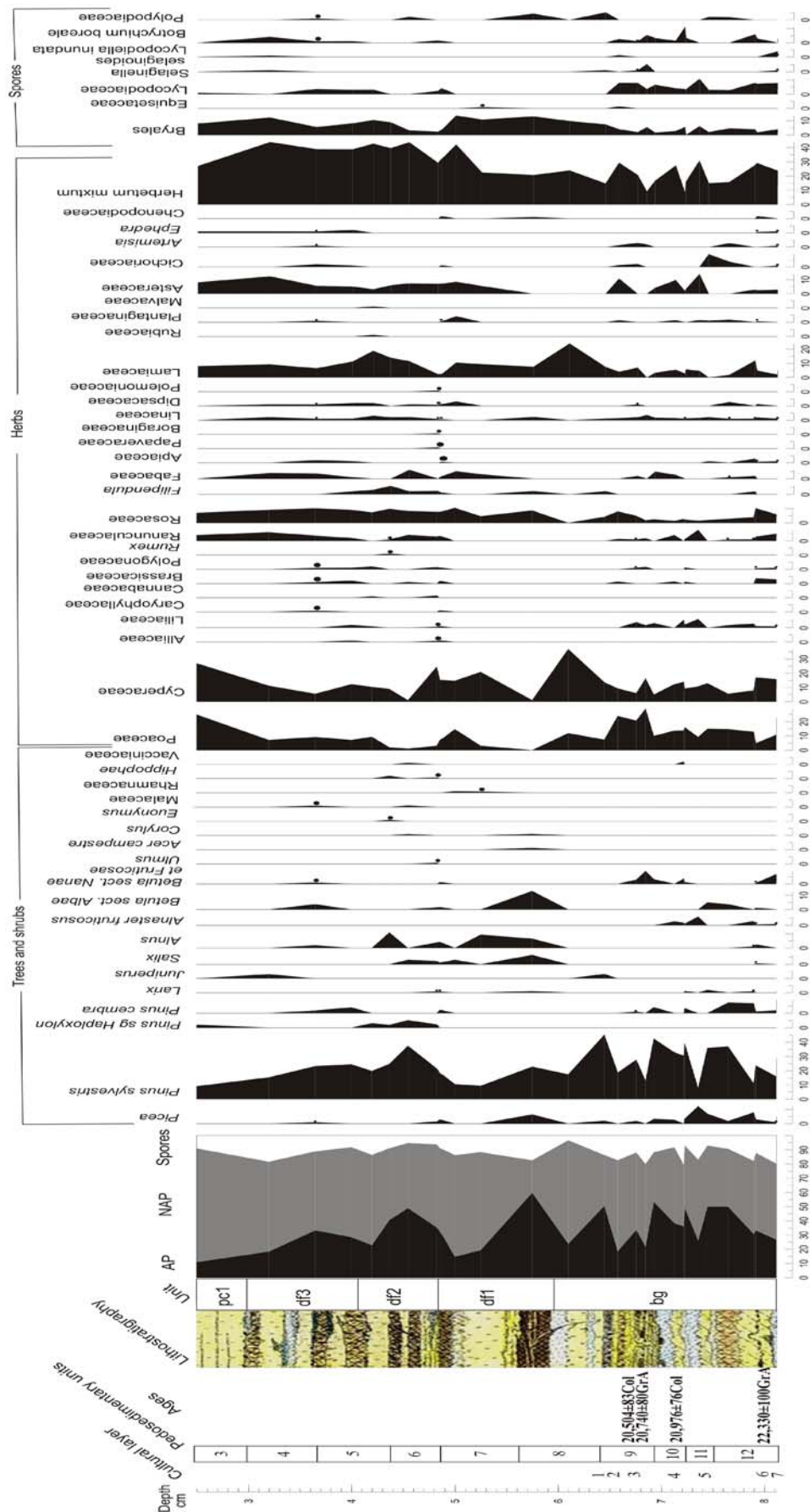


Figure 1. Pollen diagram of the Doroshivtsi III site

gravity 2.0 and 2.2. A sufficient number of pollen grains could be calculated only from 100-200 g of sediment. The pollen is mostly well preserved. Most of the samples contain re-deposited pollen grains of Pinaceae which strongly differ in their preservation compared to the air-borne pollen. The presence of re-deposited pollen shows the impact of colluvial (or even fluvial) factors on the sedimentation processes at the site. Small numbers of diatoms in many samples indicate a significant amount of ground moisture during sedimentation.

## Results and Discussion

**Bug times.** In the sandy loam at the base of the section, non-arboreal pollen (NAP) dominates and consists of mesophytic herbs and sedges. The AP (23-27%) includes that of arcto-boreal plants (*Betula* sect. *Nanae et Fruticosae*, *Alnaster fruticosus*) and boreal trees (*Pinus sylvestris*, *P. cembra* and few grains of *Picea*). Many spores of arcto-alpine plants occur (particularly from Lycopodiaceae family, *Selaginella selaginoides* and *Botrychium boreale*). The palaeovegetation was that of tundra-steppe (the percentages of Pinaceae pollen allows to suggest their transport from a far distance). Pollen from the Gravettian **layer 6** (22,300  $\pm$ 100 BP) indicates a slight climatic improvement. Few pollen of shrub *Betula* and *Alnaster fruticosus* occur. Pollen of pine and spruce become more abundant and other boreal trees (*Alnus*, *Salix*, *Larix* and *Betula* sect. *Albae*) are represented in the spectra. Arcto-alpine *Botrychium boreale*, *Lycopodium lagopus* and *Diphazium alpinum* grew, but boreal *Lycopodium annotinum* and Polypodiaceae also appeared. The vegetation was that of tundra-steppe, but trees grew more extensively in the protected river valley.

In the overlying humic soil, AP increases (50-53%), mostly at the expense of *Pinus sylvestris*, though pollen of *P. cembra*, *Picea*, *Betula* sect. *Albae* and few grains of *Larix* and shrub birches occur. Poaceae increases in the NAP, spores of arcto-alpine plants are abundant only at the base of the soil. The vegetation was represented by subperiglacial forest-steppe and, later on, by boreal forest-steppe. The climate became warmer. The dates (Fig.1) show that the soil was formed around 21 kyr BP, the same as other incipient soils in Europe (Damblon et al. 1996), including the Molodova site in the Dniester valley (Haesaerts et al. 2003). In the overlying loam (**cultural layer 5**), on the contrary, NAP prevails (mesophytic

herbs, sedges and grasses), the AP includes *Alnaster fruticosus* and shrub birches, spores are represented by arcto-alpine *Lycopodium lagopus*, *L. dubium* and *Diphazium alpinum*. Periglacial tundra-steppe spread during this time, though small refugia of *Picea* grew in the valley. Climate was cold, but relatively wet. Similar vegetation existed during formation of the overlying gleys and loams (**between the cultural layer 5 and 4**). Judging from the higher percentages of AP and arcto-alpine plants, the climate became even wetter and colder.

The gley bed with **cultural layer 4** (20,976 $\pm$ 76 BP) shows rather high AP percentage (49%) and includes *Pinus sylvestris*, *P. cembra*, *Picea*, *Alnaster fruticosus* and shrub *Betula*. Spores of only arcto-alpine Lycopodiaceae, *Selaginella selaginoides* and *Botrychium boreale* are present. The NAP includes sedges and mesophytic herbs. At this time, periglacial forest-tundra spread, with refugia of boreal trees in the valley. The decrease in AP and in palynomorphs of arcto-alpine plants in the overlying cryoturbated layers shows the drier and slightly warmer climate. The **cultural layer 3** (20,740  $\pm$ 80; 20,504  $\pm$ 83 BP) inserted in these loams, is characterised by low percentages of the AP (only far-transported pine pollen) and by an increase in Poaceae. There existed periglacial tundra-steppe with abundant arcto-alpine spore plants. The climate became drier. In the overlying humic soil (**cultural layer 2**), a slight increase in AP occurs (*Pinus sylvestris*, *P. cembra*, *Picea*, arboreal and shrub *Betula*). The NAP consists of grasses and mesophytic herbs, arcto-alpine Lycopodiaceae share dominance with boreal species. This indicates subperiglacial forest-tundra-steppe, and, thus, a wetter and slightly warmer climate. The last incipient Bug soil (**cultural layer 1**) shows a further increase in AP (pine, spruce and juniper), pollen of mesophytic herbs and sedges. On the contrary, a decrease in spores of arcto-alpine plants occurs and Polypodiaceae appear. There existed forests and meadows under a warmer north-boreal climate. Pollen from the last Bug sub-unit (a loess bed) is dominated by NAP (grasses and sedges), and only far-transported pine pollen occurs in the AP. Meadow-steppe in a cold and dry climate existed at this time.

**Dofinivka times** correspond to the interval 18-15 kyr BP (Matviishina et al. 1990). Three pedocomplexes of thin humic soils separated by loesses were formed during this time. The sub-units

df<sub>1</sub> and df<sub>2</sub> (Fig. 1) consist of the lower set of humic soils overlain by a loess. The soils have higher AP values (48-56%) than loesses (14-25%). The AP of the soils comprises pollen of boreal taxa (*Pinus sylvestris*, *P. cembra*, *Picea*, *Larix*, *Juniperus*, *Salix*, *Alnus*, *Betula*, Malaceae, Rhamnaceae and *Hippophaë*). A few pollen grains of broad-leaved forest taxa (*Ulmus*, *Acer campestre*, *Corylus* and *Euonymus*) occur. The presence of pollen and macrofossils of broad-leaved trees in the Upper Pleniglacial sediments has been shown in the eastern Pannonian Plain (Willis et al. 2000). This allows suggestion that in the Carpathian foothills, existed a few refugia for broad-leaved trees which started to produce pollen during the warmer phases that followed the LGM. During the cold phases, the pollen production stopped. During soil formation, open areas were occupied by mesophytic herbs and sedges, and during loess deposition by grasses, herbs and sedges. Spores of arcto-alpine plants occur in the loessed. Thus, during soil formation, boreal forest-steppe spread, and during loess formation, there existed periglacial and subperiglacial steppe. The sub-unit df<sub>3</sub> has cyclic alternations of incipient soils and loesses. As compared to the df<sub>1</sub> and df<sub>2</sub> soils, the soils of df<sub>3</sub> are poorer in AP, which includes mostly boreal taxa and a few arcto-boreal species. They were formed under subperiglacial forest-steppe with a mesophytic ground cover. The loesses were accumulated in periglacial steppe with elements of tundra vegetation, thus, under colder and drier climate.

**Prychernomorsk times** are represented by a loess bed, palynologically studied only in its earlier phase (15-13 kyr BP). The AP percentage is very low (11%) and includes only pine and juniper. The NAP is dominated by Cyperaceae and mesophytic herbs including the arcto-alpine *Dryas octopetala*. Spores of the cryophytes *Selaginella selaginoides*, *Botrychium boreale* and *Lycopodium lagopus* occur. This indicates the existence of periglacial tundra-steppe.

## Conclusions

Both pollen and pedolithology indicate multiple environmental fluctuations in the Middle Dniester valley during the Late Pleniglacial, and even through the LGM. During Bug times preceding the LGM, periglacial tundra-steppe on loams alternated with subperiglacial forest-tundra-steppe and boreal forest-steppe on humic soils. During

the LGM, the periglacial climate got wetter, but colder (cryophytes spread extensively): tundra with steppe elements on gleyed loams alternated with forest-tundra and forest-tundra-steppe on gley soils. During Bug times, after the LGM, north-boreal forest-steppe on incipient soil was replaced by tundra-steppe on loess. Dofinivka times (18-15 kyr BP) were marked by the alternation of interstadials (boreal forest-steppe on humic soils df<sub>1</sub> and df<sub>2</sub> and subperiglacial forest-steppe on incipient soils df<sub>3</sub>) and stadials (subperiglacial and periglacial steppe on loesses). In the Eastern Carpathians, there existed a few refugia for broad-leaved trees, which started to produce pollen at the df<sub>1</sub> and df<sub>2</sub> interstadials. In the plain part of the Middle Dniester valley, such refugia were absent (Bolikhovskaya 1995). During Early Prychernomorsk times (15-13 kyr BP), periglacial tundra-steppe re-appeared on loesses.

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## OLIGOCENE AND NEOGENE REGIOSTAGES OF THE CENTRAL AND EASTERN PARATETHYS IN UKRAINE (BASING OF BOUNDARY AND CORRELATION)

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### Abstract

New data obtained by integrated study of numerous sections of the Oligocene and Neogene in Ukraine taking into account all the published data, allowed us to substantiate regional stage division, boundaries and correlation of stratigraphic units of the Oligocene and Neogene within Paratethys and with the International stratigraphic scale.

**Key words:** *stratigraphic scheme, bio-, litho-stratigraphy, correlation, plankton, Oligocene, Miocene, Pliocene*

### Introduction

Location of Ukraine at the junction of major tectonic units - Alpine geosynclinal belt and the East European platform, predetermined the heterogeneity of structural-facial zonation and stratigraphy and difficulties of correlation.

Oligocene and Neogene sediments in Ukraine are constituents of the Central Paratethys (Balkans, Carpathians), the Eastern Paratethys (Crimean-Caucasian-Aral region) and Subparatethys (platform deposits in Northern Ukraine).

In order to work out, the detailed regional scale of Oligocene and Neogene of Paratethys, according to standards of the Stratigraphic Code of Ukraine (2012), the whole complex of regional, local and special units (regiostages, suites, layers, thicknesses, litho-, bio-, seismic-, magneto-stratigraphic) were used. Besides, main biostratigraphic markers, lithological, geochemical, seismic, cyclic ones have been applied for detailing stratification. The stages of the tectonic development of regions, global rebuilding boundaries in Oligocene and Neogene also have been taken in account. Particular attention was given to the problem of cyclicity of formational complexes. Different ranks of cyclic rhythms can be traced in various types of sections (continental, nearshore, marine). The influence of sedimentological and morphostructural factors (such as fault-block

tectonics, volcanic activity, including mud volcanism, alluvial cones and canyons, gravity processes, etc.) onto the stratigraphical structure has been analyzed. One more aspect of detailing stratigraphic structure is to identify sedimentary interruptions and unconformities in local, regional strata, diachronism of different rank boundaries, transitional boundary layers. The complex of methods including bio-, litho-, cyclo-, magneto-stratigraphic have been applied for justification of stratification and correlation.

### Materials and Methods

Based on the new data and numerous published data on microplankton, the correlation of the Oligocene and Neogene sediments of Ukrainian Paratethys have been conducted. The most complete sections of Oligocene and Neogene of the Carpathian region (Transcarpathian Depression, Folded Carpathians and Carpathian Foredeep), East European Platform (Volyn-Podolia, Dnepr-Donets Trough, Northern Pre-Black-Sea), Crimea, Kerch Peninsula and Azov-Black Sea area have been examined. Detailed analysis of the distribution of microfossils (planktonic foraminifera, nannofossils, dinocysts) in Oligocene and Neogene sediments of the Central and Eastern Paratethys enabled to establish marine plankton associations (correlation levels). These made it possible to justify the boundaries of Oligocene and Neogene, diachronism of lithostratigraphic units, perform a correlation within the Paratethys and show their relationship with the International stratigraphic scale (Gozhyk et al. 2013) (Fig. 1).

### Results and Discussion

Oligocene deposits of the Central Paratethys in Carpathian region are distinguished as Ombronian and Egerian regiostages including Menilite and Krosno series with subdivided local strata. They are Rupelian-Chatian-Aquitania-like Maikopian series as a whole. Oligocene deposits in Ukrainian part of Subparatethys are represented by Mezhygorian

and Berekian regiestages (Zosimovich, 2013). In the Black Sea Coast, Crimea, Kerch Peninsula, Azov-Black Sea area the Oligocene deposits are composed of Planorbella, Molochan, Kerleutian and Caucasian (Lower part) regiestages (Gozhyk et al. 2008, 2011; Ivanik 2003). Eocene-Oligocene boundary in these regions is substantiated by planktonic and benthic foraminifera, nannofossils, dinocysts, sponge spicules, and is placed between the Alma and Planorbella regiestages of Southern Ukraine, between Obukhov and Mezhygorian of Northern Ukraine, and between Karpian (Bystritska suite, its Eocene analogues) and Ombronian (Menilite and Krosno suites of lower part of Oligocene), in Carpathian region.

The Neogene deposits of Ukraine, in the area of Central Paratethys are upper part of Egerian, Eggenburgian, Ottnangian and Karpatian regiestages), Badenian, Sarmatian (Middle Miocene), Pannonian, Pontian (Upper Miocene), Dacian, Romanian (Pliocene).

Subparatethys Neogene consists of marine deposits (Novopetrovsk regiestage) and continental deposits (Poltavian sands of Lower-Middle Miocene, mottled clay horizon of Upper Miocene and red-brown clay horizon of Pliocene).

In the Eastern Paratethys, the Lower Miocene is represented by Upper Caucasian subregiestage, Batisifon regiestage; Middle Miocene by Tarkhanian, Chokrakian, Karaganian, Konkian and Sarmatian (partly) regiestages; Upper Miocene by Sarmatian, Meotian and Pontian regiestages; Pliocene by Kimmerian and Kuyalnikian regiestages.

The boundary of Paleogene and Neogene systems (Chattian and Aquitanian) in the Central Paratethys was established by three groups of microfossils (nannoplankton, planktonic foraminifera, dinocysts). It is placed in the middle part of the Egerian regiestage (upper part of Grushevska suite of the Transcarpathians, Krosno and Menilite suites of the Carpathians and Precarpathians). In Subparatethys, it is placed between Mezhygorian and Novopetrovsk regiestages. In the Eastern Paratethys, the boundary is set at the base of Upper Caucasian subregiestage (Andreyeva-Grigorovich, 2004).

The boundary of Lower and Middle Miocene (Burdigalian–Langhian) in the Central Paratethys is mainly transgressive and is placed between Karpatian and Badenian regiestages; within the

Transcarpathian basin is at the base of Tereshulsk conglomerates. In the Sambir zone of Carpathian Foredeep, is placed in the Balytska suite; in the Bilche-Volytsa zone of the foredeep and on the East European platform, is set at the base of the Bogorodchany and Opole suites. In the Eastern Paratethys of Ukraine, the boundary goes between Batisifon (Sakaraul and Kotsahur of Eastern Paratethys of Southern Russia) and Tarkhanian regiestages. It is fixed at the bottom of the Tarkhanian s.l. (Alma depression and the Black Sea). In the Kerch sections, this boundary is at the base of Kamyshlatsk layers of Lower Tarkhanian.

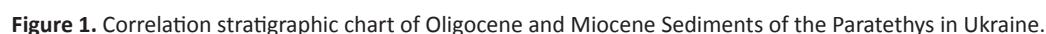
The boundary of Middle and Upper Miocene (Serravallian–Tortonian) is placed between the Sarmatian “sensu stricto” and Pannonian regiestages of the Central Paratethys. It is established in the sediments of Almaska suite of the Middle Sarmatian of Transcarpathians, in the lower part of the Berezhnitska suite (marine analog of Pannonian) of the Carpathian Foredeep and in the middle of Middle Sarmatian (Sarmatian regional stage s.l. of the Eastern Paratethys).

The boundary of Miocene and Pliocene (Messinian–Zanclean) is gone at the base of the Kimmerian sediments (Kimmerian regiestage) above Azov Layers of Pontian regiestage and is usually erosional (Semenenko, 1987; Semenenko et al., 2009).

The boundary of Neogene and Quaternary is set at the base of the Eopleistocene (1.8 MA). In the Central Paratethys, is the top of the Romanian regional stage between the Ilnytska and Chop suites. In the Eastern Paratethys, the boundary is set between the Kuyalnikian and Gurian and Akchagilian and Gurian and Apsheron regiestages (Gozhyk et al. 2013).

## Conclusions

Thus, the new data obtained by integrated study of numerous sections of the Oligocene and Neogene in Ukraine, taking into account all the published data allowed to substantiate regional stage division, boundaries and correlation of stratigraphic units of the Oligocene and Neogene within Paratethys and with the International stratigraphic scale.





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## PALEOECOLOGY AND BIOSTRATIGRAPHY OF THE OLIGOCENE FROM THE NW TRANSYLVANIAN BASIN (ROMANIA) BASED ON CALCAREOUS NANNOFOSSILS

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### Abstract

Previous studies of calcareous nannofossils in the Transylvanian Basin were done by Mészáros and Ghergari (1979), Mészáros (1984), Mészáros and Ianoliu (1989), Mészáros (1991), Melinte and Brustur (2008) and had the goal of establishing the stratigraphic sequences in the Paleogen and Neogene deposits from the NW Transylvanian basin. Mészáros and Ghergari (1979) and Mészáros (1984) have studied the calcareous nannoplankton assemblages, between Cuciulat and Hida Formations (Preluca area), with the goal of biostratigraphical calibration of Vima Formation, located between them. Based on calcareous nannoplankton, the Vima Formation, in Fântânele area, was considered to be Oligocene-Lower Miocene. In a later study, based on calcareous nannofossils, in Fântânele (Rohia), Mészáros (1991) establish the Oligocene/Miocene limit.

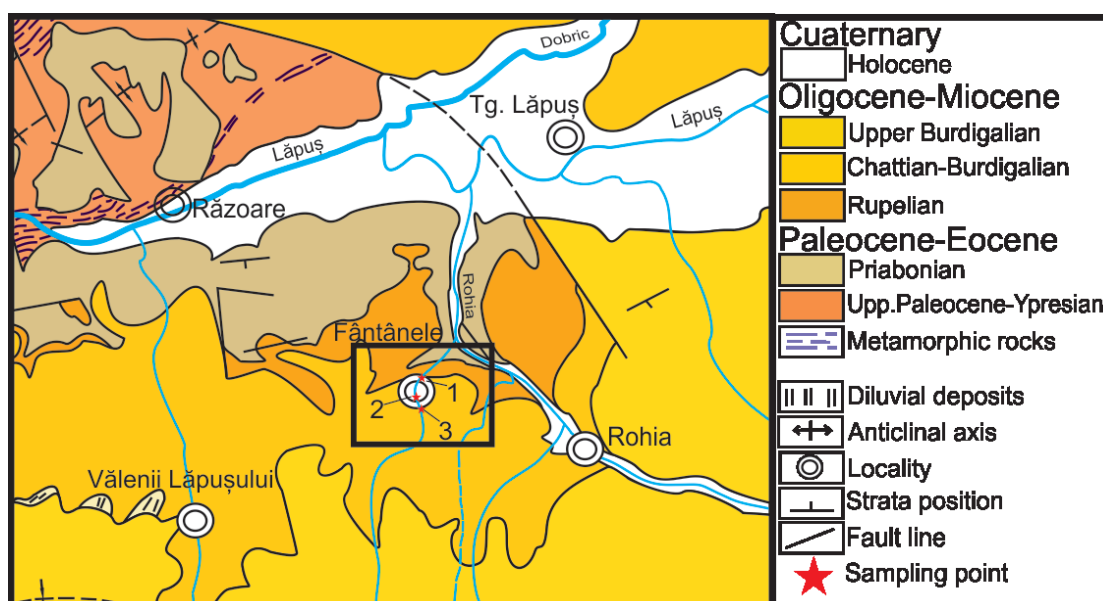
The Fântânele section is part of Vima Formation (Rusu 1969) and is located south of Preluca Masif (lat: N 47,41477 E 23,82699), in NW of

Transylvanian Basin (Fig.1). The Preluca area is characterized by continuous marine sedimentation within the Oligocene - Early Miocene interval (Melinte and Brustur 2008), which started in Early Oligocene (Rupelian) with the deposition of Cuciulat Formation (grey and brown marlstone and claystone), followed by the bituminous marls of Bizuşa Formation and by the bituminous shales of Ileanda Formation. The sedimentation continued in the Late Oligocene (Chattian) with Buzaş Formation (alternation of sandstone and marls), followed by the marlstones of Vima Formation. In the NE of this area, the Vima Formation replaced progressively the Buzaş Formation, being placed between Ileanda (in base) and Hida Formations (at the top).

**Key words:** Oligocene, NW Transylvanian Basin, calcareous nannofossils, biostratigraphy, paleoecology

### Materials and methods

The studied section is part of Vima Formation and consists of marly clays deposits alternating



**Figure1.** Geological map of Rohia-Fântânele area, page 3 Baia Mare 1:200 000 (redrawn after Giuşcă and Rădulescu, 1967).

with sandy clays and sandstones. A number of 75 samples from three outcrops (outcrop 1; lat. N 47,41477 E 23,82699, alt. 320 m, outcrop 2; located at with coordinates N 47,41356 E 23,82637, alt. 381 m and outcrop 3; lat. N 47,41195 E 23,82692 alt. 387 m), have been analysed from Fântânele section, for calcareous nannofossils study. The sampling was done at intervals of 10 cm, 30 cm and 50 cm. Smear slides for all samples were prepared using gravity settling technique (Bown and Young 1998).

## Results

The examined material contains good to poorly preserved calcareous nannofossil assemblages (Fig. 2), represented by specimens typical for Middle-Upper Rupelian and Chattian. The assemblages are generally dominated by: *Cycligargolithus floridanus* (up to 56.31 %), *R. minuta* (up to 49.09 % in 1<sup>st</sup> – 2<sup>nd</sup> profile and up to 84.64 % in 3<sup>rd</sup> profile), *Reticulofenestra lockeri* (up to 32.71%), *Reticulofenestra* gr. 3 – 5  $\mu$ m (up to 16.98 %), *R. bisecta* (up to 17.23 %), *Cy. abisectus* (up to 15.38 %), *R. stavensis* (12 %), followed by *Pontosphaera* which are represented by *Pontosphaera multipora*, *P. enormis*, *P. desueta*, *P. pygmea*. High percentages of *Braarudosphaera bigelowii* were observed in the upper part of 3<sup>rd</sup> profile. *Coccolithus pelagicus* reaches values up to max. 56.31%. Sphenoliths are very rare (up to 18.71%) and are represented by *Sphenolithus moriformis*, *S. predistentus*, *S. ciperoensis*, *S. distentus*. Continuously but in low number occur *Helicosphaera recta*, *H. intermedia*, *H. euphratis*. Rare and irregularly distributed are *Zygrhablithus bijugatus* and *Pyrocyclus orangesnis*. Stratigraphically important species *Chiasmolithus altus* and *Sphenolithus dissimilis* appear very rare.

## Interpretation

The absence of index species *Reticulofenestra umbilica* (NP16 – NP22), indicates that the lowest part of the section, respectively from sample 1 to 14, would belong to the NP 23 standard zone of Martini (1971), *Sphenolithus predistentus* Zone (Rupelian age). According to the FO of marker species *Sphenolithus distentus* in sample 7, we would suggest that the interval between samples 7 – 14 belongs to the upper part of NP23.

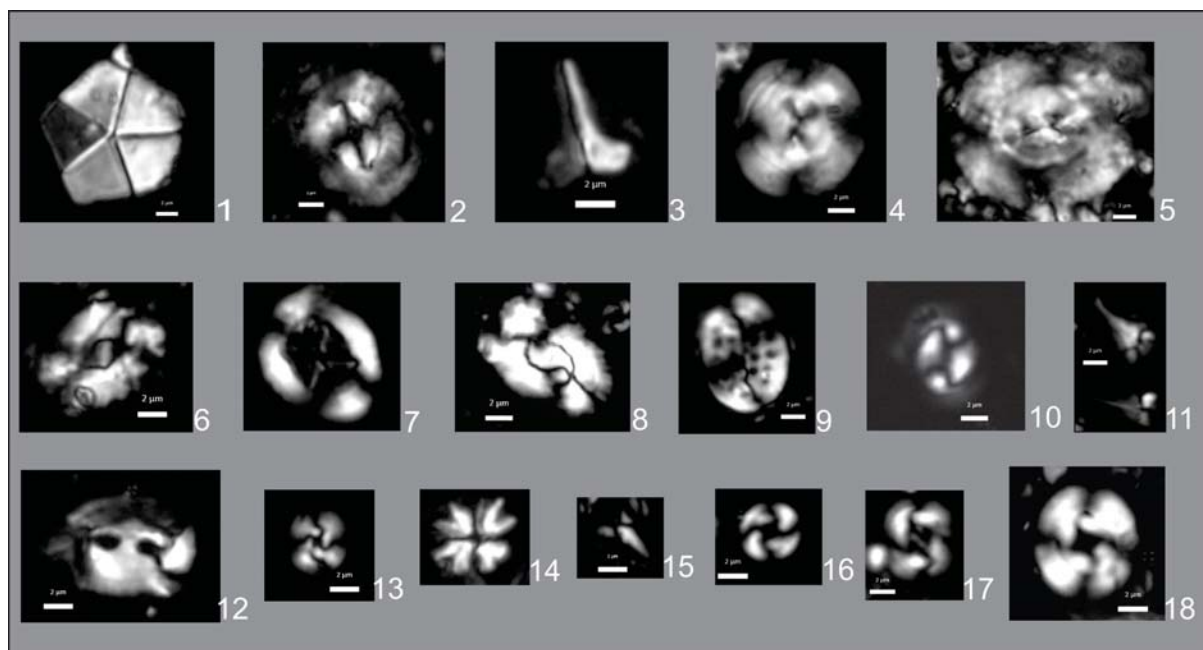
The boundary between *Sphenolithus predistentus* Zone (NP23) and *Sphenolithus distentus* Zone

(NP24) was observed in sample 15, at the FO of marker species *Sphenolithus ciperoensis*, in base of NP24 (Rupelian age). The boundary between biozones NP24/NP25 (Chattian age) was set by the LO of index species *Sphenolithus distentus* (in samples 34). As a result, the interval between samples 15 – 34 belongs to *Sphenolithus distentus* Zone (NP24). The interval between above sample 34 is attributed to the lower part of *Sphenolithus ciperoensis* Zone (NP25) (of Chattian age).

The following species were used for paleoecological interpretations: *Braarudosphaera bigelowii*, *Coccolithus pelagicus*, *Cyclicargolithus floridanus*, *Reticulofenestra* small, *Reticulofenestra* gr., *Helicosphaera* spp., *Pontosphaera* spp. Blooms of *B. bigelowii* in the uppermost part of the 3<sup>rd</sup> profile (samples F67 - F73), with more than 90 % of this species point to the fresh water influence (lower salinity) and high nutrient input. Blooms of *Pontosphaera* (*P. multipora* and *P. pygmea*) observed in the interval between samples F9 - F13 (the 3<sup>rd</sup> profile) were interpreted as shallowing. Higher percentages of *Cyclicargolithus floridanus* show episodes of stable marine environment. Sequences with lower percentages of *Coccolithus pelagicus* can be interpreted as lower nutrient input and warmer water temperature.

## Conclusions

The calcareous nannoplankton studied in Fântânele section, suggest that the material is of Middle-Upper Rupelian-Chattian age and is assigned to the nannofossils standard zonation of Martini (1971) upper NP23 - NP25. Stratigraphical attribution to Oligocene (NP23 to NP25) is confirmed by the absence of Miocene taxa. Quantitative results document fluctuations in water salinity, temperature and nutrient availability.



**Figure 2.** Calcareous nannofossils assemblage from Fântânele (Rohia) Section. All photographs are captured cross-polarized light.

1. *Braarudosphaera bigelowii* (Gran and Braarud 1935) Deflandre, 1947 (Sample 5); 2. *Coccolithus pelagicus* (Wallich 1877) Schiller, 1930 (Sample 20); 3. *Zygrhablithus bijugatus bijugatus* (Deflandre in Deflandre and Fert, 1954) Deflandre, 1959 (Sample 13); 4. *Reticulofenestra bisecta* (Hay, Mohler and Wade, 1966) Roth, 1970 (Sample 21); 5. *Reticulofenestra stavensis* (Levin and Joerger, 1967) Varol, 1989 (Sample F18); 6. *Helicosphaera euphratis* Haq 1966 (Sample 20); 7. *Chiasmolithus altus* Bukry and Percival, 1971 (Sample 20); 8. *Helicosphaera intermedia* Martini, 1965 (Sample 20); 9. *Pontosphaera multipora* (Kamptner, 1948 ex Deflandre, 1954) Roth, 1970 (Sample 18); 10. *Coccolithus pelagicus* (Wallich 1877) Schiller, 1930 (Sample 27); 11. *Sphenolithus distentus* (Martini, 1965) Bramlette and Wilcoxon, 1967 (Sample 17); 12. *Helicosphaera recta* (Haq, 1966) Jafar & Martini, 1975 (Sample 21); 13. *Cyclicargolithus floridanus* (Roth and Hay, in Hay et al., 1967) Bukry, 1971 (Sample 18); 14. *Sphenolithus moriformis* (Bronnimann and Stradner, 1960) Bramlette and Wilcoxon, 1967 (Sample 28); 15. *Sphenolithus ciperoensis* Bramlette and Wilcoxon, 1967 (Sample 18); 16. *Pyrocyclus orangensis* (Bukry, 1971) Backman, 1980 (Sample 4); 17. *Reticulofenestra lockeri* Müller, 1970 (Sample 28); 18. *Cyclicargolithus abisectus* (Muller, 1970) Wise, 1973 (Sample 20).

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## BIOSTRATIGRAPHY AND PALEOECOLOGY OF THE UPPER OLIGOCENE – LOWER MIOCENE CALCAREOUS NANNOFOSSILS FROM THE ALBANIAN-THESSALIAN BASIN (ALBANIA)

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### Abstract

The Albanian-Thessalian intermontane Basin represents a narrow and elongate marine basin composed of molassic deposits, which extends on the direction SE to NW, from the Thessaly in Greece, up to Devolli, Korça, Gora and Mokra reagions and further to the Librazhd, in Albania. Its substratum is represented by the deposits of Mirdita and Korabi zones. There are three distinct sedimentary molassic cycles: the first cycle was deposited during Middle Eocene, the second one comprise sequences from Middle Oligocene up to Lower Miocene, while the third cycle is Burdigalian to Langhian. The Oligocene to Miocene stratigraphic sequences have a thickness up to 4000 m. A number of samples from marls and silts were collected and analysed from section Bozdovec, situated near city of Korca.

Smear slides were prepared for all samples and quantitative analyses were performed by counting at least 300 specimens per sample. Different statistical methods were used for quantitative interpretations, with the goal of defining the paleoenvironmental changes using calcareous nannofossils assemblages.

The examined material contains good to moderate preserved calcareous nannofossil

assemblages, which are generally represented by: *Reticulofenestra minuta* (up to 70%), *R. bisecta* (up to 30%), *Cycligargolithus floridanus* (up to 19.67%), *Coccolithus pelagicus* (up to 17.5%), *Cy. abisectus* (up to 5%), *R. stavensis* (4%). The genus *Sphenolithus* reaches percentages up to 20.98 %, being represented by biostratigraphically important species like: *S. ciperoensis* (the marker species for top of *Sphenolithus ciperoensis* Zone NP25 and one of the index species LO which is used to define the Oligocene/Miocene boundary), *S. delphix*, *S. dissimilis*. The *Helicosphaera* genus is rare and discontinuous. We noticed the presence of: *Helicosphaera obliqua*, *H. recta*, *H. intermedia* and *H. euphratis*. Rare and irregularly distributed are: genera *Discoaster* and *Pontosphaera*, species *Ilseilithina fusa*, *Coccolithus miopelagicus* and *Zyghrabilithus bijugatus*.

For paleoecological interpretations were used: *Coccolithus pelagicus*, *Reticulofenestra minuta*, *Cycligargolithus floridanus* and *Sphenolithus* gr. High amount of *R. minuta* and *Sphenoliths* point to warm well stratified paleoenvironment.

**Key words:** Oligocene-Miocene, Albanian-Thessalian Basin (Albania), calcareous nannofossils, biostratigraphy, paleoecology



## SILURIAN CARBONATE PLATFORM PALAEOBIOGEOGRAPHY OF IRAN

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### Abstract

In terms of paleogeography, during the Silurian, the Iranian basin, has been located in the north of Gondwana and on the southern margin of Paleo-Tethys ocean. The silurian corals typical for the Iranian carbonate platform have been compared with silurian corals from other regions in the world. The whole assemblage typical for the platform carbonate settings from Iran show a high similarity with the assemblages from North America and North Asia.

**Keywords:** *Paleobiogeography, Silurian, corals, platform, Iran*

The paleogeography and the spread of Silurian rocks have caused the idea that because of vertical movements were caused the Caledonian events or the worldwide extension of glaciers and sea level fall. During Silurian, in Iran, the land had a much greater extent and that is why, the Silurian period is characterized by a gap in the sedimentary records. Nevertheless, some rocks have been reported as being of Silurian age in few regions of Eastern Alborz, Central Iran and south-east of Zagros. That is why, Nabavi (1955) believed that as a consequence of Caledonian tectonic event, the northern and north-western parts of Iran have been turned in land (Caledonian land). The eastern boundary of this land has begun from Aliabad and Gorgan and after passing through Semnan and Mahallat has reached Bakhtiari - Zardkouh Mountain, but the presence of Silurian rocks in Talesh region, made the location of this territory to be discussed (Fig. 1).

Silurian rocks in Iran are often represented by shale, graptolite-bearing limestone and sandstone showing a fauna with corals, brachiopods, trilobites and conodonts which are typical for shallow sedimentary environments. A characteristic of the Silurian period in Iran is the abundance of volcanic rocks as submarine basalts which represent the evidence for opening stage in the cratonic lithosphere of the Paleozoic platform

of Iran. Also, in some regions of Iran (south of Gorgan and south-east of Sanandaj-Sirjan zone), Silurian igneous rocks have more extent than sedimentary rocks in this period. Here we try to investigate the paleozoogeographical relation between coral fauna of the Iranian platform with other Silurian provinces in the world.

The main Silurian rocks of Iran belong to Niur Formation and the studied corals have been collected from this formation.

For first time, in order to study the Silurian rocks in Iran, Ruthner and et al. (1968) have chosen "Niur Formation" situated in the Central Iran, which is the first formation from Gushkamar Group and is composed of 446 m of coral – bearing dark brown limestone with thin interlayers of shale and partially dolomite, the type section being situated in Neivar village, south-east of Ozbak-Kuh). In this type-section, the Silurian rocks facies are not the same as in the whole region over Central Iran, so that in Shirgesht area, Neivar formatin is composed of 628 m of white sandy deposits with fossil-bearing limestone layers which has been known as Reference section. This Silurian clastic facies is typical for the most parts of Central Iran such as Jaam, Torud, north of Bafgh, Anarak, Kashan and is representative for clastic facies resulted from Caledonian orogeny.

One of characteristics of Silurian rocks in Shighesh is the presence of dark lava flow with olivine-bearing basalt which has been located often in the lower part of this formation and reminiscent of volcanic activities during Silurian in Eastern Alborz. In addition to Shirgesht, Silurian basic lavas also has formed a part of Silurian rocks in Jaam, Torud, North of Bafg and Zarand, in Kerman.

The abundance of corals, brachiopods, conodonts and various types of marine palynomorphs (acritarchs, chitinozoa within the type section and refrence section and detailed paleontological studies have confirmed a Middle – Late Silurian age for Niur Formation, in addition to emphasize sedimentary environments as a shallow sea near

to shore line.

E of Central Iran, carbonate facies and sometimes volcanic lava of Niur Formation Had considerable extent, particularly in Tabas, Jaam (Bozkuh formation, Alavi Naiini 1972), west of Kashmar, Kashan, Anarak, Neishabour, Khur, north of Bafgh, Zarand (Kerman Province), Rafsanjan. Nevertheless, north of Kerman the Silurian sediments are mainly composed of fossils-bearing limestone with dolomite, quartzite and shale which

#### Bajocian-Bathonian

Among the Silurian corals were identified the following 19 genera: *Strombodes*, *Spongophylloides*, *Coronoruga*, *Aphyllum*, *Loyolophyllum*, *Loyolophyllum*, *Streptelasma*, *Grewingia*, *Holmophyllum*, *Cystiphyllum*, *Phaulactis*, *Tenuiphyllum*, *Heliolites*, *Spongophyllum*, *Staphylopora*, *Mesofavosites*, *Halysites*, *Favosites*, *Paleofavosites*

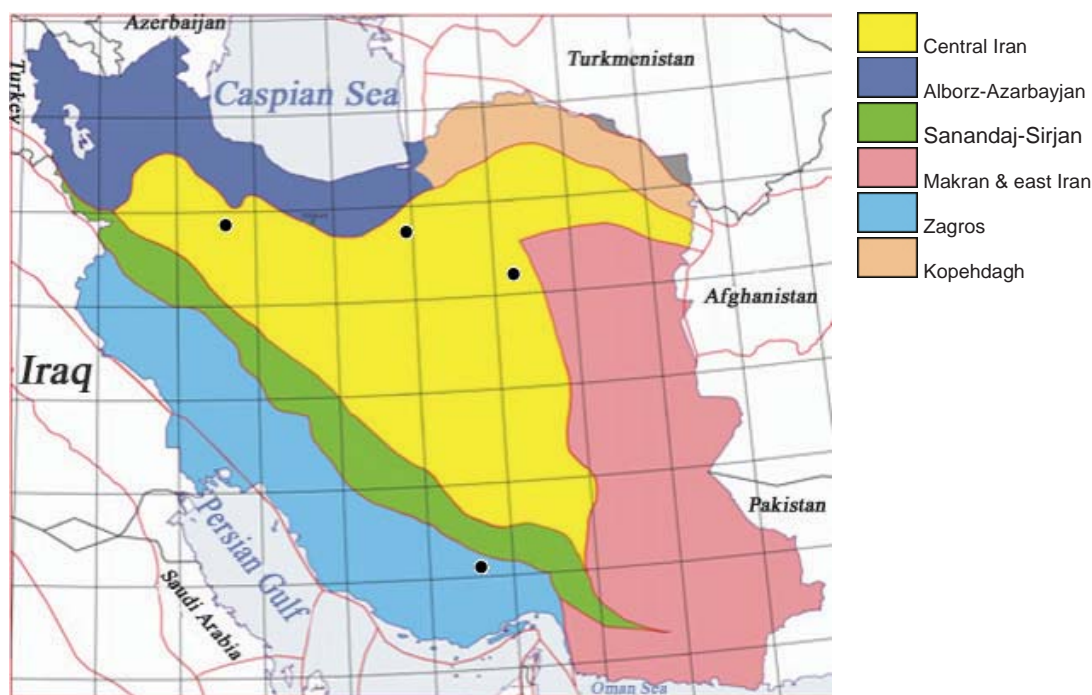


Figure 1. Formation map of Silurian

having layers of gypsum and at least three horizon of gypsum. Although, facies of these rocks are reminding the type section of Niur Formation, but the various lithology shows different conditions and sedimentary environments. Also, in Torud area, there are metamorphic rocks which have much similarities to Niur Normation concerning the stratigraphy and lithology. Hushmandzade et al. (1978) believe that these rocks have been metamorphosed as a result of orogeny phase prior to Aptian (Late Cimmerian), but probably, the age of the metamorphism of these rocks is dated

As it is observed, in Iran, the coral assemblages have most similarities with 14 common genera within the North America and North Asia Provinces. Also were found similarities with 11 genera from the provinces of Eastern Europe and East Asia, 10 genera with Australia, 9 genera with Western Europe, 7 with China and 5 common genera with Alaska (Table 1).

**Table 1.** The coral genera of Iranian basin and their distribution in the different provinces in Silurian time.

AL Alaska, AS North-Asiatic part of the Ex USSR, AU Australia, IR Iranian platform, CHI China, NA North of America, EE eastern Europe, WE western Europe, EA East Asia, NF North Africa.

<b>Provinces</b> <b>GENERO</b>	<b>IR</b>	<b>WE</b>	<b>EE</b>	<b>EA</b>	<b>NA</b>	<b>AL</b>	<b>AS</b>	<b>AU</b>	<b>CHI</b>
<i>Strombodes</i>	*		*	*	*		*		*
<i>Spongophylloides</i>	*	*	*	*	*		*		
<i>Coronoruga</i>	*	*	*	*	*		*	*	
<i>Aphyllum</i>	*				*	*	*	*	
<i>Loyolophyllum</i>	*								
<i>Streptelasma</i>	*	*		*	*		*	*	
<i>Grewingkia</i>	*	*			*			*	
<i>Holmophyllum</i>	*		*		*		*	*	*
<i>Cystiphyllum</i>	*	*	*	*	*	*	*	*	*
<i>Phaulactis</i>	*	*	*		*	*	*	*	
<i>Tenuiphyllum</i>	*			*			*		
<i>Heliolites</i>	*		*	*	*		*	*	*
<i>Spongophyllum</i>	*				*				*
<i>Staphylopora</i>	*								
<i>Mesofavosites</i>	*		*	*		*	*		*
<i>Halysites</i>	*	*	*	*	*	*	*	*	
<i>Favosites</i>	*	*	*	*	*		*	*	*
<i>Paleofavosites</i>	*	*	*	*	*		*		
similarity		9	11	11	14	5	14	10	7

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## A SEQUENCE STRATIGRAPHY APPROACH TO HOLOCENE DEPOSITS IN THE WESTERN ALBANIA DEPRESSION

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### Abstract

Quaternary deposits cover a large surface of Albanian territory, but their state of study is unfortunate still unsatisfactory. A detailed study is important particularly for the fact that all the cities of the country are constructed above those kinds of deposits. The Holocene transgression, 18 to 6.5 ka B.P. (Proust et al. 2013; APAT 2008), linked to climate changes, on the Albanian shores, affected areas hosting a huge number of population nowadays.

The process of marine transgression which follows the beginning of Holocene, was associated with a eustatic sea level rise of about 150 meters on global range, while the sea level of Late Pleistocene ending for Adriatic sea, was 110-120 meters below, compared with actual sea level (APAT 2008). Based on those data, it can be supposed that the highest sea level (the maximum between TST and HST) during Holocene, believed to be arrived 6.5 ka B.P and was up to 30-40 meters above the actual one, calculated as the hypsometric level of zero meters.

Certainly, the rapid sea transgression accompanying the first half of Holocene should leave marks on the landscape of the relief, in the zones, believed to be covered by sea at that time.

The plain between Lezha and Mamurras (Fig. 1), extends 24 km in north to south direction and 10 km east to west. In its northern and eastern periphery, is bordered by limestone hills, to a height between 280-600 meters, of Jurassic to Paleogene age, which belong to tectonic zone of Kruja (Dajti subzone) (AGS 2002, 2010&2011). Over the slopes of those hills, the erosion and corrosion caused by transgression of Holocene sea left visible marks.

Those marks appear clearly in Mali i Rencit, above Shengjini town, where cavities which follow the same level in the mountain slope can be distinguished in altitude between 10 and 20 meters. A continuous cliff, with a constant altitude, about

6 km length can be observed, from Shengjini to Lezha (Fig. 2)

On the hills of the eastern periphery of Lezha-Mamurras plain, the signs of the transgressions can be observed in the form of an arc, formed on the western slopes of the hills, with length of arc's cord (Lezha-Mamurras) about 22.5 km, and with a maximal distance of the arc's perimeter from the mentioned cord (Milot-Gurëz) about 3 km (Fig. 1).

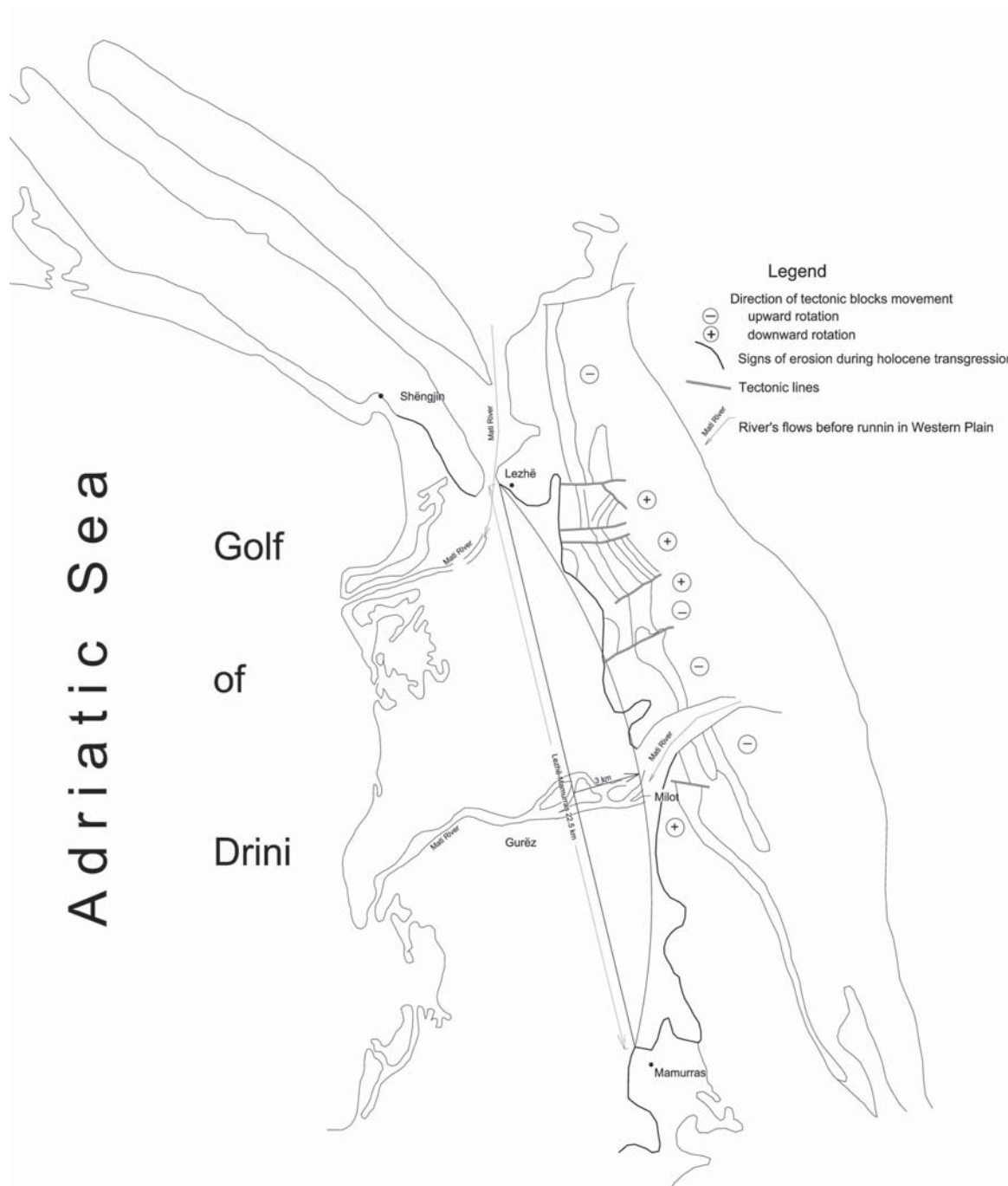
In the foot of hills, which borders the plain, not only in this area but in whole quaternary deposits of Albanian Western Depression, are situated deposits, which from their first interpretation (Nowack 1929), are considered as deluvial deposits formed during Pleistocene, as a result of wet climate. Those are mapped too, in the Geological Map of Albania of year 2002, as deluvial-alluvial deposits of Pleistocene-Holocene age (AGS 2002). But including those in a scheme of depositional environment during the Holocene transgression period, make me to believe that the definitions of 1929 and 2002 may not be correct.

Their position at the foot of the hills, an area covered by the sea during the period from TST to HTS, makes me to believe for a morphology created by influence of sea streams activity (waves or tides), against a limestone shore, highly affected by karst phenomena and fractured by climatic changes of Würmian and earliest glacial-interglacial oscillations. Also from tectonic movements, which are highly presented in this region, in longitudinal as in transversal direction, which with characteristics of an oblique slip fault, has lowered, plunged and fractured those formations, beginning from the Eocene (AGS 1999).

### Conclusions

- In the Adriatic shore of Albania, can be noted a morphology which suggest signs of erosive activity during sea transgression of Holocene (18-6.5 ka BP)





**Figure 1.** Map of area (after Sokol Marku based on AGS 1999).



**Figure 2.** Geographic extension of Shengjin-Lezhe cliff (top image) from google earth, and view of this cliff in a large landscape about 3.3 km (middle image) and its starts of cliff in Shengjin (Point 1 in top image) (image on the top is a google earth image, middle and bottom photos by Sokol Marku).

- The geomorphologic forms evident on the limestone reliefs and the deposits, until now mapped as deluvial-alluvial deposits of Pleistocene-Holocene age in Geological Map of Albania (2002) should be interpreted as linked to the erosional activity of the sea and littoral depositional processes of a clearly Holocene age.

**Key words:** *High-stand System (HST) and Transgressive System Tracks (TST), Holocene marine Transgression, Albania, Lezha-Mamurras plain*

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## MIDDLE JURASSIC FOSSIL AND DEPOSITIONAL RECORD FROM THE AREA OF THE ZIMEVITSA PLATEAU (WEST BALKAN MOUNTAINS), WEST BULGARIA

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### Abstract

Four sections were studied to reveal the fossil and depositional record of the Middle Jurassic from the area of the Zimevitsa Plateau (West Bulgaria). The biostratigraphic framework comes from the ammonite, foraminifera and belemnite occurrences, as well as auxiliary data from brachiopods. The sediments were defined by field works and microscopic observations. Our record includes four lithostratigraphic units, from the base to the top: the Ozirovo Formation (Aalenian), Etropole Formation (Aalenian–Lower Bajocian), Bov Formation (Lower Bajocian–Bathonian) and Yavorets Formation (Lower Callovian). Fossils and sediments displayed a deep-shelf to basin setting during Aalenian and Early Bajocian. Prominent carbonate productivity crisis and deepening was recorded around the Aalenian/Bajocian boundary and throughout the Early Bajocian, followed by a recovery in carbonate sedimentation up to the mid-Humphriesianum Biochron. A prolonged hiatus (submarine stratigraphic gap) until Middle Bathonian Orbigny Biochron was proved by faunal data. During the Middle–Late Bathonian, the studied area represented a pelagic plateau. It was evidenced by the reduced thicknesses of sedimentary successions due to winnowing processes, sediment starvation and condensation. The resulting sediments are thin Fe-oolid and glauconitized limestones. Well-developed hardground, combined with high fossil concentration, glauconite and phosphate enrichments, and iron mineralization was recognized at the base of Callovian, followed by stable pelagic carbonate deposition in the Middle Callovian.

**Keywords:** fossils, deposition, Middle Jurassic, West Bulgaria

### Introduction

The Zimevitsa Plateau is the highest elevated area of the Ponor Planina Mt. westwards the Iskar River Gorge (West Balkan Mts., West Bulgaria). It is a prominent outlier that is composed of thick

Jurassic–Lower Cretaceous rocks. It comprises several distinct late Alpine disharmonic folds with NW-SE structural arrangement (Moskovski 2001), which are developed on Bathonian–Berriasian hemipelagic and pelagic rocks, following upon less deformed Aalenian–Bajocian offshore argillaceous sediments, and virtually unfolded shallow-marine terrigenous-carbonate Lower Jurassic rocks. In terms of its regional stratigraphy, the Middle Jurassic strata from this area are well-defined (e.g. Sapunov and Tchoumatchenco, 1995) and subdivided into four lithostratigraphic units, in ascending order: the Ozirovo, Etropole, Bov and Yavorets Formations. However, several Middle Jurassic localities have recently provided new biostratigraphic and lithological data. The account that follows is an extension of the Middle Jurassic stratigraphic scheme for this region, as giving details that has been unknown elsewhere in the West Balkan Mts. It includes combined Aalenian to Lower Callovian fossil range data (mainly ammonites, belemnites and foraminifera) and sedimentary record, which have been obtained from the best exposed sections from the western part of the area of the Zimevitsa Plateau.

### Materials and sections

Here we present the results of the study of four stratigraphic sections: section Dobravitsa-1 (43°01'46"N; 23°14'15"E) and two related outcrops, section near Zimevitsa Village (43°01'00"N; 23°17'40"E), section across the Dobravitsa anticline (43°01'25"N; 23°15'00"E), and section to the SW of Cheparna Summit (43°00'32"N; 23°15'25"E). These sites are sufficiently fossiliferous and stratigraphically linked in order an adequate cross-section throughout the Middle Jurassic to be composed, including a sequence from the top of the Ozirovo Formation (Aalenian) to the base of the Yavorets Formation (Lower Callovian). Section Dobravitsa-1 is previously known exposure (Metodiev and Koleva-Rekalova 2008 and references cited therein), comprising the best development of the



Aalenian in Bulgaria and the Aalenian/Bajocian boundary interval in this region. The other three sections have newly disclosed the stratigraphy of the Bajocian and the Bathonian (including the Bajocian/Bathonian and Bathonian/Callovia boundaries). This work is based on the study of petrographic samples and fossils, which are part of Bulgarian Academy of Sciences collections. Fifty thin sections from nearly each rock type recognized in the field were prepared for facies analysis, and they are the data-source for the microfossil distribution. Approximately 350 ammonites and belemnites were collected, to give the best possible biostratigraphic subdivision and age assessment of the rocks.

## Results and discussion

The lowest beds of the Middle Jurassic in the area of the Zimevitsa Plateau comprise a locally preserved 4 m thick succession (section Dobavitsa-1 and the exposures) that is composed of dark stained, irregular hemipelagic marl-shale-limestone alternation of the Bukorovtsi Member of the Ozirvo Formation, which rapidly grades into the carbonate-free shales of the Etropole Formation. Lithologically, this succession mainly consists of silty marls and fine-laminated shales with sideritic concretions and phosphate nodules. Limestones occur as interbeds of micritic mudstones, mudstones to wackestones with re-sedimented iron-oooids and bioclastic floatstones and rudstones. The latter two types appear as distinct shell-beds, having a high value of fossil packing, being rich in ammonites and brachiopods, less rich in belemnites (subordinate bivalves and microfossils also appear but not studied), and recording a few levels of taphonomic condensations. Section Dobavitsa-1 keeps a sequence of valuable Graphoceratidae, and auxiliary Hammatoceratidae, spanning the Aalenian *opalinum* Zone to the Lower Bajocian *discites* Zone.

The lower part of section Dobavitsa-1 includes scattered but straight ammonite succession: *Leioceras opalinum*, *Chypholioceras bifidatum*, *C. gr. lineatum*, *Cylicoceras crassicostatum*, *Ancolioceras opalinoidea*, combined ranges of *Staufenia*, *Ludwigia* and *Pseudographoceras* species (*Staufenia sinon - sehndensis - opalinoidea - discoidea - staufensis*, *Ludwigia pustulifera - crassa - munchisonae - gradata*, and *Pseudographoceras subtuberculata*), accompanied by rare *Bredya*, *Rhodanicer*,

*Planammatoceras* and *Pseudammatoceras*. This set defines the Aalenian *opalinum* and *murchisonae* Zones. Upwards, the graphoceratid record continues with three thinner developed assemblages comprising distinctive *Brasil* and *Graphoceras* faunas. It includes *Brasil* gr. *bradfordensis-gigantea* and several allied *Brasil* species (e.g. *B. falcifera-bayley-subcava* and *B. nitens-similis-decipiens*), attending examples of *Ludwigella* and *Apedogyria* (*L. arcitenens-rudis-cornu* and *A. gr. rugosa-subcornuta*), less common *Graphoceras* (e.g. *G. cavatum*, *G. formosum* and *G. decorum*), and occasional *Pseudammatoceras* and *Accardia*. These faunas typify the Aalenian *bradfordensis* and *concaum* Zones. The topmost located graphoceratid assemblage includes *Toxolioceras* gr. *mundum-walker*, *Reynesella juncta*, *Braunsina aspera* and *Hyperlioceras* gr. *rudidiscites*. It defines the Lower Bajocian *discites* Zone and the incoming of its first members was used for drawing the Aalenian/Bajocian boundary. This assemblage contains also unidentified species of the genera *Euaptetoceras*, *Euhoploceras* and *Fontannesia* that evidence the fade of the Graphoceratidae and Hammatoceratidae, and the advent of the Sonniniidae. The Aalenian-Lower Bajocian faunal spectrum of section Dobavitsa-1 contains also frequently re-elaborated belemnites of *Belemnopsis* gr. *apiciconus*, *Holcobelus* gr. *munieri* and *Brachybelus* (aff. *subbreviformis*), as well as various brachiopods referred to least at ten genera and provisionally recorded by Motchurova-Dekova et al. (2009).

Up section, the Bajocian rocks crop out mainly in the core of the Dobavitsa anticline that faces west into a steep and wide exposure of the Zimevitsa Plateau-side. It contains much more expanded sequence of the Etropole Formation (~90 m thick) that rapidly grades into the basal sediments of the Bov Formation (2–5 m thick grey silty marls). The Etropole Formation includes a locally developed thin-bedded alternation of black shales and siltstones (nearly 35 m thick) that probably grades laterally into indistinctly bedded black shales with scattered sideritic and phosphate nodules. These rocks yielded badly preserved ammonites of the genera *Docidoceras*, *Kumatostephanus* and *Bradfordia* that indicated the Lower Bajocian *laeviuscula* Zone. The range of the Sonniniidae that was recorded at lower stratigraphic levels recedes, but the first Stephanoceratidae and Oppeliidae became visible into the succession. Upwards, this alternation evolves to the shales of the Etropole

Formation and the stratification becomes enhanced by long rows of sideritic concretions. The bulk of this pile of sediments still remains poor on fossils, giving a few stephanoceratid and oppeliid ammonites, as well as some otoitid taxa, indicating the Lower Bajocian *sauzei* Zone: *Bradfordia* gr. *involuta*, *Oppelia* spp., *Otoites* gr. *sauzei*, *Emileia* gr. *brochii* and *Skirroceras* gr. *nodosum*. Scattered belemnites of the genera *Belemnopsis* and *Brachybelus* were also recorded.

Surprisingly, the top part of the Etropole Formation, and the lowest beds of the Bov Formation yielded an ammonite assemblage that clearly referred this interval to the Lower Bajocian. We found nice and fairly common ammonites of the oppeliid genus *Dorsetensia*, composing a range of two main valuable species: *D. romani* and *D. complanata*. Less common, but also significant are the examples of several allied species (e.g. *D. regrediens*, *D. edouardiana*, *D. subtectata* and *D. liostraca*). The age assessment of this interval was supported by the occurrence of *Dorsetensia*-related forms, roughly identified as *Nannina* gr. *deltafalcata*, as well as by *Stephanoceras pyritosum* and *Teloceras* gr. *rauricum*. Sphaeroceratidae were also recorded: *Sphaeroceras brongniarti*, *Chondroceras evolvens*, *C. Polypleurum*, *Chondroceras* spp. and *Phlycticeras* spp.. Accessorily, huge belemnites of *Megateuthis* gr. *elliptica-longa* and smaller rostra of *Brachybelus* gr. *subbreviformis*, and *Belemnopsis* spp. commonly occur. This fossil association corresponds to the lower half of the *humphriesianum* Zone. It reveals that no discontinuity between the Etropole and the Bov Formations exists, and the total chronostratigraphic extent of the Bov Formation is broader than assumed previously (Sapunov and Tchoumatchenco 1995). A clear discontinuity does really exist, but it cuts out the marls of the Bov Formation and thus concerning in absence the upper part of the *humphriesianum* Zone and nearly all higher Bajocian ammonite zones. We are convinced that this break has a regional extent and can be followed all over the Middle Jurassic strata to the west of the Zimevitsa Plateau. Closely to the south of that area, this gap is further deepening as documented by the total lack of sediments higher than the Lower Bajocian *laeviuscula* Zone until the mid-*macrocephalus* Zone of the Lower Callovian.

The topmost segment of the Middle Jurassic cross-section was evidenced in the cliffs on the flanks of the Dobravitsa anticline, as well as in the sections

near Zimevitsa Village and Cheparna Summit. It embraces highly discontinuous, condensed and rapidly varying succession of the Bov Formation (0.95–3.50 m thick) that can be found only in the area of the Zimevitsa Plateau. The very base of these deposits corresponds to narrowly extended beds of dark grey radiolarian-spicule wackestones and iron-ooidal intraclastic floatstones to rudstones with phosphate nodules (reaching up to 0.5 m), surrounding scattered ammonites and belemnites (*Parkinsonia* spp., *Leptosphinctes* cf. *leptus* and *Belemnopsis* gr. *nalivkini*), as well as common benthic foraminifera (*Ophthamidium kaptarenkoae*, *O. prutensis*, *Meandrovoluta asiagoensis*, *Cornuspira* cf. *tubicomprimata*). This is apparently Upper Bajocian faunal spectrum, and the ammonites indicate the *parkinsoni* Zone. These beds are sharply overlain by red-brown, sandy Fe-ooidal bioclastic-intraclastic rudstones and packstones (thickness ranging from 0.75 to 1.20 m) that yielded a few valuable ammonites from the Middle Bathonian *orbignyi* Zone: *Cadomites orbignyi*, *Procerites mirabilis* and *Wagnericeras* gr. *suspensum*. These data demonstrate that the Lower Bathonian is missing. Therefore, it seems this absence is an extension of the break that we have already noted, except the Upper Bajocian beds that are locally preserved only.

The remaining sequence of the Bov Formation display highly unequal development with common sharp surfaces between the different rocks types observed. More expanded succession (2 m thick) of alternating thin-bedded recrystallized mudstones, sandy marls and wackestones with filaments was recognized in Zimevitsa section. It contains condensed fossiliferous levels with distinctive ammonite faunas and belemnites (*Rugiferites rugifer*, *Wagnericeras* gr. *fortecostatum*, *Wagnericeras* spp., *Siemiradzka matisconensis*, *Prevalia thressa*, *Paroecotraustes zieglerei*, *Choffatia vicenti*, *Parachoffatia arisphinctoides*, *Grossouvria* spp., *Subgrossouvria richei*, *Belemnopsis* spp. and *Hibolites* spp.). The rocks also yielded valuable record from foraminifers, including benthic and planktonic taxa (*Ophthamidium terquemi*, *Cornuspira infraoolithica*, *C. orbicula*, *Labalina occulta*, *Globuligerina bathoniana* and *G. oxfordiana*). Both ammonite and foraminiferal assemblages provided an extent that covers the Middle–Upper Bathonian (matching the interval from the *subcontractus* to the *discus* Zone, according to the ammonites). This succession is

rapidly laterally reduced to a single bed in the section at the Dobravitsa anticline, comprising ooid-bearing bioclastic-filament wackestones with some ammonites (*Siemiradzka davitashvili* and *Thraxites haemussensis*) that indicate the Upper Bathonian “*retrocostatum*” Zone. This development has not been observed in the section near the Cheparna Summit. There, a 2.30 m thick succession of medium-bedded glauconitized bioclastic packstones and wackestones, crinoidal packstones, ferruginized bioclastic-oncoidal packstones to grainstones and oncoidal-bioclastic wackestones with filaments were approximately assigned to the Middle–Upper Bathonian, by the occurrence of planktonic and benthic foraminifera (*Globuligerina bathoniana*, *G. oxfordiana*, *Nubecularia reicheli*, *Ophthalmidium terquemi*, *Glomospira* sp., and *Cornuspira* sp.).

The topmost evidence obtained in this study reached the Yavorets Formation. A thin bed of micritic limestones (filament wackestones) from the very base, was found to be bracketed by hardground surfaces, which are enclosing high faunal concentrations including ammonites and occasionally oriented belemnites (*Grossouvria cheyensis*, *G. variabilis*, *Zieteniceras* gr. *zieteni*, *Catasigaloceras* sp. and *Hibolites* gr. *hastatus*). The ammonites enabled the recognition of partly preserved Lower Callovian *macrocephalus* Zone. Upwards, the Yavorets Formation continues with no change in lithology and the scattered occurrence of hecticoceratid ammonites from the genera *Putelaiceras* and *Rossienceras* dated the rocks as Middle Callovian (“*Hecticoceras*” Zone).

## Conclusions

The faunas and the lithologies from the Aalenian and the Lower Bajocian, recorded in the area of the Zimevitsa Plateau, have revealed a deposition in low-energy environment (located below the effective wave base), and open deep-shelf to basin setting, with low sedimentation rates and frequently interrupted sedimentary influx. Brachiopod occurrences from this interval probably reflect locally raised and pulsating epifaunal sea-bottom settlements, never recorded before at this level elsewhere in West Bulgaria. A distinct crisis of the carbonate productivity occurred around the Aalenian/Bajocian boundary. This collapse is possibly keeping pace to the imposing of stressful conditions, as fossil occurrences rapidly decreased upwards, becoming extremely poor and

benthos-free for a wide extent. It seems that this development was due to gradual subsidence, since sedimentation rates apparently increased during the times of the early Bajocian *Laeviuscula* and *Sauzei* Biochrons. After that, a trend towards recovery of the carbonate sedimentation appeared, but it was not long interrupted, approximately in the middle of the early Bajocian *Humphriesianum* Biochron. Thereafter, an extensive interval of non-deposition until the middle Bathonian *Orbigny* Biochron was evidenced. The Middle–Upper Bathonian strata of the area examined are interpreted as being associated with locally developed pelagic plateau, in high-energy environments with intermittently losses of sediment supply and phases of sedimentary starvation. It is evidenced from the development of unusually variegated, condensed and coarse-grained deposits that seem to have a narrow occurrence, since outside the area of the Zimevitsa Plateau these strata grade laterally into increasingly thickening and much deeper basinwards successions. After one more short interval of somewhat uneven deposition (early Callovian mid-*Macrocephalus* Biochron), the Middle Jurassic continues with relatively stable carbonate pelagic development.

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into three facies types: Abkhazia-Racha, Odishi-Okriba and Dzirula. Late Cretaceous sediments of Odishi-Okriba facies type are spread as a discontinuous, southward bending of bow-shaped stripe and is known as the “southern calcareous stripe of Samegrelo” (Tsagareli 1946) (Fig. 1). Volcanogenic rocks are more widely spread in the southern strip of Samegrelo and in Okriba, which are already distinguished by Meffert B.F. (1931) as the “Mtavari Suite”. This suite contains reddish, brownish, yellowish-gray basaltic and porphyritic effusives and their pyroclastolites with layers of limestones and sandstones (Nadareishvili 1980). The age of the sole of the above mentioned suite throughout the area of its distribution is determined as Late Turonian. The upper limit of the suite is differently dated in different areas. For example, in some places, the roof of the suit reaches the Campanian while in other places is limited by the Turonian and perhaps partly by Coniacian (Lekvinidze 1960). The thickness of the suite varies from several tens to several hundred of meters. The “Mtavari” suite it can best be seen in the interfluvium of Rioni and Tskaltsitela, where volcanogenic rocks dominate. Within the limits of this facies type, in the vicinity of the village Gordi (basin of the river Tskaltsitela), a stratigraphic section was described.

The first suite, “Mtavari”, was investigated in detail on the basis of planktonic foraminifera. In the analyzed sections, it was possible not only to establish foraminifera assemblages, but also to establish their subdivisions.

## Materials and Methods

For a detailed stratigraphic division of the Late Cretaceous sediments of Gagra-Java zone and for specifying the volume and the age of the formations, in the facies of Odishi-Okriba facies type nappes, the sections of Tskhenistskali and Rioni river basins (vil. Gordi (r. Tskhenistskali), vil. Nokalakevi, r. Abasha, r. Tskhunkuri (r. Rioni basin)) have been studied.

The Upper Cretaceous sediments of the Odishi-Okriba facies type is represented mainly by limestones with variegated flints and tuff-gravel and tuff-stones. During the field-work 1800 samples were taken. These samples were treated in the laboratory and washed with glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) and copper vitriol ( $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ).

## Results

The general thickness of “Mtavari” suite is 80 m (in table 1 is given the correlation of the biostratigraphic

zonation for the Upper Cretaceous). The lower part is represented by brownish-pink tuff-gravel stone of different granulation. They comprise interlayers of pinkish limestones (thickness of streak 0,5-20 cm) with *Inoceramus lamarcki* Park. (determination by Ghambashidze R.A.). Herein, planktonic foraminiferal assemblages were found: *Marginotruncana pseudolinneiana* Pessagno, *M. schneegansi* (Sigal), *M. marginata* (Reuss), *Dicarinella hagni* (Scheibnerova), *D. imbricata* (Mornod), *Hedbergella delrionensis* (Carsey), *Whiteinella archaeocretacea* Pessagno, *Heterohelix reussi* (Cushman), *H. globulosa* (Ehrenberg), *Globigerinelloides bentonensis* (Morrow), on the top of the limestone layer *Marginotruncana coronata* (Bolli), *Stensioina granulata kelleri* (Koch.), *Loeblichella* spp. occur. Alongside with the species mentioned above, here is found *Tetralithus pyramidus* Gardet.

Brownish tuff-stones with streaks of red and grey limestones continue the section. In this part of the section, the following macrofauna was found: - *Inoceramus* cf. *sturmi* And. (identification of Tsagareli A.L. and Ghambashidze R.A.). Concerning the foraminifera, *Marginotruncana sigali* (Reichel), *M. renzi* (Sigal) were identified in the section for the first time, while *Marginotruncana pseudolinneiana* Pessagno, *M. marginata* (Reuss), *Dicarinella imbricata* (Mornod), *Globigerinelloides bentonensis* (Morrow), *Whiteinella archaeocretacea* Pessagno, *Hedbergella delrionensis* (Caesey), *Heterohelix reussi* (Cushman) and benthonic forms - *Stensioina exculpta* (Reuss), *St. granulata granulata* (Olbertz), *Lenticulina* sp were also found.

The Upper Okumi suite, with a thickness of 75 m, is built up of pelitomorphic, light pink, almost white, thick-layered chalky limestone. At the lower part of the sub-suite, was identified the echinoid *Micraster schroederi* Stoll., (identifications of Tsagareli A.L., Ghambashidze R.A.); in the suite, the first representatives of *Globotruncana arca* (Cush.), *G. linneiana* (Orb.), *Contusotruncana (Rosita) fornicata* (Plum.) are observed. Also *Marginotruncana marginata* (Reuss), *Heterohelix reussi* (Cushman), *H. globulosa* (Ehrenberg) are present.

The upper part of the subsuite consists of light greyish and white, medium and thick-layered pelitomorphic limestones with interlayers of greenish-grey marls and concretions of grey flint. They contain belemnites as *Belemnella mucronata* Schloth., *Belemnella langei langei* Jet. (identifications of Nazariashvili T.J.). In the limestones, planktonic foraminifera as *Globotruncana ventricosa* White., *Globotruncanita*

**Table 1.** Correlation of the Biostratigraphic Zonality for the Upper Cretaceous

STAGE	SUBSTAG E	Macrofauna zones	Calcareous nannofossil zones	Planktic Foraminifera zones		
		Western Georgia		Facies type		
				Abkhazia-Racha	Odishi-Okriba	
MAASTRICHTIAN	Upper	Pachidiscusgollevillensis	Tetralithusmurus	Abathomphalusmayaroensis	Globotruncanaventricosa	
	Lower	Belemnittelalanceolata	Lithraphiditesquadratus	Globotruncanita stuarti		
CAMPANIAN	Upper	Belemnitella langei	Tetralithustrifidus	Globotruncanamorozovae		Globotruncanaventricosa
		Belemnitella mucronata		Globotruncanaventricosa		
	Lower	Micrasterschroederi	Tetralithusaculeus	Globotruncanarca	Globotruncanarca	
SANTONIAN	Upper	Belemnitella praecursor		Contuzotruncanafornicata	Contuzotruncanafornicata	
	Lower	Inoceramuscordiformis Inoceramusundulaticplicatus		Dicarinellaconcavata		
CONIACIAN	Upper	Inoceramusinvolutus	Marthasteritesfurcatus	Marginotruncanarenzi/M.sigali	Marginotruncanarenzi/M.sigali	
	Lower	Inoceramuswandereri		Marginotruncanacoronata	Marginotruncanacoronata	
TURONIAN	Upper	Inoceramuslamarcki	Tetralithuspyramidus	Marginotruncanapseudolinneiana/M.schneegansi	Marginotruncanapseudolinneiana/M.schneegansi	
	Middle			Dicarinella hagni		
	Lower	Inoceramuslabiatus	Microrhabdulus decoratus			
CEYNOVIAN	Upper	Praeactinocamax sp. Acantocerasrothomagense		Whiteinellaarchaeocretacea		
	Lower	Mantellicerasmantelli Aucellinakrasnopolskii		Fine Hedbergella		
				Rotaliporaappenninica		

*stuartiformis* (Dalb.), *Archaeoglobigerina cretacea* (Orb.), *Heterohelix striata* (Ehrenberg), *Globotruncana arca* (Cushman), *G. linneiana* (Orb.), *Rosita fornicata* (Plum.), *Heterohelix reussi* (Cushman) were identified.

Mokvi suite is built by grey and light grey pelitomorphic, thick-layered limestones with a mixture of black flint. This suite is characterized by the presence of *Pachydiscus cf. colligatus* (Binkh.) and in the upper part of the section, remains of *Gryphaea vesicularis similes* Push are rarely found. Numerous fragments of double-keel planktonic foraminifera are also present in this suite. Observable thickness of the suite is 20 m.

## Conclusions

Thus, 5 foraminiferal assemblage zones have been established in the studied section:

1. *Marginotruncana pseudolinneiana* and *Marginotruncana schneegansi* assemblage zones are found together with the mollusk zone of *Inoceramus lamarcki* and corresponds to nannoplankton zone of *Tetralithus pyramidus*. This interval is dated as Early Turonian.

2. *Marginotruncana coronata* assemblage zone corresponds to the mollusks zone of *Inoceramus sturmi* and nannoplankton zone of *Marthasterites furcatus*. The age is determined as Early Coniacian.

3. *Marginotruncana sigali* and *Marginotruncana renzi* ("Mtavari" Suite) assemblage zones. Stratigraphically, the given complex corresponds to *Inoceramus involutus* zone and is dated as Upper Coniacian.

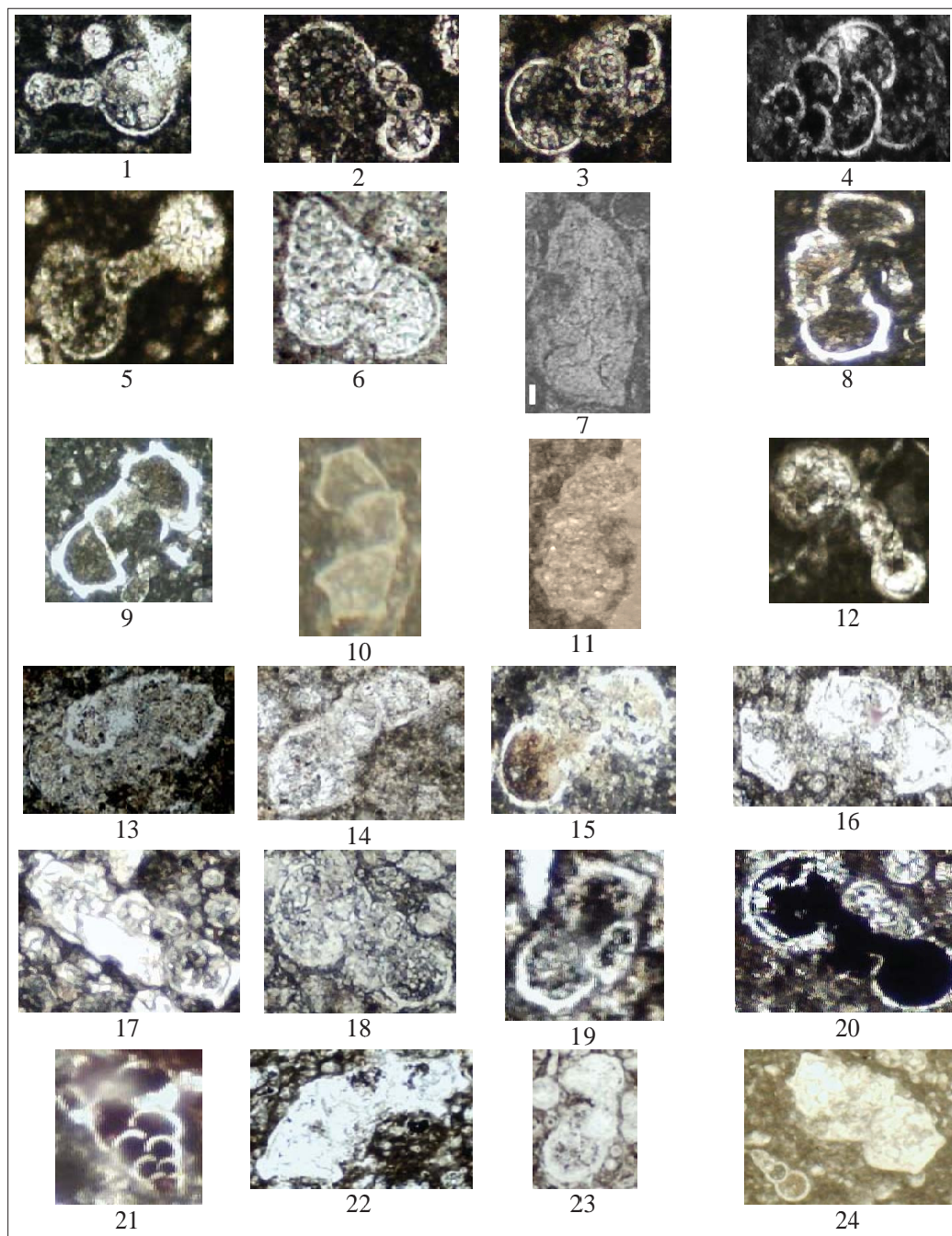
4. *Globotruncana arca* assemblage zone is characterized by the abundance of index-species and corresponds to the layer with *Micraster schroederi* and the nannoplankton zone of *Tetralithus aculeus*. It is dated as Early Campanian.

5. *Globotruncana ventricosa* assemblage zone corresponds to the layers with *Belemnitella mucronata* and to the zone of *Tetralithus aculeus* and a part of *Tetralithus trifidus* zone, by nannoplankton. The age is determined as Middle Campanian (Plate I).

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Plate I



1. *Globigerinelloides bollii* Pessagno; 2. *Whiteinella aprica* (Loeblich et Tappan); 3, 14. *Whiteinella* sp. (cf. *Wh. archaeocretacea* Pessagno); 4, 6. *Heterohelix reussi* (Chushman); 5. *Globigerinelloides bentonensis* (Morrow); 7. *Gansserina* sp. (cf. *G. gansseri* (Bolli)); 8. *Dicarinella hagni* (Scheibnerova); 9. *Globotruncana hilli* Pessagno; 10. *Marginotruncana marginata* (Reuss); 11. *Globotruncana bulloides* Vogler; 12. *Hedbergella planispira* (Tappan); 13. *Marginotruncana marginata* (Reuss); 15, 18. *Whiteinella baltica* Douglas et Rankin; 16. *Globotruncana lapparenti* Brotzen; 17. *Globotruncana carinata* Dalbiez; 19. *Globotruncana hilli* Pessagno; 20. *Rugoglobigerina hexacamerata* Bronnimann; 21. *Heterohelix moremani* (Cushman); 22, 24. *Marginotruncana pseudolinneiana* Pessagno; 23. *Whiteinella* sp. (cf. *Wh. prae-helvetica* (Trujillo));



## THE IMPORTANCE OF THE FAUNAL ASSEMBLAGE FROM THE STOLNICENI FORMATION FOR REGIONAL GEOLOGICAL CORRELATION

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### Abstract

The Stolniceni Formation is situated on the highest interfluvial areas of the Codru Highland. These deposits overlie the eroded surface of Codru (Balta) Formation (upper Miocene) and are represented by medium and fine-grained sands containing fragments of Carpathian rocks. The mineralogical and lithology of the Stolniceni Formation is quite different from that of the underlying rocks and corresponds to the younger fluvial deposits of Prut and Dniester terraces. Leordoia, Veverița-2 and Balanesti are the most representative localities bearing vertebrate assemblages in Stolniceni Formation. This fauna is Turolian (MN 12-13 units), which represents the Early Pontian in Eastern Paratethys.

From these localities a number of taxa of small mammals were firstly described in Republic of Moldova. The list of these taxa concerns: *Hylomys macedoniensis*, *Keramidomys carpathicus*, *Prospalax tordosi*, *Ischymomys* sp., *Epimeriones austriacus*, *Pliopithecus* sp. The systematic determination of some Upper Miocene fossils from the Republic of Moldova and adjacent territories was clarified. They revealed peculiar character of the faunal assemblage allowed to establish its stratigraphic position. Obtained biostratigraphic data from Leordoia, Veverița-2 and Bălănești permit development of a new stratigraphic scale for the Upper Miocene continental beds of Moldavian Plateau.

In the southern area of the Codru Highland, in a lot of localities of Cimișlia district (Mihailovca, Sagaidac, Porumbrei etc.), in the deposits of Stolniceni Formation, the following fossil vertebrates are present (*Hypolagus igromovi*, *Ochotona antiqua* etc.), that testify a younger age of Stolniceni retines in comparison with the deposits of the central part of Codru Highland.

In the faunistic association in the padding of Stolniceni Formation of the central part of Codru Highland there are representatives of various paleoecosystems: marshlands, flood - plain forests, forest steppes, that we can explain in specific taphonomy of these sites. The presence of primates is indicative for a warm temperate climate, documented also by the paleobotanical data.

The regarded faunal assemblage emerged on the Moldavian plateau during the early stage of Pontian. This peculiar mammalian complex indicates specific environmental conditions of that remote time. The faunas from Leordoia, Veverița-2 and Bălănești represent a link between middle Turolian and Ruscinian faunas. The affinity of these Moldavian faunas with the ones from the paleobioprovinces of Central Asia and Central and Southern Europe, expressed by the presence of the same faunal representatives must be noticed. Such a diverse faunal association is explained by effective biogeographical contacts with enlisted bioprovinces and migration routes that passed through the Moldavian plateau, that is quite similar to the modern biogeographical situation of the area under study.

These specificity of the investigated area allows for regional geological correlations. These localities are sharing common or similar taxa with some Turolian localities from: Ukraine (Vinogradovka, 16-th st. Odessa), Russia (Morskaya-2, Solnechnodolsk), Hungary (Tardosbanya), Greece (Pikermi, Maramena) and others.



## NOTES ON THE EUXINIAN AREA AT THE BEGINNING OF THE MIDDLE MIOCENE AND CORRELATION OF THE TARKHANIAN REGIONAL STAGE

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### Abstract

For the past decades, a lot of data on different geological aspects of the Euxinian area, part of the large Euxinian-Caspian basin (Eastern Paratethys) during the Neogene, have been accumulated.

The analysis of taxonomic composition, structure and features of fossil molluscan assemblages in NE Bulgaria suggests that the marine transgression from the Precarpathian basin occurs not only eastwards along the Black Sea – Kuban rift zone, but also southeastwards to South Dobrogea. The transgression came across a small relic basin located in the northern part of South Dobrogea, where Romanian researchers have defined scanty fauna of Kotsakhurian-type. It is very likely that the area of the Lower Kamchiya Depression (LKD) was within this basin's range. The basin transgression covered the land westwards of Dobrich town.

This inherited basin controlled possibilities of migration of the molluscs. In my opinion, the marine transgression from the Precarpathian basin side and marine molluscs migration probably happened in the beginning of the Early Badenian and extended till Middle Tarkhanian. Later on, an exchange of similar molluscan species coming from Euxinian basin occurred. However, only the species not encountering rival resistance succeed in pervading the basin. It is suggested that the higher rate of extinction of the Early Badenian species facilitates the pervasion of the molluscs from LKD.

In NE Bulgaria, the upper part of the Middle and the lower part of Upper Tarkhanian stage of the Eastern Paratethys with regards to mollusc species, correlate well with the lower substage of the Badenian, in the Central Paratethys. However, this fact does not deny the possibility of Mediterranean

Tethys transgression occurring in the eastern part of the Euxinian area, simultaneously in the Karpatian age.

The deep-water facies sediments of Lower Tarkhanian Substage (Kuvinian beds) are very similar to the Maykopian ones. It can be suggested that the reference horizon I<sup>a</sup>, which is considered as the upper boundary of the Maykopian Series might not coincide with the boundary Kotsakhurian/Tarkhanian stage (Lower/Middle Miocene). The lack of characteristic reference horizon between I<sup>a</sup> and I does not allow authentic chronostratigraphic division of the Middle and Upper Miocene sediments included in this section. The presence of stratigraphic hiatus is possible but unproved, because of the absence of angular unconformity or varied permeability mediums. As a result Middle/Upper Miocene stage, sediments might transgressively and conformably overlay the Maykopian ones at any part of the area. The reference horizon I<sup>a</sup> could not be considered a reliable chronostratigraphic marker. It can be suggested that in the beginning of the Middle Miocene, the Euxinian area was not an unified sedimentation basin. The apical parts of Andrusov Rise and Shatsky Rise probably were still on the surface dividing the basin in separate smaller basins. As a geographic barrier, they play a substantial role in the sediment distributing and preventing the fauna's migration. Two or more isolated basins which have limited or no connections probably exist at the beginning of the Tarkhanian transgression in the Euxinian area. Same scanty fauna such as *Rzehakia* and *Congerina* of so called "Kotsakhurian"-type exist in these basins.

## SILURIAN-LOWER DEVONIAN BLACK SHALES AND GRAPTOLIDS OF MUHURR-ÇAJE UNIT (ALBANIA), AND CORRELATIONS WITH CARPATHO-BALKANIDES

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### Abstract

In this paper are presented data on the Black Graptolitic Shales and graptoloids of Muhurr-Caje Unit representing the unique locality within the Hellenide-Dinaride Chains. These shales are intensively tectonized and metamorphosed, but 24 biozones ranging from Llandoveryan to Early Devonian have been identified. It is shown that the correlation between the proposed zonal scheme and the other zones used in general in Eastern and Western Europe, particularly Bohemia are possible. The Silurian-Lower Devonian Shales and graptoloid assemblages compare well with coeval sequences of Carpatho-Balkanides.

**Key words:** *Black Shales, Graptoloids, Biostratigraphy, Muhurr-Caje Unit, Albania*

### Introductions

The first graptolites were found in the Muhurr area. At the beginning of the 80<sup>s</sup>, the study on the Graptolitic Shales have started in the frame of the project "Stratigraphy of Paleozoic sediments in Albania" and they were identified as the most Paleozoic fossil fauna. Based on the research of the micro- and macrofauna mostly represented by graptolites, it was compiled the first stratigraphical scheme of Paleozoic sediments. During this time, paleontological and stratigraphical extensive researches were carried out, particularly on the Graptolitic Black Shales belonging to the Muhurr-Caje Unit Zone, where have been discovered many new localities rich in graptolites (Pashko et al. 1985). In 1998, J. Maletz described the graptoloids founded within the Wenlockian/Ludlowian boundary. The Black graptolitic shales of the Muhurr-Caje Unit contain abundant graptoloid and enable the identification of 20 biozones (Pashko 2005). The absence of some classical graptolite biozones may be attributed to collecting failure and partly on lack of outcrops.

The present paper is based on new analysis of graptolitic material with revisions of previously unpublished and published data, and gives a new biostratigraphical scheme of Silurian-Lower Devonian graptolitic shales in Muhurr-Caje Unit.

### Geological setting

The Korabi Alpine Structural Zone is a system of nappes that consists of Kollovoz, Muhurr-Caje, Mali i Korabit and Grama tectonic units. The Graptolitic Black Shales of Silurian-Lower Devonian age are found only in Muhurr-Caje Unit and represent the unique locality within the Hellenide-Dinaride chains.

The sedimentary succession of Muhurr-Caje Unit starts with Ordovician black silty-schists with quartzite intercalation but without graptoloids, followed by a Silurian-Lower Devonian sequence of graptolitic shales and more by Pragian-Eifelian intercalations of shales and limestones containing Tentaculites and Conodonts. The Graptolitic Black Shales extend from Muhurr region where are most widespread and represented by the complete Llandoveryan-Lower Devonian sequence to Buzemadhe and Nimce. They are transgressively covered by the Permian-Lower Triassic Verrucano Formation. The Muhurr Black Shales Formation (Silurian) and Fushe Muhurr Tuffaceous Shales Formation (Lower Devonian) were recognized. In general, the black shales are siliceous, organic-rich, show various degrees of metamorphism and are intercalated with thin bedded lydites (cherts) and varied intrusive beds. The lithic characteristics of the Muhurr Formation ranging from mostly black shales with thin bands of lydites to almost totally black and dark shales, whereas the Fushe Muhur Formation consists of mostly yellow, argillic tuffaceous shales. As a result of the very developed tectonics, the graptolitic shales were intensively tectonized and metamorphosed during the Late Paleozoic Hercynian orogeny. Consequently, the graptoloid rhabdosomes are deformed, affected by the cleavage, pyritised and

ORDOVICIAN

**Table 1.** The biozonal scheme of Muhurr-Çaje Unit and correlation with Generalized Graptolite Zonation of Koren' & al. (1996) and graptolite zonation of Carpatho-Balkanides (Krstić et al. 2005).

Series	Stages Ma	Graptolite Biozones		
		Standard Graptolite Biozones Koren' & Al. 1996	Muhurr-Çaje Unit	Carpatho- Balkanides Krstić & Al. 2005
Dev.	416,0 Lochkovian	Hercynicus uniformis	Hercynicus uniformis	Hercynicus uniformis
Pridoli	423,0	Tansgrediens-perneri bouceki lochkovensis-lochkovensis branikensis ultimus-parultimus	perneri  ultimus	transgrediens- parultimus
Ludlow	425, 6 Ludfordian	formosus kozłowski bohemicus tenuis leintwardinensis	formosus  bohemicus tenuis leintwardinensis primus	inexpectatus  leintwardinensis
	427,4 Gorstian	scanicus nilssoni	scanicus-chimaera nilssoni	scanicus nilssoni
Wenlock	430,5 Homerian	ludensis praedeubeli-deubeli parvus-nassa lundgreni	ludensis  nassa lundgreni-testis	nassa lundgreni-testis
	Sheinwoodian 433,4	rigidus-perneri ricartonensis-belophorus  centrifugus-murchisoni	perneri belophorus antennularius murchisoni	riccartonensis  murchisoni-centrifugus
Llandovery	438,5 Telychian	lapworthi-insectus spiralis interval griestonensis-crenulata  turriculatus-crispus guerichi	lapworthi-grandis spiralis crenulata griestonensis turriculatus linnaei	grandis spiralis (crenulata)  griestonensis turriculatus-crispus
	440,8 Aeronian	sedgwickii convolutus argenteus triangulatus-pectinatus	sedgwickii convolutus	linnaei  triangulatus
	443,8 Rhudanian	cyphus vesiculosus accuminatus	cyphus	cyphus vesiculosus accuminatus

changed in length or width. The graptoloid have been collected in detailed stratigraphic sections, whereas in the areas with the high developed tectonics were also collected in several outcrops. The biostratigraphical study of the graptoloids has made possible to distinguish the biozones mainly based on the zonal index species or on graptolite assemblages. Finally, 24 mostly assemblage

biozones have been distinguished (Tab.1).

**Silurian (Llandoveryan).** It was recognized in the Muhurr and in Buzemadhe where transgressively is overlain by Verrucano Formation. The Ordovician/Silurian boundary was identified between the black silty-schists with quartzites and black argillic silty-shales with Llandoveryan graptoloids

The **Rhuddanian** shales are marked by

*Climacograptus citocrescens*, (Buzemadhe) and *Climacograptus rectangularis*, Cl. gr. *scalaris*, *Dimorphograptus* sp. *Pristiograptus acinaces* (Muhurr) that probably have not widely identified *cyphus* biozone.

The **Aeronian** is identified by *Octavitespiralis contortus* *Monoclimacis* cf. *crenularis*, (Buzemadhe), and *Climacograptus* cf. *scalaris*, *Orthograptus ultimus*, *Torquigraptus planus*, *Pristiograptus tenuis*, *Stimulograptus sedgwickii*, *Sti. lobiferus*, *Sti. cf. halli*, *Demirastrites decipiens*, *Diversograptus capillaris* and *D. ramosus* (Muhurr), marked *convolutus* (probably) and *sedgwickii* Biozones.

**The Telychian** graptolitic black shales are characterized by the diversity and abundance of graptoloid and represent the most complete and well studied Landoverian succession from biostratigraphical point of view. Almost all Telychian biozones, mostly from the zonal species, have been identified. In Buzemadhe area, the following assemblage has been found: *Parapetalolithus elongatus*, *P. cf. tenuis*, *Spirograptus turriculatus turriculatus*, *Sp. turriculatus minor*, *Sp. spiralis contortus*, *Torquigraptus proteus proteus*, *T. proteus curvus*, *Streptograptus crispus*, *St. nodifer*, *Pristiograptus nudus variabilis*, *Pr. gr. nudus*, *Monograptus priodon priodon*, *M. gr. priodon*, *Rastrites linnaei* that represent the most graptolitic biozone of Telychian. In Muhurr area, the rich graptolite assemblages include *Climacograptus* sp. (cf. *scalaris*), *Retiolites geinitzianus angustidens*, *Stomatograptus grandis*, *Pseudoplegmatozograptus obesus*, *Ps. obesus hexagonalis*, *Ps. obesus longispinus*, *Pristiograptus nudus*, *Prs. cf. prantli*, *Prs. dubius initialis*, *Monograptus priodon priodon*, *M. priodon parapriodon*, *M. nodifer*, *M. cf. runcinatus*, *M. spinulosus*, *M. cf. anguinus*, *Cochlograptus veles*, *Octavites spiralis spiralis*, *Torquigraptus proteus proteus*, *T. planus*, *T. tullbergi*, *T. tullbergi piraloides*, *Streptograptus crispus*, *St. cf. exiguus*, *Rastrites linnaei*, *R. cf. peregrinus*, *R. longispinus*, *Demirastrites cf. pragensis*, *D. decipiens*, *Cyrtograptus lapworthy*, *Diversograptus ramosus*, *D. capillaris*, *Monoclimacis griestonensis* (frequent), *Mn. crenulata*, that in general identified all Telychian graptolite Biozones. Wenlock dark, gray-green argillic siliceous, or sericitic tuffaceous shales with minette beds mostly occur in Muhurr area and are characterized by a diversity of *Cyrtograptus*

associated of *Monograptus*, *Monoclimacis* and frequent specimens of *Retiolites geinitzianus geinitzianus*. The Llandoveryan/Wenlockian boundary is noted by the first appearance of Wenlockian *murchisoni* just on the Telychian *lapworthy-grandis* Biozones.

**Wenlock, Sheinwoodian** shales are particularly rich in graptoloids and in Muhurr area contain *Retiolites geinitzianus geinitzianus*, (abundant), *Pristiograptus dubius*, *Monograptus priodon praecedens*, *M. cf. priodon*, *M. antenularius*, *M. belophorus*, *Testograptus testis*, *Monoclimacis vomerina*, *Mc. vomerina gracilis*, *Mc. vomerina hemipristis*, *Mc. flumendosae*, *Cyrtograptus murchisoni*, *Crt. af. ramosus* identified from *murchisoni* to *perneri* Biozones, whereas in the northernmost part of Unit, in Nimce, the Sheinwoodian is marked by scarce graptoloid assemblages represented by *Retiolites geinitzianus geinitzianus*, *Monograptus gr. priodon*, *Cyrtograptus sp. indet.*

**The Homerian** shales are known only in Muhurr area and the graptoloid assemblages consist of *Paraplectograptus cf. eiseli*, *Gothograptus nassa*, *Neogothograptus sp.*, *Monograptus priodon praecedens*, *Pristiograptus dubius*, *P. ludensis*, *Mediograptus kodymi*, *Testograptus testis*, that identify the *lundgreni*, *nassa* and *ludensis* Biozones.

**Upper Silurian (Ludlovian)** consists of black or dark argillic-sericitic, with intercalations of thin chert (lydites) and minette beds. The rich graptoloid assemblages are found mostly in stratigraphic sections and also in several outcrops and the Gorstian and Ludfordian biozones were identified.

**The Gorstian** assemblages include *Spinograptus spinosus*, *Plectograptus macilentus*, *Pristiograptus dubius*, *Pr. dubius thuringiacus*, *Pr. cf. vulgaris*, *Monograptus dalejensis*, *M. cf. deubeli*, *M. cf. uncinatus*, *Colonograptus colonus*, *Saetograptus chimaera*, *Bohemograptus bohemicus*, *Neodiverso graptus nilssoni*, *Lobograptus scanicus*, *Linograptus posthumus*, that identify the *nilssoni* and *scanicus-chimaera* Biozones.

**Ludfordian** is documented and has been identified by the zonal index species as *Saetograptus leintwardinensis*, *Bohemograptus bohemicus tenuis* and *Formosograptus formosus* found in the upper part of the Hurdhe Muhur and Bulac sections.



**Pridoli** is poorly documented and has been identified only by the appearance of the zonal index species: *Pristiograptus gr. transgrediens*, *Monograptus perneri*, and *Neocolonograptus cf. ultimus*.

**Lower Devonian (Lochkovian)** consists of yellow siltstone-tuffaceous shales from Fushe Muhurr Formation with *M. uniformis*, *M. uniformis angustidens*, *M. aequabilis*, *M. microdon microdon*, *M. microdon silesicus* belonging *touniformis* Biozone, followed in abundance only by *Monograptus hercynicus* zonal species that is the latest Devonian graptolite Biozone. It is overlain by intercalations of dark shales and thin limestone layers rich in Praghian-Zlichovian *Tentaculites*. (Pashko 2004).

Comparison and correlation of sedimentary sequence and graptoloids records from Albania and Carpatho-Balkanides based on the similar lithostratigraphical characteristics and on the integrated biostratigraphy of graptoloids. The Silurian-Lower Devonian Graptoloid Black Shales of Muhurr-Caje Unit in general is similar to coeval sequence and includes the graptoloids assemblages, that were correlated with assemblages from Western and Eastern Europe, particularly from Bohemian Area. Closest comparisons are with Carpatho-Balkanides, such as Eastern Serbia (Krstic et al. 2005).

## Conclusions

In the Graptolitic Black Shale of Landoverian-Early Devonian age from Muhurr-Caje Unit were identified 24 biozones, which are common with equivalent shales from Europe and particularly from Carpatho-Balkanides area.

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## MICROFOSSIL RECORD AND FACIES TRANSITIONS OF OXFORDIAN TO BERRIASIAN CARBONATES IN THE WESTERN SREDNOGORIE, BULGARIA

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### Abstract

The study area attracted the present authors' interest for the following reasons: complex relationships and fast facies transitions between Upper Jurassic and Berriasian carbonates of three distinct depositional settings (carbonate platform, pelagic basin and flysch trough); scarcity so far of abundant paleontological data on strata, except the Kimmeridgian; new results from the recent 1:50000 geological mapping. This work presents the description of five, Oxfordian to Berriasian carbonate sections, in the Western Srednogie; the calpionellid, foraminiferal and calcareous dinocyst distribution and precise dating and facies transitions. Subject of this study are the Yavorets, Gintsi, Glozhene, Slivnitsa, Salash-Cherni Osam, and Cherni Osam Formations, their vertical and lateral passing, age determination, carbonate microfacies and evolution of the depositional environment.

Dragovishtitsa 1 section. The *Chitinoidea* Zone (*Dobeni* and *Boneti* subzones) corresponds to the upper part of Gintsi Formation and the basal 3 m of the Glozhene Formation. The *Praetintinnopsella* Zone is represented only by its index species in the lower part of Glozhene Formation. *Elliptica* Subzone in this section corresponds to a 2 m-thick interval of transitional sediments between the Glozhene and Slivnitsa formations, in both macroscopic features and microfossil content.

Dragovishtitsa 2 section. The Salash-Cherni Osam Formation represents alternation of clayey limestones and limy sandstones. The whole section corresponds to the *Elliptica* Subzone. The ammonites found are *Berriasella* (*B.*) cf. *vranensis* and *Jabronella* (*J.*) cf. *fuelopi*. The former species was only reported from its type locality in the Upper Berriasian. The co-occurrence of *Berriasella* (*B.*) cf. *vranensis* with calpionellid associations of *Elliptica* Subzone indicates its lower stratigraphic range.

Dragovishtitsa South section. The age of the micritic and grained limestones of the Slivnitsa

Formation is determined as Oxfordian based on the record of the calcareous dinocysts *Colomisphaera fibrata* and *Colomisphaera pieniniensis*. Upwards, the mainly grained and lithoclastic limestones of the Glozhene-Slivnitsa Formation are determined as Late Tithonian based on the calpionellid *Boneti* Subzone, *Praetintinnopsella* Zone and *Remanei* Subzone, as well as on the first occurrence of the foraminiferal species *Protopeneroplis ultragranulata*. Microincrusting foraminifera that are typical of the carbonate platform were redeposited in the Glozhene-Slivnitsa Formation.

Dragovishtitsa West section. The Yavorets Formation is assigned to the interval from Middle Callovian to Oxfordian based on the recorded calcareous dinocysts and the foraminiferal *Ophthalmidium strumosum* Zone. The age of the clayey nodular limestones of the Gintsi Formation is determined as Late Kimmeridgian and Early Tithonian on the record of the calcareous dinocysts *Colomisphaera nagy*, *Stomiosphaera moluccana*, and *Parastomiosphaera malmica*. The Gintsi Formation is covered with a considerable stratigraphical hiatus by the Early but not earliest Berriasian Glozhene-Slivnitsa Formation (*Elliptica* Subzone). The abundant foraminiferal *Coscinoceras* assemblage had allochthonous character in the Glozhene Formation since normally it occurs in the shallow-water subtidal zone.

Dragovishtitsa East section. The Cherni Osam Formation here represents a pre-flysch triple alternation of sandstones, clayey limestones and micritic limestones and is of Early Berriasian age (*Alpina*, *Remaniella* and *Elliptica* subzones). This evidences an Early Berriasian onset of the carbonate turbiditic deposition in the area.

Stratigraphic hiatuses. The Upper Tithonian *Chitinoidea* and *Praetintinnopsella* Zones and the Berriasian *Elliptica* Subzone of *Calpionella* Zone are documented in Dragovishtitsa 1 section. It is noteworthy that the Uppermost Tithonian *Crassicollaria* Zone and the Lower Berriasian *Alpina* and *Remaniella* subzones are absent. In

Dragovishtitsa West section parts of the Tithonian and Berriasian are missing. In Dragovishtitsa South section the stratigraphic hiatus corresponds to the Kimmeridgian and the Early Tithonian. These results differ significantly from all Oxfordian to Berriasian pelagic sections in the Western Balkan and Western Fore-Balkan in Bulgaria where the sedimentary record is continuous.

Facies transitions. The Glozhene Formation, even rich enough in chitinoideids and calpionellids, contains also allochthonous foraminifera and

debris from the carbonate platform and the shelf edge. It differs from the typical development in the distal pelagic basinal parts of the West Balkan Mts and is here designated as the “Glozhene-Slivnitsa Formation”. From NW to SE, the biogenic carbonate platform limestones of tSlivnitsa Formation pass to the pelagic limestones of the Yavorets, Gintsi, Glozhene-Slivnitsa and Salash-Cherni Osam Formations, and further to SE – to the carbonate turbidities of the Cherni Osam Formation.

## THE PRESENCE OF THE SPECIES *MAMMUTHUS PRIMIGENIUS* ON THE TERRITORY OF URZICA MARE (DOLJ COUNTY), ROMANIA

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### Abstract

The molar which represents the topic of my research was discovered by Mr. Ion Ganea around Urzica Mare, among the sands and pebbles of the bed of Desnățui river, 3 metres deep, at Fântânele point.

The village Urzica Mare is part of the commune Urzicuța, in Dolj County. It is a plain locality, situated on the right bank of Desnățui River. Urzica Mare is crossed by the national road connecting Segarcea to Băilești.

Geographically, the village belongs to Câmpia Olteniei (The Plain of Oltenia), which is part of Câmpia Română (The Romanian Plain), whereas geologically it belongs to the Moesian Platform. The deposits where the molar of *Mammuthus primigenius* was discovered belong to the last sedimentation cycle of Badenian -Quaternary of the Moesian Platform, on whose structure Urzica Mare is found.

Starting with 1908, several molars of *M. primigenius* have been discovered in Campia Olteniei and then described by scholars.

The paleontological material discovered at Urzica Mare consists in an upper molar M<sup>3</sup> from the left side. The molar was discovered in a fragmentary state, but after restoration it appears to be in very good shape, and can be considered as being whole. It contains 13 lamellas and 2 talons, one anterior and the other posterior. The length of the mastication surface is of 160.8 mm. The maximum width of the molar can be found with the third lamella - 86.8 mm. The width of the lamellas at the level of the crown is the following: lam. 1- 56.8 mm, lam. 2- 60.0 mm, lam. 3- 56.7 mm, lam. 4- 49.0 mm. The other lamellas are covered in cement. The first and the second lamellas have a common root. The average breadth of lamella 1 is of 7.4 mm, the one of lamella 2 is of 7.9 mm, of lamella 3 of 8.0 mm, and of lamella 4 of 8.0 mm. The average breadth of the enamel is of 1.2 mm with lamella 1, with lamella 2 it is of 1.5 mm, with

lamella 3 of 1.1 mm, while with lamella 4 it is of 2.4 mm. Lamella frequency is 8, and the ratio L/l is approximately 3.

By taking into account the features of the molar (high lamella frequency, thin enamel and considerable height) we may conclude that the sample definitely belongs to the species *M. primigenius*. Unfortunately, the circumstances of the discovery do not allow us to conduct a more thorough discussion regarding the stratigraphy of the site. Even so, the sample analyzed here is important as a new discovery of the genus *Mammuthus* on the territory of Oltenia, representing an undeniable piece of evidence for the existence of the species *M. primigenius* in this area.



## CAMPANIAN PERITIDAL MICROBIAL–FORAMINIFERAL LAMINITES FROM THE MAKARESHI STRUCTURE, KRUJA ZONE (ALBANIA).

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### Abstract

The Makareshi structure in the Kruja zone in Albania is a part of the Apulian passive margin, which is now placed in the External Albanides. Previous studies by Albanian geologists have already revealed the presence of Late Cretaceous peritidal limestones in this zone. Campanian deposits cropping out along the road, ca. 2 km west of Kruja, close to Sari Salltik were investigated by means of thin-section analysis. The section consists mainly of bedded peloidal-bioclastic wacke- to packstones and bindstones interlayered with rudist floatstones. Studies were focused on analysis of microfacies and microbiota from the laminated limestones. Lamination is underlined by an alternation of wackestones, packstones, bindstones (mostly foraminiferal) as well as the presence of densely laminated and clotted microbial fabrics. Due to the significant role of encrusting foraminifera and the presence of microbial laminae, some of the analysed limestones can be classified as bindstones. Fenestral structures and dolomite crystals occur locally.

The dominant microfossils are different morphotypes of nubeculariid foraminifera, which are abundant in bindstones or scattered in wackestones and packstones. They are spectacularly well preserved in a few millimeters-thick layers/

laminae, where monospecific (?) assemblages are embedded in peloidal microbialites and associated with possibly syndimentary sparite cement. In some laminae nubeculariids are ferruginized what enhance lamination. Other associated benthic foraminifera include for example the calcareous form *Rotorbinella scarsellai* Torre. *Thaumatoporella parvovesiculifera* (Raineri) – a microfossil *incertae sedis* – is common in some laminae. Based on microfacies characteristics and microfossil association, the studied limestones can be assigned to the so-called *Decastronema-Thaumatoporella* association widely reported from the Upper Cretaceous peritidal deposits of Apulian, Apenninic and Adriatic carbonate platforms. However, our observations have not revealed the presence of the calcimicrobe *Decastronema kotori* (Radoičić). Instead, we observed *Gahkumella huberi* Zaninetti described from the Cenomanian of southern Italy and tiny *Girvanella*-type tubes. Our findings suggest that some Late Cretaceous records of *Decastronema kotori* may, in fact, represent some of these microfossils or small nubeculariid foraminifera. Apart of limestones from Croatia, nubeculariids have not been mentioned in the literature as an important component of the Upper Cretaceous deposits. Nubeculariid foraminifera might, however, play an important binding role in Late Cretaceous shallow-water carbonate settings.

## THE FIRST FINDING OF THE SILICEOUS MICROFOSSILS NEAR THE SARMATIAN/PANNONIAN BOUNDARY OF FRUŠKA GORA (CENTRAL PARATETHYS, SERBIA)

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### Abstract

The Late Miocene isolation of the Pannonian basin (PB) coincides with the boundary between the Sarmatian and Pannonian regional stages. More detailed studies and the relationship between the Sarmatian and Pannonian sediments in the Serbian part of PB have been published in recent works (Ganić et al. 2010; Ter Borgh et al. 2013). Herein, for the first time in this area, based on data from the boreholes, the sediment with siliceous microfossils – diatoms, silicoflagellates, ebridians and chrysophycean stomatocysts was observed. Sarmatian diatom flora has a marine-brackish origin with dominant index species of *Coscinodiscus rugulosus* Hajos. Subdominant species belong to genera *Thalassiosira* Cl. and *Paralia* Heib. Other genera such as *Cocconeis* Ehr., *Diploneis* Ehr., *Mastogloia* Thw., *Rhopalodia* O.Müll. and *Surirella* Turp. have the greatest diversity of species. It appears that a total diatom production is highest due to the relatively stable sedimentation conditions and moderately low nutrient concentrations. Silicoflagellates and ebridians have a poor taxonomical composition (only two taxa of silicoflagellates are recognized: *Distephanus crux* (Ehr.)Hack. and *D. crux* var *longispina* Schulz). The ebridians are very abundant in depth. Chrysophycean stomatocysts occurred in all samples and are particularly abundant in the uppermost sample in the borehole B-13, as well as in the sample from the borehole B-11. Some changes in microfloral assemblages in the borehole B-13 have been noted. The diatom diagram has been compiled using taxa with abundances corresponding to 4-5 of Schrader's scale.

**Keywords:** Siliceous microfossils, Middle Miocene, Central Paratethys, Serbia

### Introduction

The Central Paratethys is an extensional system of back-arc basins existed during the Early and

Middle Miocene. Their development is driven by the roll-back of mature subducting slabs (van Hunen and Allen 2011; Ter Borgh et al. 2013). The pre- and syn-rift infill of back-arc basin systems is characterized by a transition from continental, alluvial and lacustrine to marine depositional environments (Rögl 1999). At beginning of the Late Miocene, the isolation of the Central Paratethys caused a major change in sediment fluxes as well as a regional extinction event; the Sarmatian-Pannonian Extinction Event (SPEE) (Harzhauser and Piller 2007). Absolute age of this event is uneven. High-resolution ages have recently been obtained for three Central Paratethys basins: the Transylvanian basin (11.3 Ma), the Vienna basin and the Pannonian basin (both 11.6 Ma) using magnetostratigraphy and Ar-Ar dating (Vasiliev et al. 2010; Paulissen et al. 2011; Ter Borgh et al. 2013). The principal cause for the isolation of the Central Paratethys was the uplift of the Carpathians, while sea level fluctuations may have had a minor influence.

### Geological settings

The northern field of the Filijala open pit (northern slope of Fruška Gora Mt.) contains only the Pannonian caspi-brackish deposits. However, a part where the Sarmatian sediments were drilled is situated in the so-called southern field of the pit. Three exploration boreholes IB-9, B-11 I B-13 were drilled (Fig. 1). Stratigraphically, the borehole IB-9 was already known before (Ganić et al. 2010). In borehole B-11, with a total depth of 53 m, Sarmatian deposits are found in the depth of about 20 m to the end of drilling at 53 m. They are presented by gray- dark, laminated marls with interbeds of marly sandstones. Above that, typical so-called the Beočin light-gray, poorly bedded marls, with numerous ostracodes and mollusks are found. In borehole B-13, with a total depth of 19 m, below the Quaternary anthropogenic deposits made by remains of former landfills (total thickness of 4 m) the similar Pannonian poorly bedded

marls to a depth of 7.6 m were drilled. Below that, in the lower part of the borehole to a depth of 19 m, different Sarmatian sediments represented by stripy, grayish-dark laminated marls, sandy marls and diatomites were found.

suggest the Upper Sarmatian (s.str.) age and can be correlated with the Lower Bessarabian (the lower part of Middle Sarmatian s.l from Eastern Paratethys) developed in relatively shallow water conditions (Ter Borgh et al. 2013). A lot

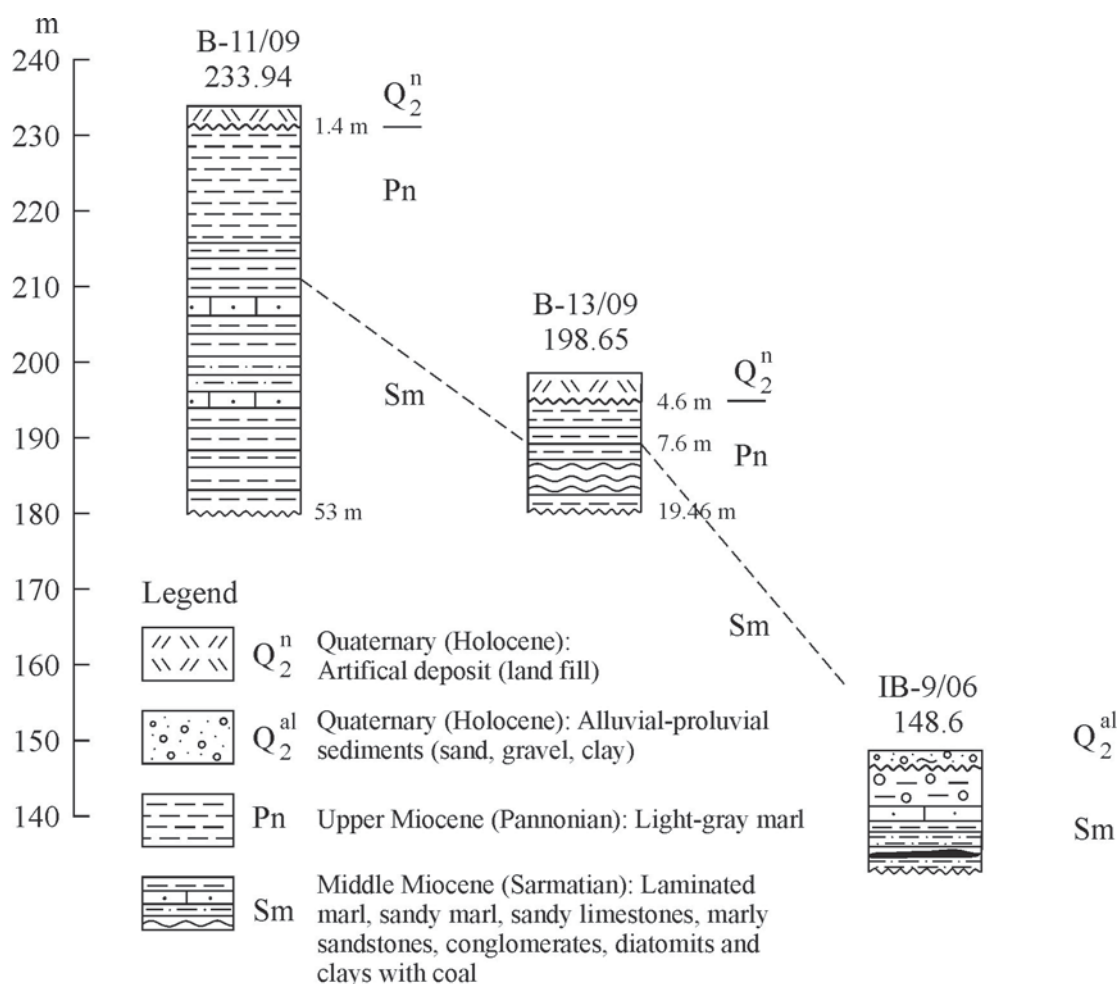


Figure 1. Stratigraphic sections of the studied boreholes (northern slope of Fruška Gora Mt., Serbia).

However, it must be emphasized that nowhere on the surface of the Filijala open pit, the Sarmatian/Pannonian transition was observed. It is determined precisely in these wells. Based on the biostratigraphic analysis of mollusks, foraminifera and ostracodes (more than 100 micropaleontological samples collected from the Filijala open pit - Ter Borgh et al. 2013) it was found that there is a continuity of sedimentation between the marine-brackish Middle Miocene (Sarmatian) and the caspiabrackish Upper Miocene (Pannonian, Lake Pannon). According to the latest biozonations (Ter Borgh et al. 2013), the base of the Pannonian is marked by an abrupt change within fossil association in relation to Sarmatian one. Foraminifera and ostracode assemblages

of Pannonian mollusks and ostracodes indicate a mesohaline, basinal development of the Lake Pannon which yielded an amazing adaptive radiation of mollusks (Magyar et al. 1999). Most of those mollusks, ostracodes, nannoplankton, dinoflagellate and the other fossils are recognized as endemic (Rundić et al. 2013).

During these recent studies, for the first time in this area, the sediment with siliceous microfossils -diatoms, silicoflagellates, ebridians and chrysophycean stomatocysts was found. Their finding, identification and biostratigraphical and paleoecological remarks are the main goal of this paper.

## Material and Methods

Five samples from the borehole B-13 (depth 11.03-12.55 m) and one from borehole B-11 (depth 21.00m) were analyzed. Diatom analysis was carried out by standard techniques (Ognjanova-Rumenova 1991). Preparation for scanning electron microscopy followed Hasle and Fryxell (1970) and samples were examined with Jeol JSM 5510. Relative abundance of diatoms was defined according to Schrader's scale (Schrader 1973). Spectra of physico-chemical tolerances based on studies of modern diatoms were used to reconstruct the sedimentary environments in the deposits. Six factors were selected: habitat, salinity, pH, nutrient, temperature, geographic distribution.

## Results and Discussion

The siliceous fossil flora is abundant, but the preservation in the sample B-11/21.00m is not good. The discovered marine-brackish diatom flora is rich and interesting. Most abundant are the representatives of class Coscinodiscophyceae. Dominant in the investigated diatom succession is *Coscinodiscus rugulosus* Hajos; this species was first introduced and described as *Coscinodiscus impressus* Hajos from Sarmatian sediments with marine origin in South Hungary (Meseke Mountains) (Hajos and Rehakova 1974; Hajos 1986). Subdominants, belonged to class Coscinodiscophyceae are species of genera *Thalassiosira* Cl. and *Paralia* Heib. The species variety in the diatom flora is due to the pennate forms. The genera *Cocconeis* Ehr., *Diploneis* Ehr., *Mastogloia* Thw., *Rhopalodia* O.Müll. and *Surirella* Turp. have the greatest diversity of species.

Silicoflagellates and ebridians are other siliceous microfossils in the investigated sediments. Their taxonomical composition is very poor, for the silicoflagellates are established only two taxa: *Distephanus crux* (Ehr.) Hack. and *D. crux* var *longispina* Schulz. The ebridians are very abundant in depth.

Chrysophycean stomatocysts occurred in all samples and are particularly abundant in the uppermost part of profile B-13, as well as in the sample B-11/21.00 m. These are the endogenously-formed siliceous stomatocystae (also called statospores and resting cysts) widely believed to be taxon specific. The cysts are not classified in different groups, according to their smooth and

scattered exterior.

Changes in microfloral assemblages in depth have been investigated in the borehole B-13 sequence. The diatom diagram has been compiled using taxa with abundances corresponding to 4-5 of Schrader's scale (Schrader 1973). From 12.55 m to 11.53 m the most abundant siliceous microfossil groups are the diatoms and ebridians. At the base of the sequence (12.55 m) the chrysophycean stomatocysts are also frequent, as well as a lot of different epiphytic diatom representatives, belonged to genera *Mastogloia* Thw., *Rhopalodia* O.Müll., *Cocconeis* Ehr. and *Licmophora* C.A., which proved more shallow environment conditions. The replacement of more epiphytic diatom forms began at 11.53 m, the relative abundance of *Coscinodiscus rugulosus*.

Hajos increased, and also the quantity of the silicoflagellates. The ebridians are developing continually but are not so abundant, which coincides with the highest frequency of chrysophycean stomatocysts at 11.03 m.

The diatom flora is marine-brackish one. Based on our finding it appears that a total diatom production is highest due to the relatively stable sedimentation conditions and moderately low nutrient concentrations.

## Conclusions

The first finding of the siliceous microfossils was observed in the area of Fruška Gora Mt. (Central Paratethys, northern Serbia), near the Middle/Upper Miocene boundary (Sarmatian and Pannonian Regional Stages). Within the whole fossil assemblages, the representatives of marine-brackish diatom flora (class Coscinodiscophyceae) are dominant. Among them, the index species of *Coscinodiscus impressus* Hajos points to the Upper Sarmatian s. str. (Lower Bessarabian). Silicoflagellates and ebridians as well as chrysophycean stomatocysts have a minor stratigraphic importance. All together, these fossils indicate a relatively stable, shallow water environment and moderately low nutrient concentrations of the Sarmatian brackish sea.



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## DEPOSITIONAL SYSTEM CHANGES IN THE BLATNÉ DEPRESSION: RATKOVCE 1 WELL CASE STUDY

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### Abstract

In the Blatné depression, the Ratkovce 1 well penetrated the Miocene sedimentary record. Biostatigraphy documents calcareous nannoplankton NN4, NN5 and NN6 zone. Foranifera CPN7 and CPN8 zones are also recognised. The source rocks analysis shows that the material from the well was derived from granitoides and gneisses of the crystalline basement and from Permian to Lower Cretaceous cover and nappe units, moreover Lower Badenian volcanic rocks are an important source in the lower part of the well. Sedimentology describes four distinct well core groups: A) is composed of conglomerates, sandstones, siltstone and claystones. Imbrication of clasts, crossbedding, and armored clay intraclasts are observed; B) consists of claystone, siltstones and conglomerate representing debris flows that pass into turbidite sequences which contain horizontal and ripple lamination. Loadcasts are also present; C) is built up of claystone and siltstone, parting lineation indicates bedforms of the upper flow regime, turbidity current are present; D) is built up by intraformation lag deposits composed of angular fragments of sandstone clasts in siltstone to claystone matrix. Spontaneous potential log (SP) reflects the change in grain size, geometry and composition of sedimentary bodies. 3 *funnel shape* cycles, 2 *serrated shape* cycles and 2 cycles with a *bell shape* were recognized. We distinguish 2 depositional systems a) fandelto – proximal to distal basin slope, b) coastal to alluvial plain and 5 sedimentary facies: 1) Deposition in fandelto to onshore environment (early Lower Badenian); 2) Proximal slope gravity sediments of the (middle Lower Badenian); 3) Distal slope to offshore turbidites of the. plus upper part and. (late Lower Badenian to early Upper Badenian); 4) Coastal plain marine to brackish sediments deposited in littoral to neritic zone (late Upper Badenian to

Sarmatian); 5) Shallow lacustrine to alluvial plain sediments of the Pannonian to Pliocene age.

**Key words:** *Blatné depression, Biostatigraphy, Source rocks, Sedimentology, Paleoenvironment.*

### Introduction

Danube Basin is situated at the East Alpine, Western Carpathians and Transdanubian Range junction and represents one of the most important depocentres of the Pannonian Basin System. Basin northern margin is divided to finger-like bays between Western Carpathian core mountains Malé Karpaty Mts., Považský Inovec Mts., and Tribeč Mts. From West to East known as Blatné, Rišňovce and Komjatice depression. In the Blatné depression, the Ratkovce 1 well penetrated the whole Miocene sedimentary record. Biostatigraphy, sedimentology and source rocks analysis of the well document changes in marine and terrestrial environments.

### Materials and Methods

All materials were obtained at the well repository of Nafta as., situated in Gbely Town. For the micropaleontological analysis, altogether 45 rock samples from the suitable well cores were taken. Samples were collected from every well core, in 40 cm interval were possible. In the well core 6, sampling was more detailed (samples every 25 cm.) due to redefining of the CPN8 (Cicha et al. 1975) planktonic foraminiferal biozone. From the rock samples, the residuum and selected foraminiferal assemblage was stored at the Department of geology and Paleontology PRIFUK.

For determining source rocks, coarse grained samples were selected and studied under a polarization microscope. Heavy mineral analysis was done using 0.25-0.10 mm fraction and studied under a binocular microscope. Selected heavy

minerals were analyzed quantitatively by a WDS, microprobe Cameca SX-100, at the Geological Institute of Dionýz Štúr, Bratislava, Slovak Republic. Measurement conditions: 15keV 20nA. Analysis of garnets were recalculated on the basis of 8 cations.

During the sedimentological analysis, all available cores and their sampler-cards were fotodocumented. 31 sediment samples were collected. Succeeding these samples were cut in half perpendicular to the bedding plane, washed, treated for preservation with dispersive glue, scanned, digitalized and finally sedimentary textures and structures were described, mainly in sense of Miall (2010).

Evaluation of the spontaneous potential (SP) core log was also applied. The curve was originally constructed by Moravské naftové daly, n. p., Karotáž HODONÍN (1969). We interpret the log with the help of published literature (Rider 1986; Emery and Myers, 1996).

## Results

**Biostatigraphical analysis** draws from calcareous nannoplankton and foraminifera biozonations documenting presence of calcareous nannoplankton of the NN4, NN5 and NN6 biozone. From the foraminiferal point of view, we can follow FO events of planktonic species: Early Badenian *Globigerinoides quadrilobatus* (d'Orbigny), *Globigerina regularis* d'Orbigny represent the biozone CPN7, FO *Orbulina suturalis* (Brönnimann) is linked to the CPN8. The Late Badenian was determined with *Globigerina druryi* Akers together with *G. woodi decoraperta* (Takayanagi and Saito).

Based on these results and published lithostratigraphical data we believe that the sedimentary sequence in the Ratkovce 1 well, begins with the Middle Miocene strata deposited discordantly on the pre-Cenozoic basement (in the well present from 2016 to 1991m). The Miocene sedimentary sequence is represented by Lower Badenian Špačince Fm. with basal Jablonica conglomerate Mb. (1991-1060 m), Upper Badenian Báhoň Fm. (1060-410 m) and the Sarmatian Vráble Fm. (410-257 m). The above deposited Late Miocene succession is build up by the Pannonian Ivánka Fm. (257-135 m.). The Late Miocene-Pliocene sediments are represented by Volkovce Fm. (135-35 m) and the Quaternary strata (35-0 m).

The source rocks analysis shows that the material from the Ratkovce 1 well was derived from granitoids and gneisses of the crystalline basement and from Permian to Lower Cretaceous cover and nappe units derived from adjacent mountain ranges. Moreover Miocene, Lower Badenian volcanic rocks become an important source with epiclastic material in the lower part of the well, reaching about 500 m in thickness. We speculate about volcanoes exceeding the sea level. The closest one is most probably buried near Trakovice village.

**Sedimentology of the well cores.** Above all sedimentary textures and structures were described from bottom to top (Fig. 1). The **basal part** is composed of conglomerates with intercalations of sandstones, siltstone and claystones. Fine to coarse grained conglomerates, with carbonate, quartzite, granitoid and volcanic pebbles (some clasts reaching up to 5 cm in diameter) occur and are subangular to well rounded. The matrix is composed from coarse to fine grained sandstone. On some samples imbrication of clasts, cross-bedding, indistinct fining upwards and armored clay intraclasts were observed. Occasionally, the conglomerates pass into coarse grained lithic sandstone and brown claystone. Hummocky bedding of heterolithic sediments indicates onshore environments. Siltstone with claystone intercalations are on some places laminated and also ripple cross bedding was observed. Claystones, in the upper part of the coarse sequence having abundant mica, macrofauna fragments (echinoid) and carbonized plat fragments were observed.

The overlying sequence of the pale brown to gray claystones and siltstones, with abundant mica and carbonized plant fragments in the middle part intercalate with medium to fine grained sandstone with small sized load casts. A sample shows small sized ripples and layered diamictite (pebbly claystone) with macrofauna (bivalves) pointing out dynamic events in the neritic offshore sedimentary environment. Pebbly claystone with carbonized plant fragments and macrofauna (echinoderm fragments) as well as poorly sorted conglomerate layers (clasts reach up to 5cm in diameter) represents debris flows (proximal slope environment). Bioturbated siltstone and sandstone with carbonized plant fragments occasionally pass into turbidite sequences with sandstone and claystone layers with horizontal and ripple lamination, abundant load casts at the bottom of

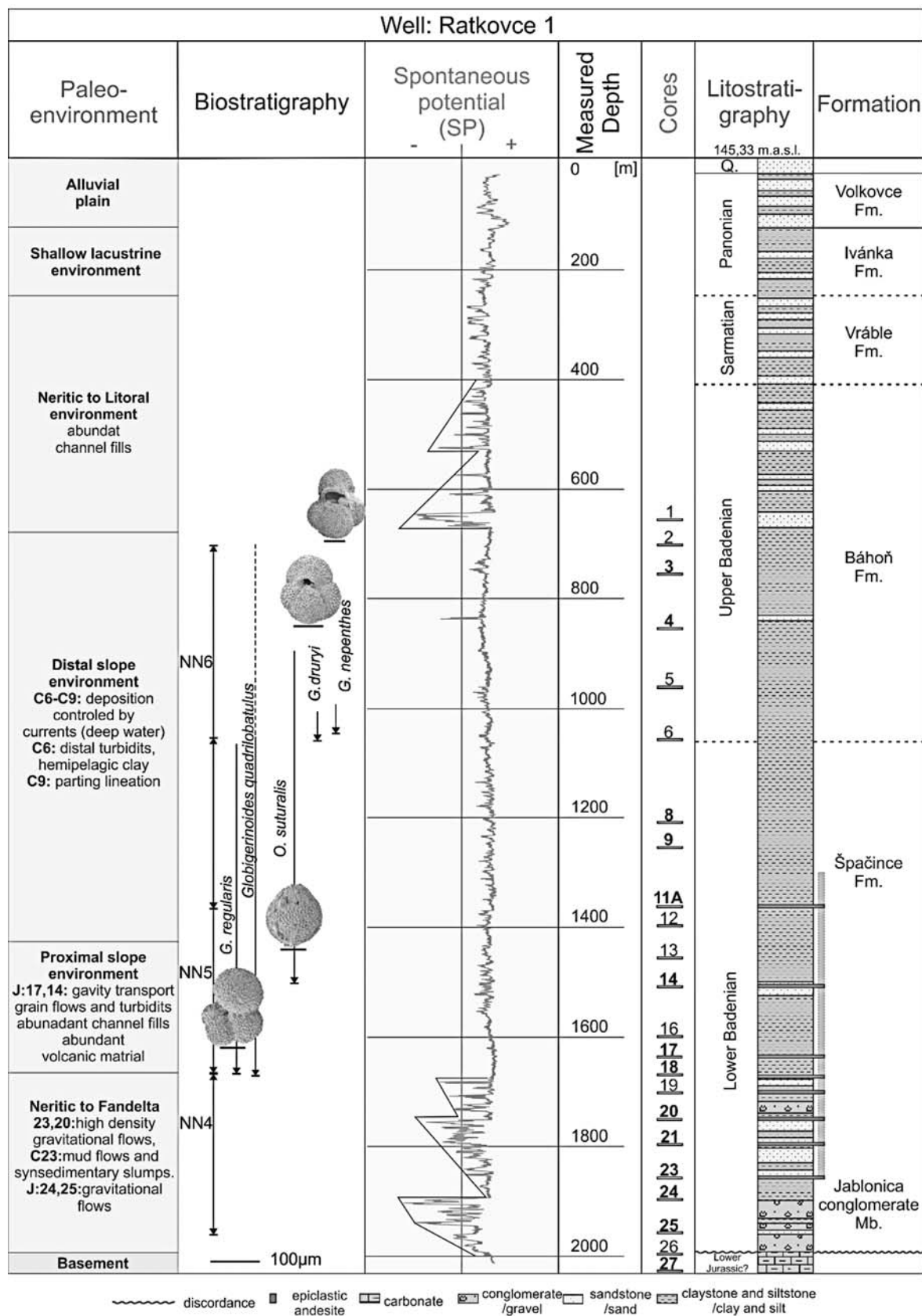


Figure 1. Passport of the Ratkovce 1 well, lithostratigraphy explored from Biela et al. (1987) and Gaža (1969).



layers were documented. The upper part of the offshore predominantly pelitic sequence is built up of pale brown to gray claystone and siltstone, rare layers of fine grained sandstones are present. The sedimentary succession at places contains parting lineation indicating bedforms of the upper flow regime and turbidity current transport (this could also be confused with traction marks).

The top of existing well cores sedimentary material is build up by intraformation lag deposits composed of angular fragments of laminated sandstone clasts in siltstone to claystone matrix, carbonized plant fragments are abundant.

**Spontaneous potential log (SP) curve shape** (Fig. 1) reflects the change in grain size, geometry and composition of sedimentary bodies. The Ratkovce 1 well SP curve begins with 3 *funnel shape* cycles with characteristic change from a positive anomaly to negative anomaly, sharply bordered at the top. This coarsening upwards cycles indicates delta front facies. Middle part of the curve has a *serrated shape* and represents alternations of thin layers of sandstone and claystone, indicating frequent changes of depositional conditions in distal turbidites of basin slope environments. Regrettably deeper shelf environment influenced by storm activity cannot be excluded. Toward overlying strata, the log posses 2 cycles with a *bell shape*, representing retrogradation interpreted as a change from dynamic to calm environment. Principally the curve shows fining upwards and refers to a transgression or tidal environment. In the case of Ratkovce 1 well, the tidal environments of coastal plain is more probable. The rest of the log is again represented by a *serrated shape*, interpreted as a gradation connected with the development of alluvial floodplains.

## Conclusions

The study allowed us to distinguish two depositional systems: **a)** fandelto, proximal to distal basin slope. **b)** coastal to alluvial plain and five dominant sedimentary facies (Fig. 1).

From the base to top of the well: **1)** Jablonica conglomerate Mb. deposited in fandelto to onshore shallow marine environment of early Lower Badenian age. **2)** Proximal slope gravitational current sediments belonging to Špačince Fm. of middle Lower Badenian age. **3)** Distal slope to offshore turbidites and gravitational currents of the Špačince Fm. upper part and Báhoň Fm. lower

part, e.g. of upper Lower Badenian and early Upper Badenian age. **4)** Coastal plain marine to brackish sediments interfingering with deltaic environments deposited in littoral to neritic zone of late Upper Badenian to Sarmatian age. **5)** Shallow lacustrine to alluvial plain sediments of the Pannonian to Pliocene age.

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## PALEOENVIRONMENTAL RECONSTRUCTION BASED ON EARLY MIOCENE FORAMINIFERAL ASSEMBLAGES FROM THE NORTH-WESTERN TRANSYLVANIAN BASIN (ROMANIA)

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### Abstract

The purpose of this study is the paleoenvironmental characterization of the Miocene deposits and possible correlation with other sections from the Transylvanian Basin. Twenty-seven samples were taken from two representative Lower Miocene formations from the north-western Transylvanian Basin: Chechis Formation (outer shelf settings) and Hida Formation (deep-sea settings) (Krézsek and Bally, 2006; Filipescu 2001). The studied area is located near the Gălpâia Village (Sălaj County), where two outcrops were sampled. Previous studies revealed rich foraminiferal assemblages represented by both benthic and planktonic foraminifera (Popescu 1975).

Planktonic communities are dominated by *Globigerina praebuloides*, *Globigerina lentiana*, *Globigerina ottnangiensis*, *Globigerinoides trilobus*, *Tenuitellinata angustiumbilitata*. The assemblages suggest an Early Miocene age, belonging to the *Globigerinoides trilobus* Biozone (Popescu 1975).

The benthic assemblages are well represented by both calcareous and agglutinated forms. These were divided into epifaunal, shallow-infaunal and infaunal dwellers in order to characterize the paleoecological factors such as bottom-water oxygenation and organic matter flux to the seafloor (Jorissen 2002). Although infaunal forms are abundant and diverse (e.g., *Uvigerina popescui*, *Praeglobobulimina pyrula*, *Karreriella*

*chilostoma*, *Laevidentalina elegans*), the presence of several epifaunal species (*Cibicidoides pachyderma*, *Cibicidoides pseudoungerianus*) suggest well-oxygenated bottom-waters and mesotrophic conditions. The abundance and diversity of benthic foraminifera show a decrease towards the top of the second outcrop, where agglutinated foraminifera dominate the benthic community due to the deepening of the basin.

Univariate (species diversity, Planktic/Benthic ratio) and multivariate analyses (hierarchical clustering and non-Metric MultiDimensional Scaling) have been also applied to the benthic assemblages in order to identify relationships between samples and the controlling environmental factors such as oxygenation, organic matter flux, temperature and paleodepth.

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## THE STRATIGRAPHY OF THE CRETACEOUS DEPOSITS IN THE REGION OF RAHOVEC

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### Abstract

The Cretaceous deposits cover the most of the surface of Rahovec Region and include a part of the Internal Dinarides and External parts of the Vardar zone and have a wide spread displaying different facies formed in different environmental settings. Based on the presence of Cretaceous members, their unequal position in relation to older deposits and their different lithofacial features, within the deposits of this age were separated two tectonostratigraphic units.

In the western belt (MU-Malisheva Units), the Cretaceous carbonate rocks are widespread around Gremnik-Shkoza-Pagarushë, Zatriq and Nishori. The Cretaceous in this area is presented in two series: Lower Cretaceous and the Upper Cretaceous and is mainly characterized by shallow water sediments and in part by pelagic sediments as follows: shallow water sediments, reefal and sub-reefal sediments (turbidites) and pelagic sediments. The Upper Cretaceous deposits have a wider spread than those belonging to Lower Cretaceous. Based on biostratigraphic and lithofacial studies undertaken in some selected outcrops, we have distinguished the following divisions here below:

- Conglo-breccia facies (Lower Cretaceous)
- Carbonate facies (Barremian, Aptian and Albian)
- Clastic facies ( Senomanian)
- Dolomitic and sandy limestone with *Cyprina* and *Orbitolina* and pelagic limestone (Turonian)
- Marly limestone with chert nodules, thin-bedded limestone, mudstone with chert lenses (Santonian)
- Limestone with *Globotruncana*, limestone with rudists, marly shale (Lower Maastrichtian-Upper Maastrichtian)

Cretaceous carbonate-clastic sediments of eastern belt (DU-Drenica Unit) consist only of Upper Cretaceous deposits which are mostly represented by clastic turbidites and less by carbonate sediments. The Upper Cretaceous flysch series is developed Rahovec region within the psamitic and brecciated facies.

Psamitic flysch facies (Upper Maastrichtian) represents the Upper Cretaceous younger flysch sediments (Upper Maastrichtian) and are spread outside the region of Rahovec with a NNW-SSE orientation comprising the eastern edge of Santonian limestone with the gradual deployment on these carbonate sediments.

Brecciated flysch facies (Lower Maastrichtian) constitutes a relatively wide area of the field study. The size of the terrigenous component varies from microscopic size to blocks of several m<sup>3</sup>. The western belt breccia is partially withdrawn through the psamitic flysch facies and partly covered by Pliocene sediments. Most frequently, the breccia blocks consist of marble, brecciated marble and conglomeratic schist.

**Key words:** *Stratigraphy, deposits, cross section, belts and fossil*

## A NEW APPROACH TO STRATIGRAPHIC INTERPRETATION - RAHOVECI REGION

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### Abstract

The Mesozoic deposits are widespread in Rahoveci region and cover an area of approximately 35-40% of the 1600 km<sup>2</sup> total surface. The Triassic deposits outcrop in southeastern and central parts of the region. They are represented by metamorphosed limestones, schists, intracontinental basalts, etc, and their relationship with the underlying Paleozoic formations is tectonic. The Middle Triassic limestones are dated on the following conodont fauna: *Enantignathusziegleri*, *Prioniodinalatidentata*, *Spathognathoduskockeli*, *Gondolella* sp. cf. *G. navicula*.

The Jurassic deposits outcrop in the western part of the Rahoveci region, along the River "Drini i Bardhe". The oldest Jurassic formation is the "blocks in matrix" – type *mélange* and consists of blocks of different lithologies in a shaly matrix. The predominant lithology of the *mélange*-blocks is sandstone, the sandstone blocks consisting of fine to very coarse-grained, dark gray to yellow arenites. The age of the *mélange* according to the stratigraphic position is related to Middle – Late Jurassic. The limestones including abundant *charophyta* overly the ultrabasic rocks and outcrop within a limited area of this region. Their presence indicates a rapid shallowing of the basin. The age of the limestones with *charophyta* can be related to Late Jurassic. Both the ultrabasic rocks and the *mélange* "blocks in matrix" are unconformably overlain by ophiolitic breccias. The presence of ophiolitic breccias marks the disruption of the underlying ophiolitic formations. The radiolarian cherts found at the top of the ophiolitic breccias are being referred here as Çupeva cherts. They show a thickness of about 40 m and outcrop on the right bank of the River 'Drini i Bardhe'. The presence of the radiolarian cherts indicates the homogenization of the deep water. The Çupeva cherts consist of beds of radiolarites of 5-30 cm thick alternating with few mm of siliceous shales;

thick levels of tuffs and rarely tuffitic sands are also present.

The samples from the Guri i Zi and Çupeva e Nalte section contain radiolarian assemblages which indicate ages from Middle-Late Oxfordian to Kimmeridgian-Early Tithonian. The Çupeva cherts are subsequently covered by the Volljaku flysch which represents siliciclastic turbiditic deposits, dated Late Kimmeridgian-Early Tithonian by foraminifera and calcareous algae. The following microfossils are recognised: *Clypeina sulcata* Alth, *Parurgonina caelinensis* Cuvillier, codiacean algae, *Cresciantiella* sp., *Textularia* sp., ostracods, *Sacoccoma*-type fragments etc. The flysch shows a 450m thick sequence and can be subdivided in two members: the lower member is mainly composed of clast and matrix supported pebbly sandstones and mudstones; the upper member is mainly composed of arenites with minor siltstone and marly beds. The ophiolitic breccias, the Çupeva cherts and the Volljaku flysch represent the oldest depositions lying above the ophiolite; they marked the ocean-basin closure.

The Cretaceous deposits are widespread in this region. They outcrop to the east of the ophiolitic unit of Rahoveci. The Cretaceous deposits are mainly made up by basal conglomerates, platform and pelagic limestones and flyschoidal deposits. In previous studies, two lithostratigraphic units were individuated. For the first time, in this paper, the following three lithostratigraphic units have been individuated: Grebniku unit, Ponorci unit and Dresniku unit.



## OSTRACODA ASSEMBLAGE OF THE MIDDLE-LATE MIOCENE KUŞADASI FORMATION, SÖKE BASIN, WESTERN ANATOLIA, TURKEY

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### Abstract

Söke Basin is located about 40 km west of the Aydın City, in western Turkey. The basin started to form during Early Miocene like several other basins in the “Western Anatolian Extensional Province” and exhibits a thick Neogene succession. The Kuşadası Formation unconformably overlies the Early-Middle Miocene Söke Formation and is represented by clast-dominated lithologies at the lower and middle parts. The lower part mainly consists of pebbles, while the middle part comprise sandstone-claystone alternations. The formation gradually passes to carbonate-dominated lithologies towards the upper parts and it is unconformably overlain by the Late Pliocene-Pleistocene Fevzipaşa Formation. The total thickness of the formation is approximately 120 meters.

Six stratigraphic sections were measured along the middle and upper parts of the formation and sixty-seven samples were collected. Ostracoda fauna assemblage, composing of sixteen taxa belonging to nine genus (*Paracandona*, *Candona*, *Ilyocypris*, *Prionocypris*, *Herpetocypris*, *Cyprinotus*, *Potamocypris*, *Leptocythere* and *Limnocythere*), was recovered from only thirty-five samples. As well as Ostracoda, *Leuciscus* sp., *Barbus* sp., cf. *Scardinius* sp. and *Cobitis* sp. fish remains belonging to Cyprinidae family, *Valvata pulchella*, *Bythinella badensis* and *Bythinella* sp. shells belonging to gastropoda fauna are also obtained from the samples.

Chronostratigraphic ranges of the obtained Ostracoda genus indicate a Late Miocene age. Also Hisartepe Volcanics, cutting clast-dominated lower and middle parts and overlain by the carbonate-dominated upper parts, are radiometrically dated (<sup>40</sup>Ar/<sup>39</sup>Ar) as  $12,31 \pm 0,09$  Ma (Serravallian/late Middle Miocene) by Sümer et al. (2013). By the evaluation of all the data, the age of the formation is calibrated as Middle-Late Miocene.

Ostracoda and gastropoda records and lithological features indicate that Kuşadası Formation was deposited in permanent and shallow to relatively deep freshwater lake conditions. Furthermore, it is determined that periodic salinity increases and an ingression influence existed, as it is recorded by an increase in the abundance of the marine species *Leptocythere psammophila*.

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## FRESHWATER OSTRACODA IN THE PLEISTOCENE SEPIOLITE DEPOSITS OF POLATLI BASIN, ILICA/POLATLI (ANKARA), CENTRAL ANATOLIA

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### Abstract

This study was carried out along the Ilica stream valley and its tributaries, located in Ilica region, Southwestern Polatlı. A series of stratigraphic sections were studied and a number of 22 samples was collected for micropaleontological analysis. Excepting the ostracoda fauna, were also obtained twelve samples containing charophytes, gastropods and fish remains. Among ten ostracoda taxa that have been determined, seven are represented by known species (*Candona candida*, *C. neglecta*, *Fabaeformis candona fabaeformis*, *Pseudocandona sucki*, *Cypria reptans*, *Llyocypris bradyi*, and *Cypridopsis vidua*), while three of them are left to the open nomenclature (*Candona* sp.1, *Candona* sp.2 and *Cyprideis* sp.). According to the chronostratigraphic ranges of the Ostracoda genus, the age of the investigated levels were dated as Pleistocene. Ostracoda species obtained in this study are common in freshwater lacustrine and fluvial environments all around the world (Meisch 2000; Bronshtein 1988).

While the dolomites and sepiolites usually have been observed at the base of the sequences, plenty of limestones which includes macroscopic ostracods and gastropods (20-40 %) have been observed partially in thin layers between these dolomites and sepiolites levels and also generally

in the upper levels of these units. It is stated that the sepiolites, dolomites and smectites were formed in shallow restricted alkaline lake environments, but limestones were formed in fluvial-lacustrine environments, especially in more dilute depositional conditions when compared with smectites and sepiolites. The depositional environment has been affected by varying oxic/anoxic conditions. While white sepiolites have been formed under oxic conditions, the organic matter-rich black and partially brown sepiolitic claystones have been formed under anoxic conditions. The sepiolite deposits of fluvio-lacustrine origin have been formed in a closed, alkaline, shallow-lake environment. (Karakaya et al. 2011).

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## DIATOM BIOSTRATIGRAPHIC SYNTHESIS RELATED WITH PALAEOENVIRONMENT IN GOTSE DELCHEV NEOGENE BASIN, SW BULGARIA

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### Abstract

Comprehensive sedimentological and paleontological investigations were performed on the sediments belonging to Baldevo and Nevrokop formations, in Gotse Delchev Basin, Southwest Bulgaria. The diatom flora consists of abundant *Aulacoseira* species with very interesting and unusual morphology. The phases in the lake history are presented herein, based on the ecological spectra of the diatom species and the results of the sedimentological analysis.

**Key words:** Late Miocene-Early Pliocene, Gotse Delchev Basin, palaeoecology, sedimentology, diatoms

### Introduction

Gotse Delchev Basin is a Neogene one, located along the river Mesta in SW Bulgaria (Fig. 1). Although it was subjected to numerous palaeontological and sedimentological studies during the last couple of decades, our last studies on the diatom flora and sedimentary filling complete our vision on the basin evolution during the Late Miocene-Early Pliocene. The aim of this study was to add up the results issued from sedimentological and palaeontological analyses and to reconstruct the phases in the lake history.

The sediments in the Gotse Dechev Basin were deposited mainly in fluvial environment, with development of swamps and a lake in the north and northeastern parts. Vatsev (1980) and Vatsev and Petkova (1996) subdivided them in four formal lithostratigraphic units (Fig. 1). The lowermost Valevitsa Formation is 100 m thick and contains mostly conglomerates and less sandstones. The formation outcrops at the NE border of the basin. The age of these sediments is probably Maeotian. In the northern and northeastern parts of the basin it is covered by the Baldevo Formation and in the

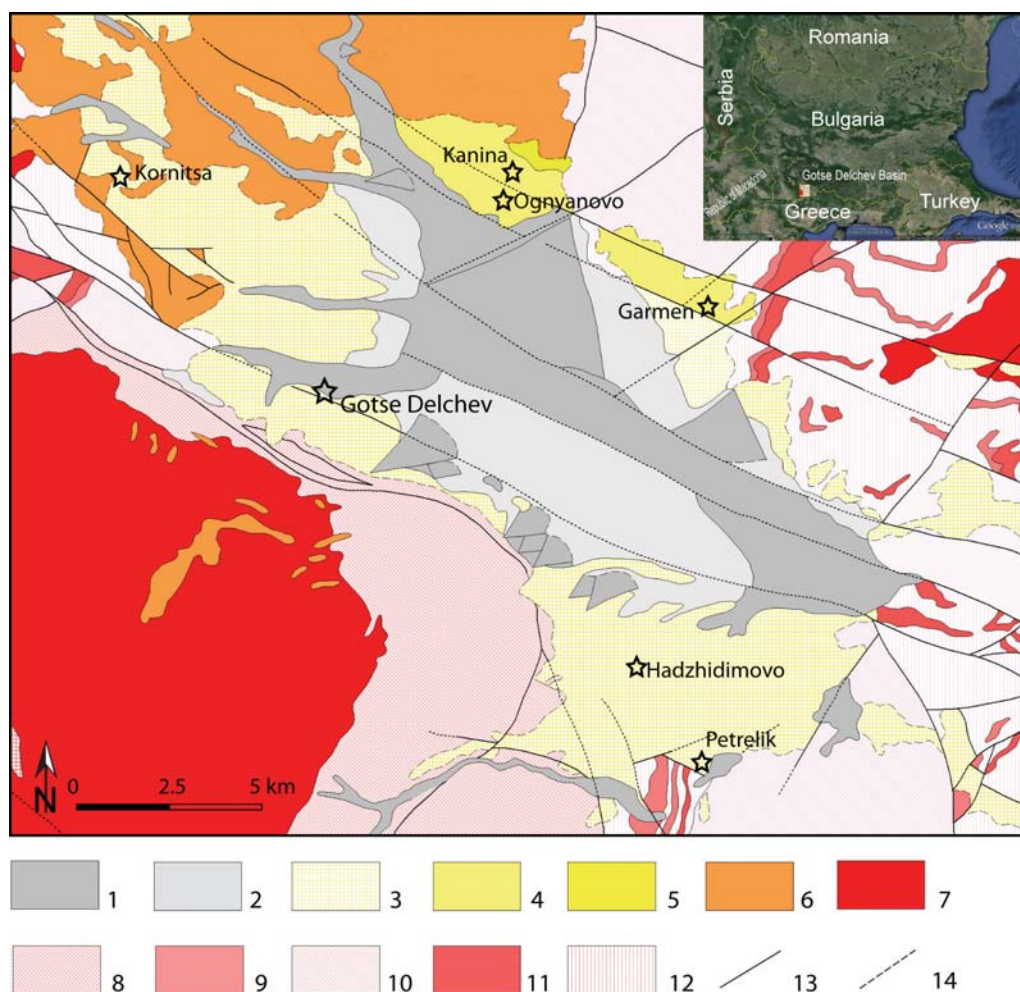
other parts by the Nevrokop Formation. Baldevo Formation is 40-120 m thick, and is represented by siltstones, clays, coal beds and diatomites, and thin sandy lenses. These sediments are cropping out in the NE and NW parts of the basin. The age of Baldevo Formation is Pontian-Dacian, based on diatoms, pollen, macroflora and mammal fossils. Sediments of Nevrokop Formation cover the sediments of Baldevo Formation in the north-eastern part of the basin, whereas in the other parts they were deposited above the Valevitsa Formation or the basement rocks. Nevrokop Formation is about 200-300 m thick. It represents a typical fluvial succession composed of irregular alternation of conglomerate, sand, silt and clay, and represents the most part of the Neogene basin sedimentary filling. The age of this formation is reported as Pontian-Dacian based on the mammal fauna. Sredna Formation is the youngest one, 30-100 m thick, and comprises breccias and conglomerates with gneiss and marble pebbles and cobbles. It is cropping out only on the highest NW areas of the basin borders. The age is probably Pliocene.

### Material and Methods

Samples collected from sediments belonging to Baldevo and Nevrokop Formations were studied. We choose sand, silty sand and sandy silt, and diatomite to be subjected to grain-size analysis, mineralogical analysis of light and heavy mineral fraction, X-ray fluorescence analysis (XRF), and X-ray diffraction analysis of clay fraction. The preparation and analysis of fossil diatoms followed standard techniques: light and scanning electron microscopy, quantitative analysis, ecological spectra of diatom species, included active water reaction (pH), temperature, trophic state, type of habitat and salinity.

### Results and Discussion

In this study we focused our efforts to clarify



**Figure 1.** Geological map of the Gotse Delchev Basin (according to Kozuharov and Marinova, 1994): 1) Holocene; 2) Pleistocene; 3) Nevrokop Formation (Pontian-Dacian); 4) Baldevo Formation (Pontian-Dacian); 5) Valevitsa Formation (Maeotian); 6) Paleogene volcano-sedimentary formation; 7) Upper Cretaceous granites; 8-12) Precambrian: (8-marbles; 9-metamorphosed basic volcanic rocks and orthoamphibolites; 10-gneisses; 11-massive and layered marbles; 12-gneisses, schists, marbles, amphibolites; 13-fault; 14-probable fault).

the distribution of the deposits of the Baldevo Formation and particularly of the diatomite layers in both E-NE (sites Ognyanovo, Kanina and Garmen) and NW (site Kornitsa) parts of the Gotse Delchev Basin.

According to their grain-size composition, the sands of both formations are very similar – poorly to very poorly sorted ( $\sigma_1$  between 0.5-2.5  $\phi$ ), with mean size 0.8-4  $\phi$ , and near symmetrical distribution. Grain-size analysis of diatomite show dominance of the pellite fraction (53-75%), followed by silt (25-47%). A great deal of the fraction 0,002-0,032 mm is from diatom frustules. Mineralogical composition is very uniform too: quartz, plagioclase, potassium feldspar, mica (muscovite and biotite), chlorite, amphibole, epidote, zoizite, titanite, zircon, rutile, tourmaline, apatite, kyanite, andalusite, garnet and opaque

minerals. Quartz is prevailing in sand from northern and north-eastern parts, whereas in sand from southern and southwestern parts the quantities of quartz, plagioclase and potassium feldspars are almost equal. Feldspar grains are fresh or slightly weathered, which along with preserved prismatic or angular shape indicates a short transport (Yaneva and Donkova 2013). The composition of heavy minerals is uniform with few exceptions: garnet, rutile and tourmaline are missing in south and southeastern parts, but chlorite and biotite are the dominant minerals there, which points to the source area of dominantly metamorphic rocks from the south and southeast. The prevalence of micas in sand from eastern part also evidenced the decomposition of metamorphic rocks in the source area. Clay fraction is composed of kaolinite, smectite and illite with prevalence of kaolinite in the E and NE parts of the basin and of smectite in



the W and SW parts; illite keeps the same amount (Yaneva 2002). Chemical composition shows that sediments from the eastern part are low-alkaline and with higher chemical index of alteration (CIA), whereas those from western part are with normal alkalinity and lower CIA.

The fossil diatom flora of Gotse Delchev Basin is distinguished by its relatively poor species composition (Temniskova-Topalova and Ognjanova-Rumenova 1983; 1997; Yaneva et al. 2002; Ognjanova et al. 2012a). The abundance and diversity of the planktonic genera of class Coscinodiscophyceae are most important for the biostratigraphic subdivision, due to their well known evolutionary history. The fossil diatom flora is established in the sediments belonging to Baldevo Formation. The diatom preservation is good, the diatom tanathocoenoses are monotaxonic and comprised of variable roughly silicified *Aulacoseira*/*Melosira* species. During recent decades they have been determined according to Jousé (1952) as *Melosira praegranulata* Jousé, *M. praeislandica* Jousé and *M. praedistans* Jousé. The biostratigraphic correlations have been complicated by the taxonomic inconsistencies within taxonomy of genus *Aulacoseira*. Pertinent taxonomic and morphological data of *Aulacoseira* taxa, the dominant group of diatoms, are reviewed and discussed. Our observations suggest that there may be several fossil *Aulacoseira* species but their taxonomy is far from being clear. The nomenclatural confusion of the *Aulacoseira* taxa within Gotse Delchev Basin led us to reinvestigate the type materials of *Melosira*/*Aulacoseira*, housed in the Pantocsek Collection, Natural History Museum Budapest, and the Ehrenberg Collection, Natural History Museum Berlin, and their relationships with our fossil *Aulacoseira* morphodemes (Ognjanova-Rumenova et al. 2012b). In addition, we have re-examined several sediment sequences from the diatomite layers in Pontian-Dacian. Second interesting centric form with biostratigraphical significance belonged to newly described genus *Conticribra* Stachura-Suchoples and Williams, which recently is considered as a synonym of genus *Spicaticribra* Johansen, Kociolek and Lowe (Khursevich and Kociolek 2012). In addition, the total diversity of class Coscinodiscophyceae and the evolutionary rates of diatoms could be completed by the presence of *Melosira undulata* (Ehr.) Kützing and *Ellerbeckia kochii* (Pant.) Moisseeva.

## Conclusion

During the Latest Miocene - Early Pliocene (Pontian-Dacian) Gotse Delchev Basin was a large fluvial system with local development of swamps. These swamps evolved into a lake in the northern area. The lake was large, the mass development of *Aulacoseira* species proved more eutrophic conditions. The periphytic subdominants confirmed the development of shallow littoral zone. The salt content ranged between 0.2-0.3 ‰. The active water reaction was neutral to slightly alkaline which corresponds to the results from geochemistry of the sediments. The temperature of the water was similar to those of the moderate latitude lakes; only a few tropical elements were present. The uniformity of the mineralogical composition of sand and clay led to the conclusion about relatively constant source area during Pontian and Dacian. The mineral composition of sand from different parts of the basin reflects the rock composition of the source areas: Paleogene volcanic rocks to the north, metamorphic rocks to the east, and granites to the west. Clay mineralogy and chemical composition suggest the possibility that sedimentary material from the east came from the area characterized with relatively plain relief and with advanced weathering processes. Most of the minerals are fresh and not weathered, with angular and subangular shape. Minerals which are not resistant to transportation prevail in the heavy fraction from the sand. This supposes relatively short transport from the source area to the basin.

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## ICHTHOLOGICAL RECORD OF ECOLOGICAL CONDITIONS DURING MIDDLE–LATE JURASSIC PELAGIC SEDIMENTATION IN THE FATRICUM DOMAIN OF THE TATRA MOUNTAINS, SOUTHERN POLAND AND NORTHERN SLOVAKIA

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### Abstract

Content of food, one of the basic ecological factors influencing burrowing organisms, generally diminishes offshore. This hypothesis is verified in the Middle–Upper Jurassic sediments of the Fatricum Domain, where a gradual deepening and transition from hemipelagic to pelagic deep sea environment is well expressed. These changes have been caused by opening of the Western Tethys, further rifting and the general transgression.

The basin during Bajocian and Bathonian was characterized by horsts and graben topography, which resulted from the Early–Middle Jurassic extensional block tilting. *Subsiding parts of the basin* were filled with grey spotted limestones and marls, followed by grey nodular limestones with thin-shelled bivalves *Bositra*. Condensed *Bositra*-crinoidal limestones with glaucony were deposited on the horsts. The Late Bathonian–Kimmeridgian radiolarites and radiolarian limestones are an evidence of deepening with sedimentation between the ACD and CCD or below the CCD. The Upper Kimmeridgian red nodular and platy micritic limestones reveal recovery of carbonate sedimentation.

Ten ichnogenera include fodinichnia (*Zoophycos*, *Teichichnus*, *Phycodes*), chemichnia (*Chondrites*, *Trichichnus*), pascichnia (*Planolites*, *Phycosiphon*), and domichnia-fodinichnia (*Thalassinoides*). They belong to the *Zoophycos* ichnofacies, which characterizes deeper shelf-basin plain settings in pelagic and hemipelagic sediments. Abundance and diversity of trace fossils decrease up the studied succession. In the lower part, most beds of Bajocian spotted limestones and marls and Upper Bathonian–Lower Callovian spotted radiolarites display typical spotty structures, i.e. relatively dense and diverse cross sections of trace fossils visible as variable spots. *Chondrites*, *Planolites*, *Thalassinoides*, and

*Zoophycos* are common.

Other trace fossils are rare or very rare. Up the succession, in the upper part of radiolarites and red nodular limestones, the spots decrease in density, contrast and diversity, up to disappearance. The commonest trace fossils are *Chondrites* and *Planolites*. *Thalassinoides* and *Zoophycos* are rarer. The changes are not ideally linear, but fluctuations in these features do not discard the general trend. They are not related to grain size or lithology.

The primary lamination occurs only in a few thin horizons, which colour is not darker than in other horizons. It can be referred to incidental rapid sedimentation marked by a subtle increase in grain size, or a short anoxia. The changes of ichnological features up the studied interval are caused mainly by decrease in food content in the sediments. With deepening of the basin and decreasing sedimentation rate associated with generally advancing flooding of epicontinental areas, less and less food was supplied to the basin from shallower areas and less and less buried in sediment. In more eutrophic conditions (lower part of the interval), organisms penetrated deeply in the sediment, where distinct trace fossils were produced. Thicker layer of nutritional sediment gave an ecospace for a higher diversity of burrowing organisms. In more oligotrophic conditions (higher part of the succession), the organic matter was concentrated in the soupy sediment near the sediment–water interface, where preservation of distinct trace fossils was limited or impossible.

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## GEOCHEMISTRY OF A NEW PERMO-TRIASSIC BOUNDARY SECTION IN SERBIA

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### Abstract

We present geochemical data from a newly discovered (2011) Permian-Triassic (P-Tr) boundary section exposed along a road cut in the Jadar Block tectonostratigraphic unit in Serbia, about 90 km SW of Belgrade. This new P-Tr section, named Sitarička Glavica, is lithologically different from other Serbian P-Tr boundary sections which typically have Lower Triassic dolomite micro-breccia. Importantly, this new section appears to be continuous across the P-Tr boundary and is lithologically similar to the Bellerophon-Tesero Oolite P-Tr sections in the Southern Alps. During the Permian-Triassic period, this Serbian P-T section was situated in the Paleotethys along the passive margin of Laurasia. The lower beds are about 7 metres of interbedded calcisiltites and dark grey shales similar to the Bellerophon Formation and are dominated by a diverse fauna of crinoids, algae, foraminifera,

molluscs, bryozoans, brachiopods, etc. The upper beds are about 8 metres of calcareous shales interbedded with micaceous calcisiltites similar to the Werfen Formation, and with only a molluscan fauna. Preliminary conodont studies show only rare specimens of *Hindeodus-Isarcicella* fauna in lower part of the section. Foraminifera studies are in progress. The P-Tr contact is provisionally placed at the base of a sandy micaceous calcarenite in this unit: about 6 metres above, a 30 cm thick lensitic oolitic limestone is similar to the Tesero horizon of the Alps. The oolitic limestone shows a positive Eu anomaly which may be associated with volcanism. Stable isotopes (C, N, S), mineralogy, major and trace elements of this Serbian P-Tr section show similar patterns of secular variation as in other marine Late Permian sections, suggesting major changes in sediment provenance and marine environmental conditions prior to the Early Triassic, where geochemical proxies indicate prolonged seawater anoxia.



## DEEP EXCAVATION AND SLOPES STABILIZATION IN TIRANA, ALBANIA

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### Abstract

This study aims to give a summary of geotechnical problems during deep excavations in Tirana, their realization and elimination of risks for facilities that are adjacent to the new facility. The main issues of this study are:

- Geotechnical study for characterization of layers that are present in the building site (important during the studies is to combine the field tests with the laboratory tests. More important is the accurate determination of shear strength ( $\phi$  &  $C$ ) and water pressure.
- Prediction of engineering measures effective and economic for protecting the slopes of deep excavation.
- Monitoring the stability of the slopes of deep excavation.
- The correction of errors in calculation of engineering measures and improvements during construction.

This study also provides new techniques that are used for geotechnical studies in Tirana, modern monitoring of equipment that are used in several buildings in the city of Tirana during deep excavation.

Some positive examples to aid take by monitoring and adjustment of calculations in real time.

Examples of deep excavations that are not monitored and that have brought negative economic consequences and loss of human life.

The optimal solution requires not only time and know-how but also a faithful partnership between all parties and specialists.

**Key Words:** *Geotechnical investigation, deep excavation, slopes stability calculation, monitoring and back analysis*

## GROUNDWATER-VULNERABILITY MAPPING IN ALBANIA

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### Abstract

Groundwater that represents a major source of water for domestic, industrial and agricultural uses in Albania, is recently suffering a deterioration of its quality especially in the regions with extensive demographic and industrial development, due to excessive groundwater withdrawal and the presence of different contaminants coming from the surface. Over the past 30 years, the groundwater vulnerability maps have been compiled in many countries as a basis for developing land use strategies that take into consideration aspects of protection of groundwater from pollution. The final goal of vulnerability maps is the subdivision of the area into several hydrogeological units with different levels of vulnerability.

The aim of this work is to assess the vulnerability of groundwater for the whole territory of Albania. The major factors (Depth to Water-D, Net Recharge-R, Aquifer Media-A, Soil Media-S, Topography-T, Impact of vadose zone-I, Hydraulic Conductivity-C) that affect and control the groundwater contamination were incorporated into the DRASTIC model. Moreover, a Geographical Information System (Arc Gis 9.2 INFO) was used to produce the groundwater vulnerability map of Albania.

This involved: (i) data (hydrogeological, geological

and pedological) collection, (ii) transferring of DEM to slope data, (iii) creating the attribute table, (iv) analyzing the DRASTIC factors for evaluation of Drastic Index, (v) rating these areas as to their vulnerability to contamination and deriving a Graduated Map.

The determination of the DRASTIC index number (pollution potential) for a given area involves multiplying each factor rating by its weight and adding together the resulting values:  $\text{DRASTIC Index} = \text{DrDw} + \text{RrRw} + \text{ArAw} + \text{SrSw} + \text{TrTw} + \text{IrIw} + \text{CrCw}$ , where  $r$  = rating for area being evaluated (1–10), and  $w$  = importance weight for the factor (1–5). The higher the DRASTIC index is, the greater is the relative pollution potential.

In order to reduce the subjectivity in the selection of rating ranges and to increase the reliability, the methods of sensitivity (SI), variation index (Vxi) and effective weight (WXi) were applied to assess the validation of the aquifer vulnerability method.

As a result of the vulnerability assessment, 20% of the territory was classified as being very highly vulnerable, 30% highly vulnerable, 30% vulnerable at moderate to low levels and, finally, around 20% of the basin has very low vulnerability. The areas with high and very high categories, i.e. the more vulnerable areas to contamination belong to karstic and shallow alluvial aquifers, whereas the lowest vulnerable areas are related with the molassic and flyschoidal formations.

## SCANNING METHOD WITH LAND SCANNERS FOR ANALYZING SUSTAINABILITY IN ENGINEERING OBJECTS

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### Abstract

To avoid the risk, the forecasting and evaluation of buildings and engineering constructions is necessary from time to time. It is important to monitor and model them continuously either by standard, classical or modern surveying methods with advanced technology.

The object of the study is the group of objects whose lifetime is very long and specifically, a bridge designed and built in 1967 at the intersection of the railway - highway Rrogozhine-Lushnje over Shkumbini River. This river is subjected to frequent changing of water level and flow course, something that is reflected in changes to riverbed, thus increasing its potential destruction to engineering works built upon it. The foundations of the bridge are embedded in QH Quaternary formations which are represented by gravel deposits whose thickness varies from 3 to 20 m. The bridge has a length of 270 m, width 9.5m and its beams are placed on 2 abutments and 7 piers.

Nowadays, geodesy provides the modern as well as classical methods of measuring and monitoring, using statistical processing, digital, etc. in order to determine on time the real value of dynamics of changes affecting these objects.

The main reason for monitoring this engineering object is the collapse of an automobile bridge in 2008, which is 70 m away from the bridge under study. The designer's opinions for the possible causes of the damage of this bridge are the changes in the riverbed affecting footing and soil.

The monitoring method in this survey, by scanning with image and points is being used for the first time. It aims at making comparisons of classical methods of standard monitoring. For implementation of this survey, are used surveying

instruments of digital technology such as satellite systems GPS TopconGR-3, Topcon Image Scanner IS203 and the respective software Top Surv, Topcon Tools and Image Master Pro have been used. The survey is carried out based on measurements referred to a geodetic foundation which consists of 6 fixed points and 36 horizontal and vertical marks set on both sides of the bridge, built in 2009. The classical method monitoring procedure started in September 2009. During this year, the bridge was monitored using the modern scanning method with a land scanner.

From the comparison of monitoring methods during this study, we came to the conclusion that this method guarantees high precision in determining the parameters of the monitoring, the displacement, velocity and greater monitoring of frequency, both in terms of density points monitored and time of monitoring, while the cost of implementation for this process is lower than the implementation of classical method. Based on the results, the object represents a construction sustainability, but it is vulnerable to the phenomenon of riverbed corrosion, on which piers No. 4, 5, 6, are constructed. As observed during the project, the terrain in these piles has a settlement ranging from 1.5-5.0 m.

In conclusion, we can summarise that the use of survey with scanning method is of great interest not only in constructions similar to this, but for all the engineering structures on ground or underground. We believe that this new method of monitoring can also be used in the study of natural phenomena such as landslides, erosion, etc.

## USE OF GEOLOGICAL-ENGINEERING METHODS FOR PROTECTION AGAINST WATER PENETRATION IN COAL EXPLOITATION IN SECTOR SITNICA OF MIRASH MINE

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### Abstract

In this work we present the process of geologic-engineering methods in order to provide protection from water penetration along the coal-bearing Sitnica sector. This sector is located east of Mirash mine. This area is very apt for coal exploitation. Geology is relatively simple and consists of Pliocene and Quaternary - Holocene sediments. In geological terms, the collectors are divided in two zones. The first hydrogeological collector is located directly over the coal layer, while the second collector that represents the peripheral sector, is not in direct contact with the coal layer. Insulation in this sector represents gray clays. Groundwater is fed from rainfall and this is confirmed from monitoring levels of groundwater especially during the years when the rainfalls were very scarce. Sitnica river-bed awaits groundwater horizons having a direct communication link with them. Character of plumbing mutual communication is variable, in dry seasons when groundwater levels drop, the river feeds the alluvial aquifers and conversely. The average groundwater level was 2.5m. Exploiting sector from Sitnica River was impossible which defines this sector as well as groundwater. For this purpose and to ensure the use of coal in this sector, the deviation of the river-bed was essential as well as undertaking geological-engineering measures for

the protection of underground water penetration in this area. In this case, 355 vertical drillings located in a linear segment of 1450 m long and 6m wide, were performed. The distance between drillings initially was planned to be every 4m but after drilling, results showed that this distance should be every 2 m. To achieve the highest factor of safety and better bonding mass injection, the average depth of drilling changed, depending on the contact with the coal layer. The average depth of drilling was 10m. Diameters of drillings were  $\Phi 146$  mm while drilling control was made with  $\Phi 101$  mm diameter. In this case, the composition of the used solution was 80% ash, 10% cement, 10% bentonite and water. In the alluvial layer, the drills were made 4m deep while in coal layer they were made to a maxim depth of 2m. The drilling method used was from the top down, using a pressure of 6 bars.

**Key words:** sector, coal, drilling, layer



## PRELIMINARY INDICATIONS ON THE FACTORS INFLUENCING THE UNEXPECTED WATER LEVEL LOWERING AT BADOVC LAKE, KOSOVO\*

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### Abstract

This study is focused on the investigation of hydrological and geological factors affecting the unexpected lowering of water level in Badovc Lake, Kosova. Existing historical data and measurements performed during the period 2013-2014 were used. Badovc Lake, which has a watershed surface of 104 km<sup>2</sup>, occurs 7 km southeast of Prishtina city and is among its main drinking water resources. Badovc Lake catchment area is located between ca. 600 m and 1100 m above sea level. The lack of water in this lake presents a serious concern for water supply municipal authorities. Based on the recent hydrological monitoring data, the water level has shown a tendency toward minimum levels, while the maximum level is rarely reached during heavy rainfall. The mean historical values of precipitations, temperature and air humidity are 642.0 mm, 10.4 °C and 71.3%, respectively. Historical monitoring data showed that the runoff coefficient and runoff module are 0.41 and 8.13(l/sec/km<sup>2</sup>), respectively.

For the scope of the assessment of the possible water "loose" from the Badovc Lake, all the components of the hydrologic balance of its basin are considered. Four rainfall gauges were installed seven months ago within the lake catchment area to monitor precipitation. At the same time, the water discharge and water intake are under a continuous monitoring.

Geodetic measurements conducted at the end of 2013 including the bathymetry of the lake, showed a low (around 1.000.000 m<sup>3</sup>) water volume decrease compared to the initial volume of the lake, which represents about 3-4% of its total volume. Bathymetric analyses showed that sedimentation of fines took place mostly close to the dam.

The lake floor is composed of serpentinites, gabbros, diabases, ophiolitic melange etc., while the dam is placed on serpentinites. From the tectonic point of view, all the above geological formations are involved by a very developed faulting system, where the hydrothermal alteration took place. In particular, the serpentinites of the dam zone are characterized by abundant northeast-southwest orientation cracks that continue towards the depth. Three active mines of lead and zinc are also located in the surrounding area of Badovc Lake whose tunnels drain continuously considerable quantity of groundwater. This later, along with the unexpected water level lowering in the lake, may be an indication of the potential water loss from the lake through cracks towards the mine tunnels. A detailed assessment of the hydrologic balance of the lake watershed and of the water intake from the lake will further clarify the possible water loose from the lake bottom. Comparison of chemical and isotopic composition of both lake water and groundwater draining from the mines represent another manner for the study of the bottom water infiltration from the lake. The results of this study will be helpful for the decision making authorities in order to better plan and manage the water intake from the lake.

**Key words:** Badovc Lake, hydrology, geology, water balance

\*This designation is without prejudice to positions on status, and is in line with UNSC 1244 and the ICJ Opinion on the Kosovo declaration of independence.

## EVALUATION OF POLLUTION LEVEL IN TIRANA RIVER

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### Abstract

The geochemical data-pollution studies of the river of Tirana refers to the levels of  $\text{PO}_4$ , Active Cl,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{NH}_3$  and water pH as general indicators of pollution.

Tirana river is located across the south Tirana – Ishem area depression with a length of 17 km.

Its valley is flat at highlands area and slowly expands at lowlands.

During the early ‘90 rapid demographic changes (end of the Communist controlled era), accompanied by a boom in construction, mainly private buildings and illegal in the area Tirana - Paskuqan - Babru.

This area is crossed by the flow of Tirana river, and is associated with significant effects on water quality of this river; deterioration due to polluted emissions.

The main deterioration comes from urban uncontrolled/ illegal discharges.

For the evaluation of the pollution levels, we took 13 samples along its flow which were analyzed for the contents levels of phosphates, active chlorine, nitrates and ammonium. Temperature and pH were evaluated.

The aim of the study is to identify the river’s water levels of pollution, pollution trends and try to predict the trend under its flow.

Water temperature and pH were measured directly at sampling site. The analysis of active chlorine, phosphates, nitrates and ammonium in the river’s water were carried out at the laboratory of the Faculty of Geology and Mining with the photometer Multiparametric HI 83000.

Data processing was carried out with AQUACHEM and Microsoft Excel software.

The result interpretation is done through data confrontation and comparison with the literature and with local geochemical data background.

**Keywords:** *Pollution, River, Tirana*

## LANDFILL DESIGN FOR ŞIRNAK COAL MINE DUMPS - SHALEFILL STABILITY AND RISK ASSESSMENT

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### Abstract

GEO5 FEM program with four rockfill slope modeling and stability analysis was performed for S1, S2, S3 and S4 slopes where landslides of the shalefills were limited. Topographic maps of 1:1,000 scale and structural cross section were produced based on analyses of bulk soil samples. The experiment was performed with following conditions: Effective angle of internal friction ( $\phi^\circ$ ) 17°-22.5°, the effective cohesion ( $c'$ ) from 0.5 to 1.8 kpa, the maximum rate 1.87-2.25 g/cm<sup>3</sup> unit weight, saturated unit weight g/cm<sup>3</sup> 1.78-2.43, 1.9-2.35 g/cm<sup>3</sup> natural unit weight, dry unit weight 1.97-2.40 g/cm<sup>3</sup>, one unit weight ( $\gamma_s$ ) 2.47-2.60 g/cm<sup>3</sup>, the permeability coefficient of  $1 \times 10^{-4}$  -  $6.5 \times 10^{-4}$  cm/s, and also the grain size distribution determined is tested. In cross-sections of the slope, using GEO 5 FEM program, possible critical surface tensions were examined. Rockfill dump design was made to prevent sliding slopes. Bulk material designated geotechnical properties using also GEO5 program FEM and stability program via a safety factor determined and calculated according to the values S3 and S4 No. slopes are stable S1 and S2 No. slopes were close to stable state that has been found to be risk. GEO5 programs with limestone rock fill dump through FEM program was found to exhibit stability.

Around 3 km<sup>2</sup> working area was investigated and an engineering map of the area was made at 1:1,000 scale. Also the drillings and laboratory geotechnical engineering properties of materials were determined by experiments. No residential units appropriate, at the bottom of streams and ponds nature will save condition heap slope design and geotechnical properties by examining the stability analyzes with different methods GEO5 programs FEM program was carried out by (Anonymous 2009, Anonymous, b 2013).

Within this project, urban use, which will open

workspace and environment covering 3 km<sup>2</sup> area 1/1.000 scale engineering map of field and laboratory studies prepared as a result also the polar coordinate system using a field study with four slopes of the topographic maps have been created.

Şırnak to the south of the city center is located on a sloping topography was observed. Field generally formed of claystone and siltstone formations were observed. Germav Şırnak center is known that in the formation. Germav formation, corrosion due weakness quickly eroded; with steep slopes create a topography that is caused to occur locally landslides. Therefore, summarizing the central province of Şırnak, usually because of old landslides sandy, calcareous, clayey, silty resulting from the blending of the units are located on disturbed Germav Formation. Rubble slope of the creek to the south extends to the boundaries of the study area. A Field observation of the Miocene limestones of the debris was determined. Thickness is highly variable. Decrease in the slope of the land where relatively little outcrops.

**Key words:** Slope stability, GEO5 Stability Analysis, Rockfills, Rock stability

## SHORELINE DYNAMICS AND PERFORMANCE OF PROTECTION WORKS IN THE SOUTHERN PART OF DURRËSI BAY

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### Abstract

In the southern part of Durrësi Bay, the sandy beach has suffered strong erosions phenomena during the last 25 years. In particular, in different segments situated in the Karpen - Qerret lowland, during the last few years, the annual erosion rates reached values of up to 40 m/year.

The purpose of this study is the identification of the main factors causing such high erosion rates and to recommend appropriate measures for the beach and land protection.

In order to determine the protective measures for the study area, the erosive effects along a coastline of 3 km were taken into consideration. This study was conducted according to the following steps: 1) study of the coastal dynamics and spatiotemporal changes in coastal morphology using historical data from previous map publications, aerial photography and field measurements. Five shoreline positions corresponding to four time intervals (1944-1980, 1980-2007, 2007-2009 and 2009-2010) were analyzed; 2) Design of protective measures. The sediment budget is used in order to predict the changes of the coastline position after the groins construction; 3) Monitoring process after the groins construction. This process includes bathymetric measurements and interpretations, sediment analyses and the calculation and interpretation of Annual Rates of Changes for periods between shoreline positions mapped in June 2011, September 2011, October 2012, November 2012 and June 2013.

Bathymetric maps and the study of the shoreline dynamics are elaborated in G.I.S. Annual Rates of Change are processed using Digital Shoreline Analysis System (DSAS) created by Thieler and Danforth (1994).

The used shoreline data sets provide sufficient information to calculate the primary direction of change and the rate of either accretion or erosion at every point, from the time of a data-set to the next. For the interval of time 1944-1980, an accretion is observed. After this, during the period from 1980 to 2010, a dominance of erosion along the whole length of the shoreline under study is observed. Dividing this time interval in shorter periods such as 1980-2007, 2007-2009 and 2009-2010, increases in the annual rates of shoreline changes are observed in the lasts intervals of time.

The construction of groins is associated with deposition in the southwestern part of each groin and approximately an area 3500 m<sup>2</sup> is gained in 160 m of shoreline extension. The total volume of sand gained is 9.937 m<sup>3</sup> in a time interval of 2 years. The mean annual rate of accumulation is about 14 m/year.

Downward from the groins, the erosion is observed. The mean annual erosion rate is about 3 m/year.

The above mentioned results indicate that the groins are the most appropriate protective measure to be applied in Durrësi Bay. The groins create the possibility to recreate the beach in its south-western side while in the north-eastern side erosion is observed. However, the deposited volume is greater than the eroded one, indicating a bimodal alongshore sediment transport in the area.

In order to have a good configuration of the coastline, these protective measures must be designed and constructed in groups covering greater lengths of shoreline than each private property, as is commonly the case in Albania.



## DYNAMICS OF THE VERTICAL VARIATIONS OF RIVER BEDS IN ALBANIA

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### Abstract

The monitoring process of the riverbed morphology provides us with the information regarding the phenomena that occur in the river bed, their evolution in time and space, as well as the impact of the human factor on these processes. In order to have a real scenario of the process, periodic measurements are performed which allows to confront the data and to construct the evaluation of the river bed profile through the time. The results of monitoring of the vertical evolution of the river bed, will be used to construct the model of prediction and as a sure base for the decision making of the river bed treatment aiming to improve the situation.

In Albania, several problems were encountered during the last 10 years along the valleys of the rivers, mainly in their lower and middle flow course. The most important consequences are the riverbed lowering due to the vertical erosion, soil erosion, pollution of surface and groundwater, demolition of civil or industrial engineering constructions, loss of biodiversity, water flooding, damage of the forests and the whole ecological system, landslide in the river banks, etc.

The change of the profile configuration from successive measurements to the initial one, determines the sedimentation and/or erosion areas across the riverbed. The difference of accumulation surfaces (+) and those in erosion (-) gives the trend of the profile.

The results of monitoring of the river dynamics showed that in most of the river profiles, the process of erosion prevails (Fani, Ishmi, Erzeni, Semani and Vjosa River), 10 of them are characterized by accumulation and other 9 have stable profiles as shown by the rhythms of sedimentation or erosion which do not exceed  $\pm 10\text{cm}$ . The river flow is the main factor that influences the dynamics of relief modeling and its forms. The aggregate extraction represents another important factor that influences the river bed lowering which could be easily observed where the natural river profile is fixed. The removal of large amounts of sand and gravel from the river bed has activated the cutting back erosion. The geological or neotectonic factors have their impact on the river bed variations in the long term monitoring.

The number of profiles is still limited (47 monitoring profiles under surveying distributed on the rivers of Albania) give a complete scenario of the river bed dynamics. The increase of the number of profiles and the possible automation of monitoring will improve the performance of the process. As a result, a more detailed information on the dynamic changes in the riverbed will be provided in real-time. The monitoring results will help to distinguish areas where the aggregate extraction can be applied from those where the erosion dominates and which must be conserved.

## ISOTOPE AND CHEMICAL INVESTIGATIONS OF SULPHUR-RICH SPRINGS FROM THE LIPNICA (ORAWA, POLAND)

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### Abstract

Water from two springs situated in the vicinity of Babia Góra Mt. (Orawa, southern Poland) was investigated. Chemical analyses have shown increased chloride and sodium content in water from Siary spring suggesting the presence of ascending water of diagenetic origin. Lumped-parameter models applied to tritium data allowed to estimate the contribution of tritium-free water in total spring discharge. However, the estimated contribution of this component and its expected chemical and isotope parameters, based on the existing data for Polish Flysch Carpathians, form internally inconsistent system. The results of isotope and chemical analyses can be reconciled assuming the presence of three components in the spring discharge: (i) the tritium-containing young water of infiltration origin, (ii) tritium-free water of infiltration origin having similar stable isotope composition and, (iii) water of diagenetic origin which chemical and isotope parameters need to be further investigated.

**Keywords:** *Carpathians, diagenetic water, stable isotope, tritium*

### Introduction

Eight springs of sulphur-rich water appear in the villages Lipnica Wielka and Lipnica Mała located in the Orawa region (Beskid Żywiecki Mts., southern Poland). The springs are situated in the tectonic zones within the Magura Nappe of the Inner Flysch Carpathians. Their total mineralization varies between 0.2 to 2.4 g/dm<sup>3</sup> and the H<sub>2</sub>S content is between 3.4 and 14 g/dm<sup>3</sup>. Two springs, Jacek and Siary, were selected to conduct chemical and isotope analyses. Jacek is a near-channel, sub-slope fracture spring in the Lipnica Wielka village, with water of the HCO<sub>3</sub>-Cl-Ca-Na+H<sub>2</sub>S type and total mineralization of about 0.6 g/dm<sup>3</sup>. Siary spring, situated within sandstones occupying fault zone is

located on the southern slope of the Babia Góra Mt. It is enclosed in the form of a 3.5 m deep dug well. Water is of the Cl-Na+H<sub>2</sub>S type and contains 2.4 g/dm<sup>3</sup> of dissolved solids. The occurrence of H<sub>2</sub>S in some Carpathian groundwaters is a result of sulphate reduction which is the product of pyrite weathering (Rajchel et al. 2005).

### Field Sampling and Laboratory Methods

Water samples from Jacek and Siary springs were collected during sampling campaigns performed between 2000 and 2007 and in 2012. Several parameters were measured in the field: temperature of water, pH, bicarbonate ion content. During 2000-2007 campaigns the samples from Siary spring were collected from the upper part of the water column. In 2012 the sample has been taken from the bottom of the well.

Chemical analyses of water were carried out in the chemical laboratory of the Department of Hydrogeology and Engineering Geology, AGH University of Science and Technology. The ICP-MS technique was used. The <sup>3</sup>H and stable isotope composition of water was determined at the Isotope Laboratory of the Department of Applied Nuclear Physics of the same university. Deuterium and <sup>18</sup>O content of water samples were measured using established techniques: Zn reduction for <sup>2</sup>H and CO<sub>2</sub>-equilibration for <sup>18</sup>O assay (Coleman et al. 1982; Epstein and Mayeda 1953). Tritium content in water samples was measured using electrolytic enrichment and liquid scintillation spectrometry. The isotope ratios <sup>2</sup>H/<sup>1</sup>H, <sup>18</sup>O/<sup>16</sup>O are reported as per mil deviations (δ<sup>2</sup>H and δ<sup>18</sup>O) from the respective isotope ratios of the internationally accepted standard (V-SMOW). Tritium concentration is expressed in "tritium units" (1 atom of <sup>3</sup>H per 10<sup>18</sup> atoms of <sup>1</sup>H).

### Results and Discussion

Results of investigations are presented in Table 1 and 2 and in Figures 1 and 2. In contrast to

the earlier sampling campaigns, in 2012 water sample from the Siary spring was collected from the bottom of well. Chemical composition of this sample indicates the presence of ascending, highly mineralized water. To date, the Siary spring is the only spring in the Orawa region in which the presence of mineral water has been recognized.

Tritium, the radioactive isotope of hydrogen is widely used as a tracer in hydrogeology. Its concentration in precipitation and thus, in infiltrating water, increased considerably in fifties and sixties of the last century as a result of thermonuclear weapon tests in the atmosphere. Measurements of tritium content as a function of time in a given groundwater creates a possibility of estimation of its age i.e. the time elapsed between its recharge and appearance at the outflow. Based on analytical data presented in Table 2 such estimations were performed using FLOWPC

the total outflow. Also for the Siary spring, the ages resulted from different models are similar. However, the goodness of fitting of the DM model is much better than the EPM model. Depending on the applied model, the contribution of tritium-free water in this spring should be in the range between 16 and 22%. The calculations performed clearly demonstrate the presence in both springs of water with short transit time making them potentially susceptible to antropogenic pollution. Stable isotope composition of waters in the Jacek spring and in the upper part of water column in the Siary spring is typical for the area. In Siary spring, the elevated chloride content suggests the presence of ascending water of diagenetic origin. However, its presence in the upper part of the water column is not marked by the characteristic shift in stable isotope composition (gray square in Fig. 2). Other waters representing pure diagenetic component

**Table 1.** Chemical composition of waters. Concentration of ions and  $H_2S$  are expressed in  $mg/dm^3$ ; n.m. – not measured.

Spring	Jacek			Siary		
Sampling date	22.09.2002	01.07.2007	01.08.2012	22.09.2002	01.07.2007	01.08.2012
Temp. °C)	8.9	7.9	8.6	10.0	14.2	11.4
pH	7.6	7.42	7.14	8.1	7.6	7.69
Na <sup>+</sup>	15.5	38.6	27.7	802	880	1258
K <sup>+</sup>	1.0	2.3	1.4	7.0	9.3	9.3
Ca <sup>2+</sup>	73.3	70.3	72.6	51.8	63.5	79.9
Mg <sup>2+</sup>	11.4	14.9	12.3	8.6	20.7	24.5
Cl <sup>-</sup>	21.2	41.7	30.3	1232	1495	1973
SO <sub>4</sub> <sup>2-</sup>	35.4	56.6	25.5	18.8	21.0	7.9
HCO <sub>3</sub> <sup>-</sup>	247	264	265	185	178	197
H <sub>2</sub> S	3.9	n.m.	n.m.	5.7	n.m.	n.m.

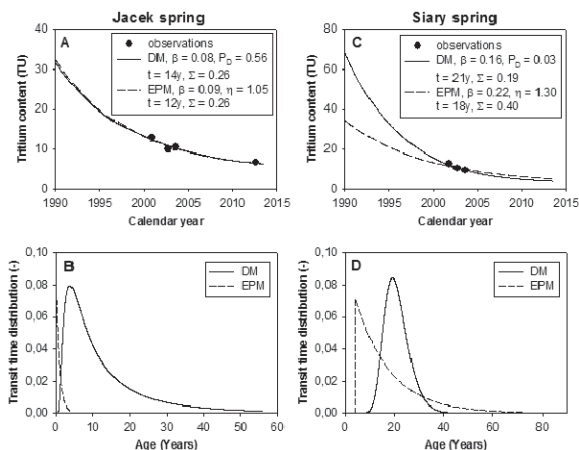
**Table 2.** Tritium content and stable isotope composition of spring waters.

Spring	Sampling date	$\delta^{18}O$ (‰ V-SMOW)	$\delta^2H$ (‰ V-SMOW)	Tritium content (TU)
Jacek	02.12.2000	-10.48	-74.7	12.9 ± 0.8
	22.09.2001	-10.34	-72.0	10.0 ± 0.6
	25.07.2003	-10.43	-73.9	10.5 ± 0.6
	01.08.2012	-10.32	-73.7	6.7 ± 0.4
	21.10.2001	-10.18	-74.3	12.7 ± 1.0
Siary	22.09.2002	-10.07	-71.9	10.5 ± 0.6
	25.07.2003	-10.14	-73.0	9.5 ± 0.5
	01.08.2012	-9.90	-72.1	6.3 ± 0.4

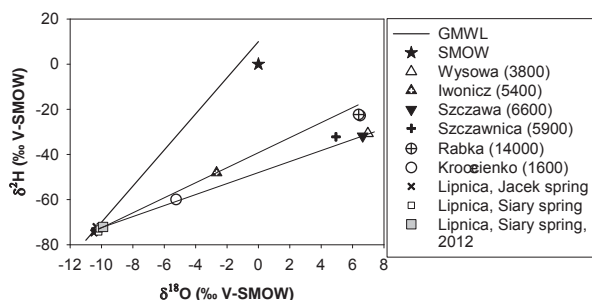
computer software (Małoszewski and Zuber 1996). Sample from the Siary spring taken from the bottom of the well in 2012 was excluded from the calculations. The results of lumped-parameter modeling are presented in Figure 1.

For the Jacek spring both dispersion (DM) and exponential-piston (EPM) fitted models are characterized by almost identical transition time, equal 12-14 years. The best fits require assumption about the presence of a tritium-free component which should constitute 8-9% of

in other parts of the Polish Flysh Carpathians are also presented in Figure 2. Two straight lines form an angle determining the possible positions of waters containing diagenetic component. The data point representing bottom water from Siary spring lies within this angle. Both lines cross GMWL in the point forming the vertex of an angle ( $\delta^{18}O = -10.3‰$ ;  $\delta^2H = -73‰$ ). These values are practically identical with the mean isotope composition of water from Jacek spring and represent the infiltration component. Assuming that the tritium-



**Figure 1.** Lumped-parameter modeling of Jacek and Siary springs. A and C - best fit of experimental data (DM – dispersion model, EPM – exponential-piston flow model). Fitted parameters:  $\beta$  – the contribution of tritium-free water in the total discharge,  $P_D$  – the dispersion parameter,  $\eta$  – the ratio of the total volume of investigated system to the volume with the exponential distribution of transit times,  $t$  – mean transit time of water,  $\Sigma$  – the parameter describing goodness of the fit (see Małoszewski and Zuber 1996). B and D - transit time distribution functions for Jacek and Siary springs.



**Figure 2.** Stable isotope composition of the investigated springs. The isotopic composition of springs representing pure diagenetic waters, found in other regions of the Polish Flysch Carpathians (Wysowa, Szczawa, Szczawnica and Rabka) is also shown. Marked are also waters containing significant contribution of diagenetic water (Iwonicz, Krościenko). Numbers in parentheses denote chloride concentrations (in mg/dm<sup>3</sup>). Mean isotopic composition of the global ocean (SMOW) is marked by star. Heavy line indicates the position of the Global Meteoric Water Line (GMWL).

free water is of diagenetic origin, the mass-balance calculations reveal large discrepancy between the amount of diagenetic water present both in Jacek and Siary springs, resulting from lumped-parameter modeling and its chloride concentration and stable isotope composition. This discrepancy can be eliminated if the presence of third component (tritium-free water of infiltration origin) is postulated. In such scenario the diagenetic component becomes reduced to few percent which makes it non-distinguishable in the stable isotope signal.

## Conclusions

Results of chemical and isotope investigations of sulphur-rich springs in Lipnica (Orawa, Poland) indicate the presence of three water components: (i) fresh infiltration water, (ii) tritium-free water of infiltration origin, and (iii) diagenetic water. At present stage of investigations it is impossible to determine precisely the chemical and isotope characteristic of the diagenetic component contributing to the discharge of investigated springs. The available data suggest that this water should be dominated by Na<sup>+</sup> and Cl<sup>-</sup> ions in high concentrations.

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## DEVELOPMENT OF A SOFTWARE FOR THE PSHA CALCULATION AND RELATIVE GRAPHICAL RESULTS - A SEARTHQUAKE HAZARD

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### Abstract

The goal of many earthquake engineering analyses is to ensure that a structure can withstand a given level of ground shaking while maintaining a desired level of performance. But what level of ground shaking should be used to perform this analysis? There is a great deal of uncertainty about the location, size and resulting shaking intensity of future earthquakes. Probabilistic Seismic Hazard Analysis (PSHA) aims to quantify these uncertainties and combine them to produce an explicit description of the distribution of future shaking that may occur at a site.

The most common way to express the results of PSHA is the Seismic hazard Curve, which gives the rate of exceedance of a selected shaking parameter. The peak ground acceleration is the selected parameter in this case. Unfortunately, the process of calculations as are necessary to obtain the value cited above is long and needs a large number of mathematical steps. This work attempts to simplify this process through a software designed and developed from us. This software builds the Seismic Hazard Curve across the steps described below:

1. Identify all earthquake sources capable of producing significant level of shaking at the site of interest.
2. Use of the Gutenberg and Richter's recurrence relationship to characterize the distribution of earthquake magnitudes.
3. Characterize the distribution of source-to-site distances associated with potential earthquakes.
4. Use of GMPE (ground motion prediction equation) to calculate the values of peak ground acceleration as function of the magnitude and distance. Different GMPE can be used (Cornell 1979; Sabetta and Pugliese 1996; Ambraseys 1996).

5. Combine uncertainties in earthquake size, location and peak ground acceleration, using a calculation known as the total probability theorem.

To implement the first two steps, we use an algorithm to parse the CSV file containing the data collected. First of all, we load the csv file and apply some calculations to determine the amount of earthquakes for each magnitude. These results are presented in two tables. In the end, after the activation of a button the Gutenberg-Richter law is calculated.

To satisfy the third point, the software collects from the user the coordinates of the area of interest, the coordinates of the source, the ranges of subdivision and finally calculates the probability for each interval.

While implementing the fourth and fifth point, the user must give the software some values such as minimum and maximum values of acceleration. In addition, the user must also choose which GMPE function the software has to use.

After completing all the steps, the software produces the results in tabular form, which can be exported in excel format. The software also provides a chart library, written from using C++, that builds charts based on the results obtained. The chart is constructed on a window within the GUI (Graphic User Interface) and can also be manipulated in real time. Seen that, to obtain the results, are used different GMPE functions, in the same window you can build different charts. This is to provide a comparison of results obtained with different GMPE functions. At the end, charts created can be printed or exported to jpg, png or bmp format.

The software desktop window base, is user friendly and has a very simple GUI. To develop the software we have used C++ programming language and .NET framework. This software can be used from different users under trial ware license.

## LIQUEFACTION ASSESSMENT IN GOLEM AREA, ALBANIA BY MEANS OF IN SITU TESTS

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### Abstract

The liquefaction is a very significant phenomenon in clayey silty soils, silty sands and sands. The high potential of liquefaction is generally recognized when these types of soils are located under the hydrostatic water table. Low plasticity silts, silty sands and sands are encountered extensively as recent alluvial deposits in the western coastal part of Albania, especially in the sandy beaches of Adriatic Sea near Durrës city.

This is an overpopulated area and several buildings are constructed close to the seashore. Their foundations are embedded in the above mentioned types of soils.

The aim of this study is to evaluate the soil liquefaction potential in the area of Golem. This area is located in the Periadiatic Depression, denoted as PL-zone, strongly affected by post-Pliocene compression movements, in direct convergence with Adria microplate. It is characterized by a high seismic activity. According to the seismic regionalization of Albania, the maximum acceleration of the area is 0.138g (Sulstarova et al. 2010).

The main types of soils in this area are loose silty sands to sandy silts, medium dense sands to silty sands and water ground may vary from 1.00 to 2.00 m below the zero level, but depending on the distance from the sea, it may be closer to the ground surface.

Cone Penetration Test (CPT) and Dilatometer Test (DMT) are widely used for the site-specific evaluation of liquefaction potential of soils.

In this work results of the analysis of liquefaction potential based on CPT values are presented. 10 CPTs and 1 DMT are considered and the liquefaction potential was evaluated by means of a factor of safety.

Evaluation of the liquefaction potential is made by means of the potential index of liquefaction ( $P_L$ ).

The procedure essentially compares the cyclic resistance ratio (CRR) at a given depth with the earthquake-induced cyclic stress ratio (CSR) at the depth for a specified design earthquake.

The cyclic resistance ratio (CRR) is calculated based on the method proposed by Robertson and Wride (1998). The measured tip resistance  $q_c$  is normalized versus initial total effective overburden stresses, measured in other sites hit before by an earthquake with magnitudes equal to 7.5 and characterized by the same soil profile (clean sand). It is compared with the cyclic resistance ratio equivalent ( $CRR_{eq}$ ), which is correspondent to the considered earthquake for these calculations.

The soil behavior type index  $I_c$  is used to identify the layers with high potential of liquefaction from the CPTU data in this area, as well as to calculate the CRR.

The cyclic stress ratio (CSR), induced by the earthquake is calculated for a given seismic hazard level expressed in terms of acceleration, with the probability of exceeding the same acceleration during the life-span of engineering structures (usually 50 years).

The results of liquefaction potential analysis show that the soils in the area of the Golem have a high risk of liquefaction.

## PROJECTING OF THE CORRIDOR FROM LEVEL 830 M IN STARITËRG TO 835 M LEVEL “TREPÇA”, MAZHIQ.

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### Abstract

Lead-zinc metallogenic fields in Kosovo are subject to the highest level of exploration, more than any other metallogenic units. Even so, this level is incomplete for allowing a definitive technical-economical evaluation and to have a definitive perspective of these mineral resources. In “Trepça” region, Stantërg is known as the largest Lead – Zinc deposit in Kosovo, distinct for the ore quality and quantity of reserves, which spread over a wide area, even outside the “Trepça” mine area, in Stantërg. Trepça mine has in total of 11 open horizons, 4 of them being active horizons with three depressive points in horizons X, VII and IV. The old Mazhiq mine is opened from the level 915 m in depth and is connected to a gallery at level 835 m through a blind shaft. The latter level of drift continues to the main shaft that outcrops in surface, but it is not functional because of the falling of surrounding rocks of the shaft. Mazhiq mine is meant to joint Trepça mine-the level of the first horizon there is an open drift of over 3000 m in length that connects the first horizon from “Trepça” Stantërg with Mazhiq mine. This drift has been opened and is subject to mining activity by the opening of a chimney from the level 610 m, respectively the first horizon of actual mine “Trepça”-Stanterg, to the level 835 m old Mazhiq mine. The chimney has remained without meeting between the open facilities as it will discussed in this presentation.

The other mining facilities that are not described here are the level 830 m geographically located in the Eastern part of Stantërg.

Designing the drift from level 830 m will be also used for exploration because through this drift it will be explored also the mineral-bearing zone from Maja e Madhe, Xhidome and Rashani. The designing of this drift will connect this mine, from the gallery of level 830m, with the level of old Mazhiq mine and it will contribute to the solution of the ventilation problem in these two mines, which are not connected until now. The designing of this drift, with a length 1180m, will be done also for functionality purposes, to create the possibilities to open the mines without joining each other and the extension of explorations in these two separated geographically zones. Two mines, actually, are passive and their ventilation is non functional. The opening of this drift will solve the ventilation problem, for a certain period of the development of these mines, to its permanent solution.

## EVALUATION AND MONITORING OF GROUNDWATERS OF ALBANIA

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### Abstract

In Albania, the quantity of groundwater used for the supply of population is around 14 550 to 18 190 lit/s. The aquifers with greater exploitation of groundwater are: Quaternary porous aquifer with utilization coefficient  $k = 0.3 - 0.9$  and sandstone-conglomerate aquifer with utilization coefficient  $k = 0.7$ .

Aquifers with the smallest exploitation are: carbonate aquifers with an utilization coefficient  $k = 0.03$  and magmatic aquifer with an utilization coefficient  $k = 0.3$ .

Quaternary porous aquifer is under human impact in terms of its exploitation without any criteria, lack of implementation of sanitary protection and damage of their nutrient areas through the exploitation of inert materials in the river beds. From these phenomena depends the deterioration of the aquifer hydraulic parameters and physical-chemical properties of groundwater of the aquifers of Lezhe, Tirane-Fushe Kruje, Erzen, Lushnje, Vjose etc. Carbonate aquifers are at risk due to the failure of sanitary protection, as well as by the open pits for limestone exploitation.

**Key words:** *Aquifer, Monitoring, groundwaters, utilization coefficient, amplitude*

### Introduction

Geological surveys in several porous aquifers started in our country during the 80's. After 2000 the monitoring records the greater development and today, a water monitoring network with 87 points (drillings and representative springs) exists. The hydrochemical monitoring is complete, since the monitoring net is extended in the entire territory of Albania with a monitoring frequency of 2-4 times per year. The hydrodynamic monitoring is not at the right level since its network monitoring is based only on 20 wells; in three of them is established self-recording apparatus data-logger from which we receive data on the water level and conductivity each hour.

### Methodology

The used monitoring methodology consists in a monitoring network composed of existing and new wells; pumping stations and key representative springs; level measurement through manual measurements and stationary self-recording devices in 20 wells; information on exploitation of these aquifers from pumping stations; water sampling and analysis of the chemical composition in 87-120 water points.

### Results and discussions

The groundwaters of Albania are classified in several major aquifers and the water exploitation for each aquifer is given in TSable 1.

**Table 1.** The major aquifers in Albania and the quantity of the water exploitation

Aquifers	The exploitation amount	Utilization coefficient
<b>Porous aquifers</b>	<b>Q (l/s)</b>	<b>K</b>
Shkodra aquifer	1200-1300	0.33-0.5
Nenshkodra aquifer	500-800	0.33-0.5
Lezha aquifer	700-900	0.3-0.35
F.Kuqe aquifer	1250-1300	0.35-0.5
Tirana aquifer	1000-1300	0.85-0.95
F. Kruja aquifer	600-700	0.85-0.95
Elbasani aquifer	1200-1250	0.25-0.3
Lushnja aquifer	590-600	0.78-0.9
Korca aquifer	465 -500	0.3-0.5
Berati aquifer	350 - 450	0.35 - 0.6
Drinos aquifer	90-110	0.4-0.5
Kafaraj aquifer	700	0.4-0.5
Novosela aquifer	720	0.5-0.7
Orikumi aquifer	50	0.4-0.7
Vurg-Mursi aquifer	180-200	0.4-0.7
Carbonate aquifer	4530-6110	0.03
Conglomerate - sandstone aquifer	430-570	0.7
Magmatic aquifer	345-630	0.3
<b>Total</b>	<b>14550-18190</b>	<b>0.2-0.6</b>

### Groundwater regime in porous aquifers



Groundwater regime is mainly related to natural factors which are represented by atmospheric precipitations, temperature, infiltration, evaporation and artificial factors which are intensive exploitation and changes in hydrographic network. Fluctuation amplitude of the UN level

for the year 2010-2013 range:

- Amplitude for the Quaternary aquifer of Shkodra varies  $A = 3.55 - 4.52 - 6.94$  m (Figs. 1 and 2)
- Amplitude for the Quaternary aquifer of Fushe Kuqe varies  $A = 1.21 - 1.78$  m (Figs. 1 and 3)
- Amplitude for the Quaternary aquifer of Lushnja varies  $A = 1.34 - 3 - 5.78$  m (Figs. 1 and 4)
- Amplitude for the Quaternary aquifer of Tirane-Laknas varies  $A = 0.58 - 6.25$  m. This aquifer is actually under extreme exploitation.

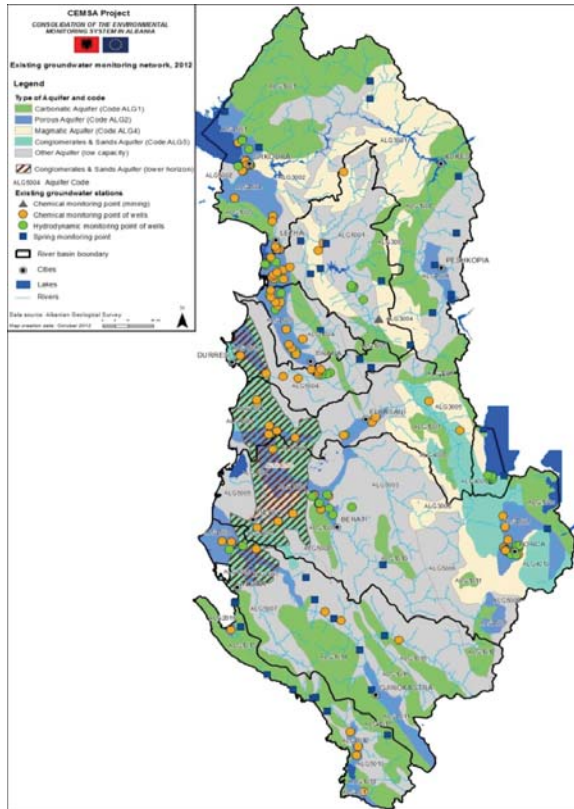


Figure 1: Hydrogeological schematic map of Albania and monitoring points

*Chemical composition of groundwater of the aquifers is as follows:*

Monitoring of the chemical composition of the groundwater aquifer is done through sampling for chemical analysis with a frequency of 2-4 times per year. Based on the results of the analysis we conclude that the pH of groundwater in all aquifers varies from 6.5 to 8.5, typical of weak alkaline waters.

*Hydrochemical monitoring for porous aquifers (Quaternary aquifers)*

Groundwaters of Quaternary aquifers have in general good physical-chemical properties. Some stations have content over the allowed maximum for some indicators as Cl, Na and especially the stations of Barbullonja, Pish-Poro and Kafaraj (the most western well station), (Figs

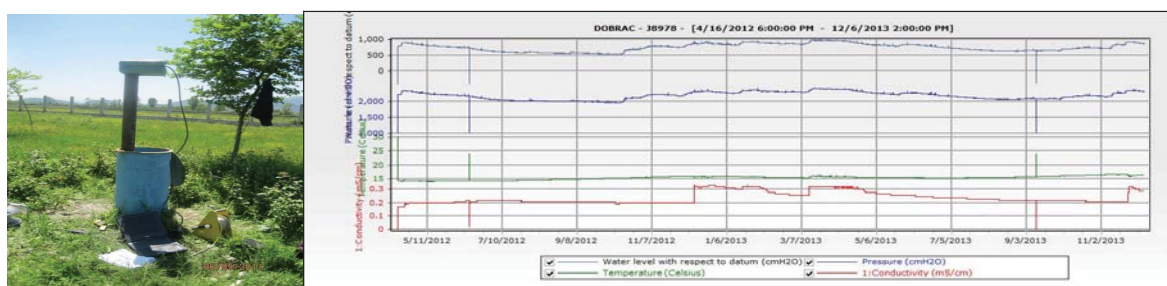


Figure.2: Graphic of hydrodynamic monitoring for Dobrac-Shkode aquifer.

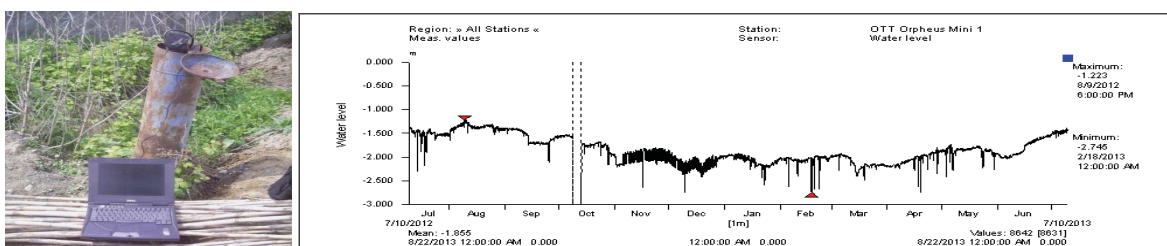


Figure 3: Graphic of hydrodynamic monitoring for Fushe Kuqe-Lac aquifer.

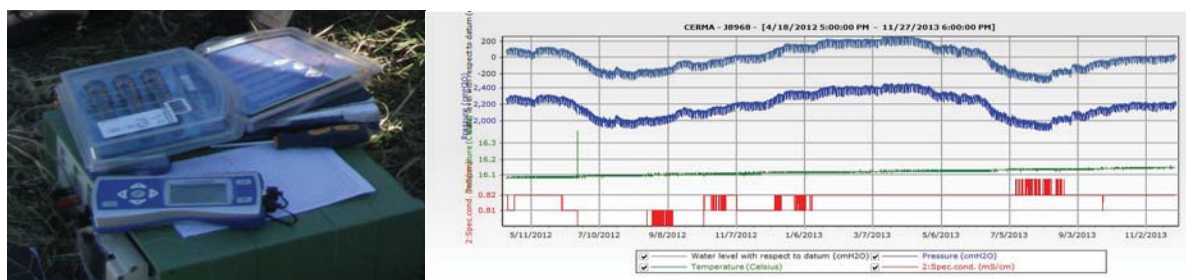


Figure 4: Graphic of hydrodynamic monitoring for Çërme-Lushnja aquifer

5 and 6)

Stations with chemical indicators over the allowed maximum of drinking water are Barbullonja of Lezha, Pish Poro for villages of Fier and Qeparo. The presence of  $\text{NO}_2$  or  $\text{NH}_4$  in many pumping

Bulgarec-Korce and Kafaraj-Fier is the result of non-respecting of penalty areas and sanitary protection for water stations. The penalty areas and sanitary protection must be the subject of another project. Only in the station of Konjati there is

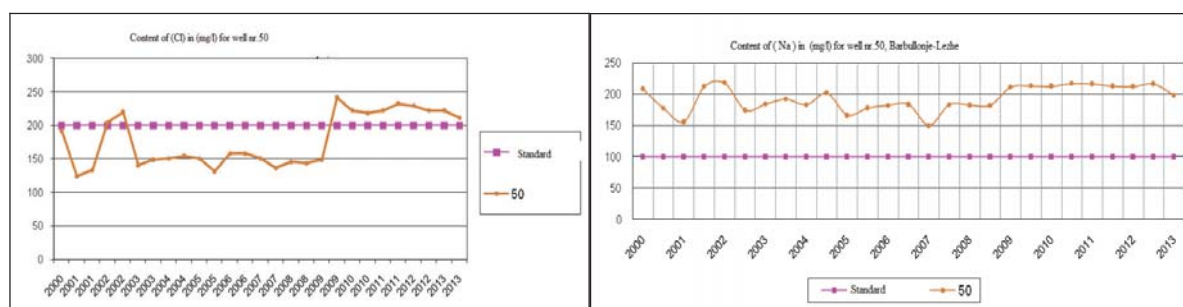


Figure 5. Graphic of Chlorine (Cl) content in Mg/l and Na of the water pumping station of Barbullonje-Lezhe.

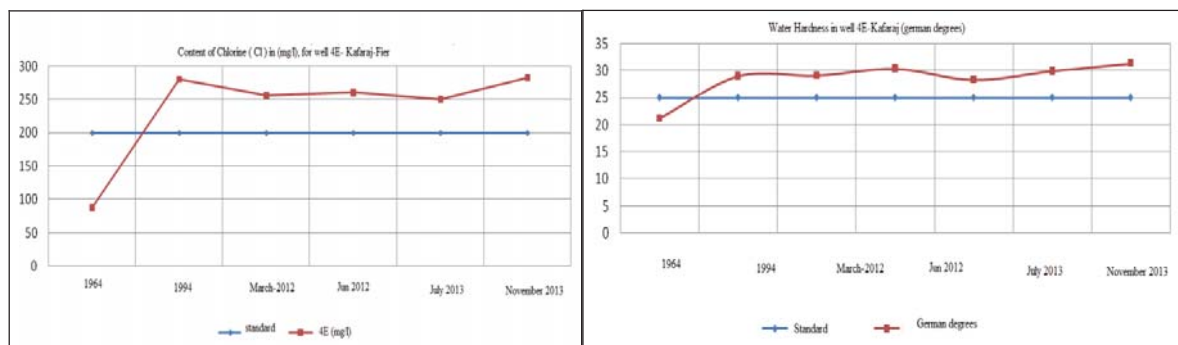


Figure 6. Graphic of Chlorine (Cl) content in (mg/l) and general hardness in (°dH) of water in well 4E- Kafaraj-Fier.

stations as Velipoje, Hoteli i Gjuetise, Barbullonje-Lezhe, Gramez-Fush Kruje, Çërme-Konjat,

water contamination with  $\text{NH}_4$  consistently, which we think comes from the discharge channel with

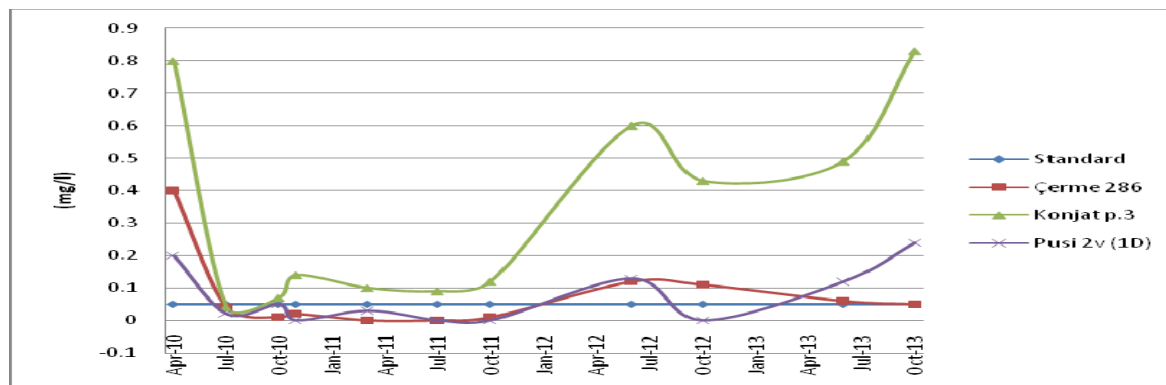


Figure 7. Graphic of Amoniac ( $\text{NH}_4$ ) content in Quaternary aquifer of Lushnja

mixed waters passing near the station (figure 7).

### *General hardness*

Groundwaters of this aquifer display medium hardness, strong and very strong and only in Lezha aquifer the hardness is very soft. In particular sectors and drillings, the waters are very strong as in the pumping stations of Gramez, Tirana, Vidhas, Peqin and Rrogozhine where the hardness varies from 25 to 32 °dH of German scale.

### **Conclusions**

- The rate of water exploitation of aquifers was determined.
- The water pumping stations which have parameters outside of the standard for drinking water.
- The reasons that led to the decay of hydrodynamic and chemical parameters of the different aquifers were determined.
- The perspective of water - bearing areas for improvement of water supply was determined.

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## LANDSLIDE MITIGATION AND REHABILITATION MEASURES AT THE TIRANA – ELBASAN MOTORWAY

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### Abstract

During the excavation works of the Tirana – Elbasan highway, a tension crack was observed at the excavated slopes accompanied with upstream activation of earth movement. The sliding event took place at the uphill area of the highway axis within the agricultural fields, and the landslide kinematic consisted of two discrete and interacting sliding masses with N-E and E direction, which probably caused sequential events.

In this presentation, a detailed mitigation and rehabilitation technical solution to be applied at the area of the landslide event is proposed, incorporating creative combination and reasonable mixture of appropriate remedial and stabilization measures on a basis of best practice and optimum cost balance. The mitigation design is based on the geotechnical assessment and evaluation of the current status at the slide area, taking into account the following key parameters:

- findings of the detailed site investigation,
- in situ evaluation of the geological and geotechnical conditions and observations on the natural ground morphology,
- hydrogeological conditions,
- existing structures in the proximity of the landslide area,
- causes, the failure mechanism, the landslide depth and scale,
- post-landslide response of the natural terrain and the adjacent structures (monitoring recordings),
- seismic hazard of the area under study (peak ground acceleration  $PGA = 0.35 \cdot g$ ),
- environmental and social impacts,
- international best practices, design standards and guidelines (e.g. BS standards, Eurocodes).

The landslide event along the highway affected an area of approximately 8.000 m<sup>2</sup>, while the main scarp of the slip zone is located about 100 m

upslope the highway axis. In terms of the immediate assessment and evaluation of the situation, the following actions were implemented:

- thorough site inspection and field investigation for the broader area of the incident.
- new detailed and extended topographical survey properly mapping the limits of the landslide, the occurred tension cracks and the existing structures.

According to the macroscopic evaluation of the sampling boreholes performed in the area of the landslide event prior and after the activation of the sliding mechanism, it is evidence that the predominant siltstone component of molasses is subject to deterioration and weathering process which penetrates down to the depth 10.0-15.0m decreasing the stability of the underlying bedrock. Within the landslide area there is a clear distinction between the upper weathered mantle and the molassic bedrock, and the interface between the above two formations, as from the core sampling boreholes, is located at depth 10.0m.

On the other side, the pseudo-inclinometers installed within and outside the landslide area have shown no movement re-activation. However, from engineering point of view and by considering all the available geotechnical data, it is estimated that the failure surface, i.e. the slide zone, is represented by the interface between the upper weathering mantle and the underlying molassic bedrock, where the disintegrated upper material slide upon the sound siltstone.



## GEOPHYSICAL STUDY FOR DETERMINATION OF THE QUATERNARY LITHOLOGY IN A SECTOR OF TOROVICA MARSH, LEZHA DISTRICT

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### Abstract

The studies conducted in the Balldren village within the Torovica wetland using Vertical Electrical Sounding method (VES) showed a high efficiency and were able to determine with high precision the vertical section and the lithology of Quaternary deposits. The results presented here are obtained using the Vertical Electrical Sounding (VES) method in three profiles.

**Keywords:** *Vertical Electrical Sounding; Quaternary deposits*

### Introduction

The geophysical survey in Torovica area aims:

1. Determination of thickness of Quaternary deposits.
2. The lithology of Quaternary deposits.

To solve these tasks, a number of 9 points of Vertical Electrical Sounding (VES), in three profiles (Fig. 1) was performed.

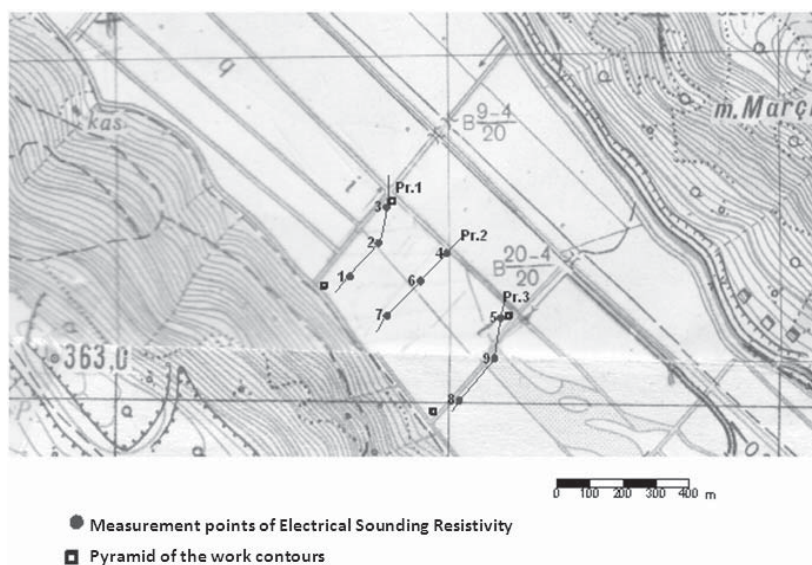
### Methodology of geophysical works

Vertical Electrical Sounding (VES), Wenner scheme, with maximum aperture distance up to 180 m is considered as rational scheme for solving the above-mentioned problems

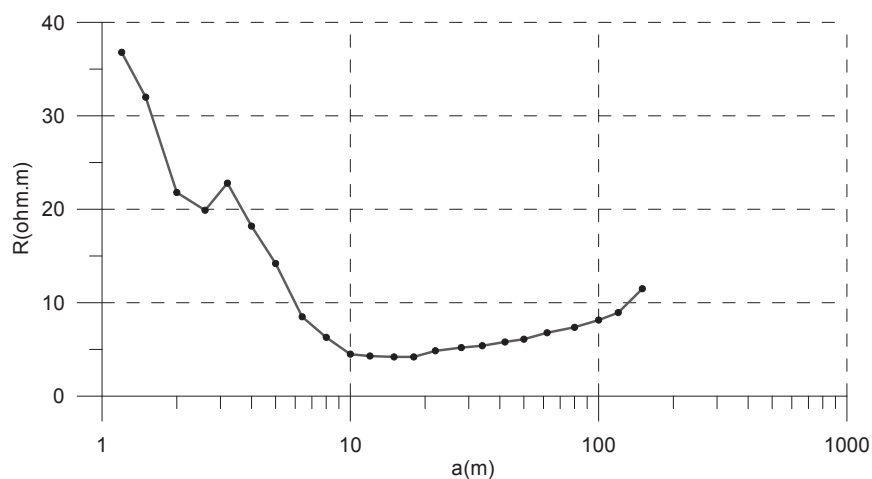
The used scheme provides depth study, sufficient for solving the specific tasks. Quantitative interpretation of the resistance curves is done by means of special computer programs (Resist), (Koefoed 1979, Dorn 1985). Based on data of these interpretations are built geological-geophysical cross-sections for each profile (Fig. 3), thus giving lithology and Quaternary thickness map (Fig. 4).

### Geology of the area

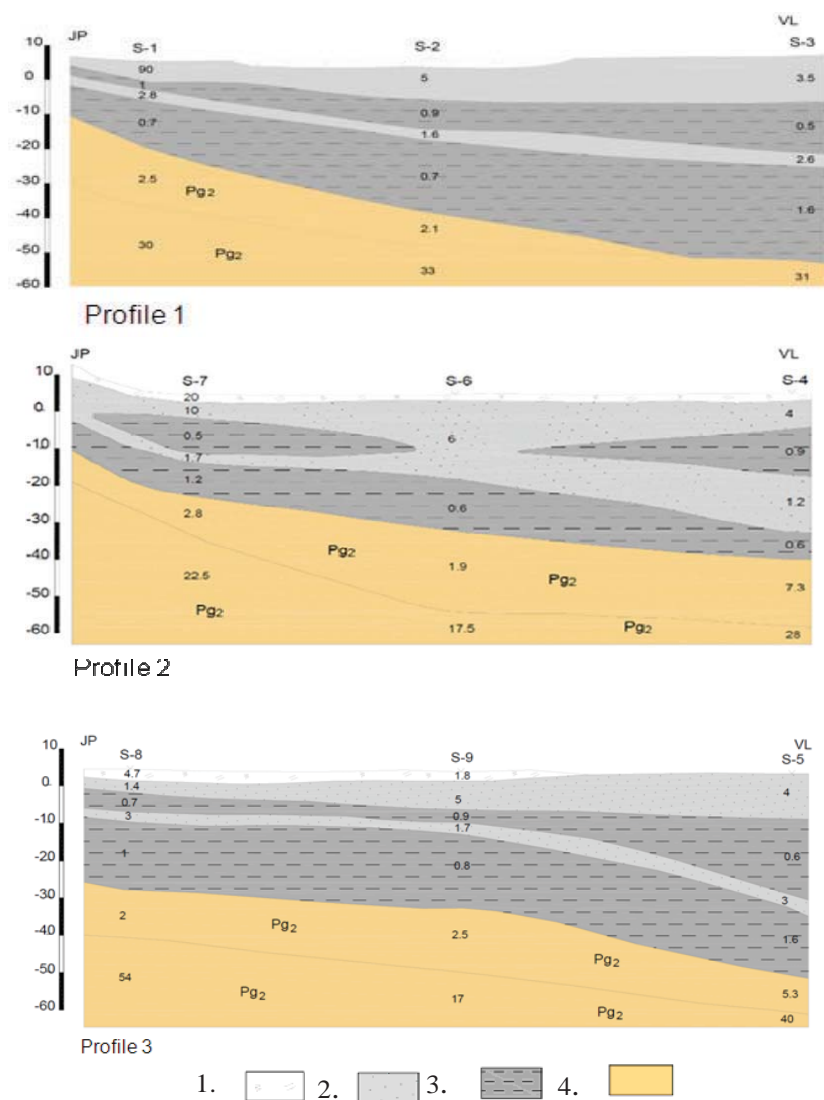
The area consists of Quaternary, Paleogene (Eocene) and Upper Cretaceous deposits. Our study focuses on the Quaternary deposits which are described here below.



**Figure 1.** Topographic map with profiles and measurement points, Torovica area.



**Figure 2.** Curve of Electrical Sounding of Resistivity.



**Figure 3.** Geological and geophysical sections of profiles 1, 2 and 3 of Torovica area.

1. Silt; 2. Coarse and fine-grained sand; 3. Saturated salt marshy clay; 4. Flysch, argillaceous - siltstone with sporadic sandstone and limestone.

## Quaternary

These deposits display an alluvial - marshy character and mainly consists of clay, sand and rare gravel. Different intermediate lithofacial types are also encountered within the above mentioned types. At certain intervals, the lithological composition is different due to the facial changes. These phenomena are present in both striking and dipping directions and are also confirmed in drilling and well reflected in Vertical Electrical Soundings. The most typical section has a thickness up to 1 m and this upper part consists of silt brown to beige in color, while its lower part consisting of plastic and gray moist silt, the last 20-30 cm being represented by clay silt, this lithology continuing down to 3.5 m. The section continues downwards with fine-grained sand, about 10 m thick, associated with clay intercalations and organic debris. Within this part of the section are encountered intercalations of coarse gravels and facial changes are often present. The formations are saturated with water and appear averagely compressed. The thickness ranges from 10 to 15 m. Downwards the section there are found compact grey clay, almost homogeneous. (Muceku, Y., Zeqo, V., 2001). In this sector, the marshy alluvial deposits reach a thickness of 25-60 m. These formations are underlied by the formations belonging to Kruja zone. At the contact between the Quaternary formations and the underlined Kruja zone formations, a coarse grained clastic and weakly cemented formation is developed proving the transgressive setting of Quaternary deposits on the underlined formations.

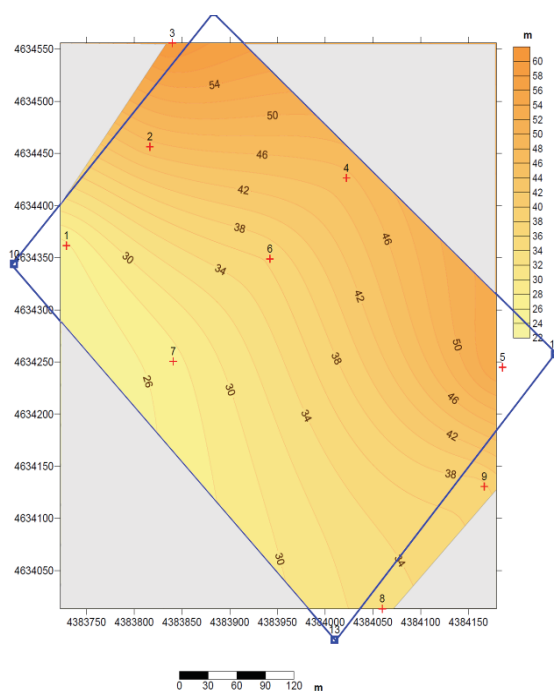
## Analysis of the results of the electrometric studies

As mentioned above, the electrometrical studies are completed with the Vertical Electrical Sounding (VES) method, the Wernner scheme. A particular network conducts each point of VES. The interpretation was done according to the respective program and on their basis was created the map of Quaternary thickness. The curve in the figure 2 illustrates the shape of a VES provided in a profile point. Three geological-geophysical cross-sections are compiled for the study area (Figures 3). From a general overview of the cross sections, we conclude that the Quaternary deposits display very low values of resistance, varying within the limits of 0.6-5 OMM. According to the survey of the neighboring areas and also from literature, such values are characteristic for clayey

– muddy formations, peat or formations saturated in sea water as sands etc. (Kavaja et al. 2004; Jata 2004).

In general, these sedimetary formations show a gentle dipping towards east. Based on the geophysical data it is shown that the upper part of the section is predominated by coarse and medium grained sands with an average thickness of 10-12 m, in some cases maximum 20 m (Figure 3, profile 1).

Below the succesion described above, clay silt formations dominate and are represented by two parallel layers with a thickness up to 10-15 m (the upper layer) and 15-25 m (the lower layer). The thickness of these formations varies from 25-30 m in the south-western part of VES 1, 7 and 8 and reaches 45-60 m in the north-eastern part of VES 3, 4 and 5 (Fig. 3). As mentioned above, the thickness of the Quaternary formations varies from 25-30 m and reaches a maximum up to 60 m. The Quaternary deposits overlie Eocene deposits which reflect an electrical resistance higher than those of Quaternary deposits (Figure 3, profile 2).



**Figure 4.** Map of thickness of Quaternary formation, Torovica area

In the upper part of the Eocene section occurs a layer with resistance values varying from 2.0 to 7.3 Omm. The thickness of this layer is 10-12 m, rarely 15-20 m and is represented by slumping horizons

with numerous olistoliths with different shapes and blocks of limestone and marly flysch as well. The top of this layer represents the basement of Quaternary formations. The formations underlying this layer belong to Eocene and are represented by argillaceous - siltstone - sandstone with sporadic limestone layers. The thickness of this formation reach up 500-600 m (Jata et al. 2008)

### Conclusions

Based on the geological - geophysical works carried on the area we conclude:

1. The formations in the studied area are 20-25 m thick and rarely up to 60 m thick.
2. Lithological composition of Quaternary deposits consist of fine to coarse grained sand, clay and silt clay saturated with salt water.

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## ASSESSMENT OF HUMAN ACTIVITY IMPACTS ON THE WATER OF OPEN AND CLOSED LAKE SYSTEMS. CASE STUDY: LAKE SHKODRA AND BELSHI, ALBANIA

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### Abstract

The lakes of Shkodra and Belshi may be considered as open and closed hydrological systems based on their hydraulic communication with other water bodies. This research tends to compare their water quality taking into account several chemical parameters indicating the state of water quality like O<sub>2</sub> dissolved, BOD, NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>, PO<sub>4</sub>, Cl.

20 water samples were taken from the Lake Shkodra and 18 water samples from Lake Belshi. The samples were taken at depth 50 cm from the water surface in order to avoid any interference of the accidental contamination. The temperature and pH of water were measured on the site. Chemical analysis was performed at the Chemistry Laboratory of the Albanian Geological Survey and at the Geochemistry Laboratory of the Faculty of Geology and Mining, Tirana. The spatial elaboration of the data was made by using the Geographical Information System (GIS) which allows the interpolation of the water quality parameter at unknown location and creates a continuous surface that helps us to understand the scenarios of water quality parameter of the studied area.

There are various interpolation methods, but in this study, the IDW technique, adopted to create the spatial distribution maps of water quality parameters is applied.

In both lakes, the water is slightly alkaline (7.84 - 8.37 and 8.67 - 8.8 for Lake Shkodra and Belshi, respectively), but the values of pH show higher variation in the water of Lake Shkodra ( $\sigma = 0.14$ ) against the lowest variation ( $\sigma = 0.03$ ) for Lake Belshi. The higher values (166-198 mg/l) of the dry residue in Lake Belshi against that of Lake Shkodra (126 to 157 mg/l) are explained with the lack of the hydraulic communication of the lake Belshi with other water bodies. The content of dissolved O<sub>2</sub> in water is higher (9.2 mg/l) in Shkodra Lake than in Belshi Lake (5.64 mg/l) due to both intensive waiving and the great recharge from the karstic springs for the lake Shkodra. In addition, the BOD<sub>5</sub> values are lower (0.66 mg/l) in the water of Lake Shkodra than in Lake Belshi (0.87 mg/l). This value of the BOD<sub>5</sub> for the water of Lake Shkodra could be lower if the water sampling was done all over the water body. In fact, the sampling was done only in the discharge part of the lake where several sewerage are present. The total phosphorus content is almost the same in the waters of both lakes with a slight tendency to increase in Lake Belshi. Ammonia and nitrites are missing or are found as trace amounts in both lake waters, while nitrates are higher (11.63 mg/l) in the water of Lake Shkodra than the Lake Belshi (6.35 mg/l) probably because of a more intensive agricultural activity accompanied by a greater application of chemical fertilizers.

## GEOCHEMICAL CHARACTERISTICS OF THE KAVAJA BASIN GROUNDWATER (PRE-ADRIATIC DEPRESSION, ALBANIA)

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### Abstract

The basin of Kavaja is part of the Rrogozhina aquifer, which is a multi layered aquifer consisting of intercalations between water-bearing Pliocene sandstone and conglomerate with impermeable clay layers and spreads out over the Albanian pre-Adriatic depression. This aquifer occurs under typically artesian conditions because of its impermeable clay basement and semi-impermeable Quaternary cover. The precipitations represent the main recharge source, but other recharge sources of the aquifer are the overlying Quaternary alluvial aquifers, the river beds and the boundary aquifers.

The groundwater shows a variable geochemical composition due to the different mineralogical composition of its medium and the vast extension of the aquifer. However, the mainly magmatic-carbonate mineralogical composition of the water-bearing sandstones and conglomerates has determined a geochemical composition of groundwater mostly consisting of HCO<sub>3</sub>-Mg-Ca groundwater type. Such a geochemical composition characterizes the groundwater of Rrogozhina aquifers chemically immature groundwater, which mainly plots near the center of the Piper plot. The groundwater evolves gradually from HCO<sub>3</sub> type to Cl type, from southeast (Shkumbini river) towards northwest (Adriatic Sea) that is from the recharge to the discharge zone.

The dissolution of minerals seems to be the major geochemical processes in the formation of the groundwater composition followed by cation exchange between groundwater and clay

formations that result in the Na enrichment of the groundwater. The mainly magmatic composition of sandstones and conglomerates is also responsible for the high content of iron in the groundwater of this aquifer. Iron content is higher in sandstone related groundwater where the silt fraction is mainly composed by iron-bearing minerals such as magnetite, epidote, garnet, sphene, amphibole and pyroxene.

The Total Dissolved Solids and General Hardness of groundwater show an increase of their values from the surface to depth, ranging from 500 to 800 mg/l and from 11 to 25°dH, respectively. In general, up to the depth 250-300m, all the hydrochemical parameters of the groundwater fit the Albanian and EU limits for the potable water. In some cases, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, etc., are found in concentrations higher than the limits of drinking water. In the diagram (not shown) of Total Dissolved Solids (TDS) versus the depth (H) was found that groundwater can maintain TDS values less than 1.0g/l up to a depth that ranges from 400 to 500 m according to the well location with respect to recharge and discharge zone.

The variation of TDS values follows the variation of the hydraulic conductivity values of the Kavaja aquifer. Thus, the highest values of the TDS and General Hardness correspond to the lowest values of the hydraulic conductivity. All the main ions, especially Cl<sup>-</sup> and alkaline ions increase from the southeastern to the northwestern part of the aquifer, i. e. from the recharge to the discharge zone.

## HYDROCHEMICAL DATA FOR THE GROUNDWATERS IN THE RADOVIS VALLEY ON THE AREA BETWEEN THE VILLAGES TOPOLNICA AND GORNO ZLEOVO, FYR OF MACEDONIA

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### Abstract

To determine the quality of ground water in the Radovis valley on the area between the villages of Gorno Zleovo and Topolnica, single samples were taken from 45 locations, 25 water wells, 6 springs, 2 boreholes and 12 hand pumps.

The measured values of pH indicate that water is weakly acidic to neutral (6.5 to 7.6), and the value of TDS, K<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> indicates possible contamination of ground water from fertilization on agricultural land as well as communal wastewaters.

Knowing the quality of ground water on the investigated area is of particular importance because these springs and water wells are used by residents of this region as drinking and irrigation water.

**Key words:** cations, anions, pH, MPC, temperature, water hardness

### Introduction

Groundwater quality in recent decades has been steadily deteriorating, so it is necessary to make efforts to preserve it. In many parts of the country, the exploitation of ground water as drinking water is denied, because of their contamination by various human activities.

Investigated area is located in the eastern part of Macedonia and covers part of Radovis valley. (Fig. 1).

In the geological structure on the wider environment on the investigated area can be found Precambrian rocks represented by different types of gneisses, micashist, marble; Ryphean-Cambria rocks are represented by schists and phylites, old paleozoic rocks are represented by shist carbonate series, marbles, cipollins, schists,

phylite and metasandstone, coarse porphyritic metarhyolites and aplitoid granites; cretaceous rocks are represented by limestones and tertiary rocks are represented by clays, sandstone, flysch, andesite and pyroklastite.

### Methods and materials

To determine the quality of groundwater in the investigated area during March-April 2012, single samples were taken from 45 locations, 25 water wells, 6 springs, 2 boreholes and 12 hand pumps. pH values were determined with a field digital pH meter, and cations with AES-ICP, Libery 110, Varian. For determination of anions were used standard EPA methods (gravimetric - TDS, volumetric - Cl<sup>-</sup>, spectrophotometric - NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> and turbidimetric - SO<sub>4</sub><sup>2-</sup> with spectrophotometer 6715 UV/VIS, Jenway).

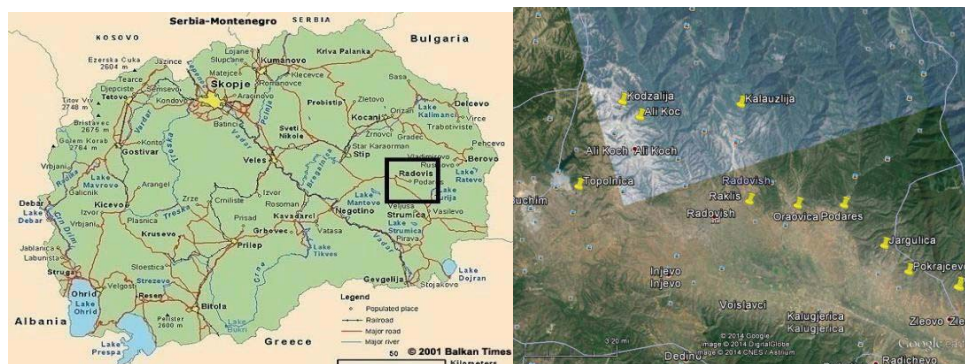
### Results and discussion

The spatial position of the measured data is displayed in graphical form, based on measured Gauss-Krüger coordinates (x, y) from the locations where the samples were taken.

The measured data are compared with national standards, which were made by pattern of European standards (MPC-Official Gazette of R. Macedonia Nr. 57 of 27. 08. 2004 g.).

pH is an important environmental factor which provides information about many types of geochemical balances (Shyamala et al. 2008). The measured pH values for groundwater are examined in the range of 6.5 (Kodzaliya I-1) - 7.6 (from Raklish wells, Pokrajchevo and Zleovo) with median 7.3. In all tested samples, the measured values (Fig. 2) are within MPC (maximum permissible concentrations) used by national standards for comparison.

TDS is used to estimate the total dissolved salts in



**Figure 1.**  
 Geographical location of investigated terrain.



water (Purandara et al. 2003), which might have an impact on the taste and suitability for applying water for various purposes. The measured values of TDS in the tested water are in range from minimum 97 mg/L in Kodzalija I-1 to maximum value from 2047 mg/L in Pokrajchevo B1 with median 537 mg/L. In all waters except Pokrajchevo B1, TDS values do not exceed the recommended MPC for drinking water, 2000 mg/l. (Fig. 3). Increased concentrations for total dissolved ionic substances is a consequence from the geology of the ground, but indicate possible about the contamination with communal wastewater.

According to WHO, water which contain more than 500 mg/l TDS are not recommended for drinking and can cause some diseases due to excess part of the dissolved salts. (EPA 2002; Ballester and Sunyer 2000).

**Calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ).** Contents of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  determine the hardness of the water, which is an important parameter for reducing the toxic effects of some elements. In the three samples examined specific content of  $\text{Ca}^{2+}$  exceeding MPC for drinking water (Ca 200 mg/l), while in 6 tested samples content of magnesium is higher than 50 mg/l in drinking water.

On average, a larger number of samples where the measured concentrations for magnesium is higher than 50 mg/l, compared with calcium (Fig. 4 and 5). The high values for total hardness on the tested waters mainly due to the dissolution of the carbonate rocks.

**Sodium  $\text{Na}^+$ .** Sodium concentration is with minimum value of 4 mg/l in Kalauzlija I-1 until a maximum 153.6 mg/l in the Pokrajchevo B2 with median 22 mg/l. In the all tested water (Fig. 6), the content of sodium is lower than MPC for drinking water (200 mg/l).

**Potassium  $\text{K}^+$ .** Particular range from concentrations of the potassium is very wide (Fig. 7). The minimum value is from 1.08 mg/l in Oraovica Source 3, to the maximum 189.4 mg/l in Podares B4 with median 5.45 mg/l. The content of the potassium is higher than the MPC for drinking water (12 mg/l), in 16 samples.

**$\text{HCO}_3^-$ .** Values for alkalinity of the the waters is expressed as hydrogen carbonate anions indicates the nature of the salts present in the water. The reasons for alkalinity of the water is dissolution of the minerals from the soil into the water. Different ions have a stake in alkalinity, such as hydrogen carbonate, hydroxide, phosphate, borate, and organic acids. These factors are typical for water resources and natural processes which occur (Sharma 2004).

Particular range from concentrations of the hydrogen carbonate determined as alkalinity is with the minimum value from 38 mg/l in Podares B2 to the maximum 262 mg/l in Pokrajchevo B1, with median 174 mg/l (Fig. 8).

**Chloride  $\text{Cl}^-$**  commonly encountered as NaCl,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  in a large range of concentrations

in natural waters. They can also be pollutants of the groundwater, whose source can be sewage water and waste (Shaikh and Mandre 2009).

Chloride (Fig. 9) is determined in a concentration range from 24 mg/l in Kodzalija source to 512 mg/l in Pokrajchevo B2, with a median 104 mg/L.

Maximum permissible concentrations (MPC) for chlorides in drinking water, according to the rulebook safety of drinking water in Macedonia is 250 mg/l. According to the measured content of chlorides in 10 of the tested samples were measured content higher than 250 mg/l.

**Sulphates  $\text{SO}_4^{2-}$ .** Sulphates can be an indicator of water pollution in mining waste water. Concentration range for the tested sulphates in water (Fig. 10) is from minimal 1.65 mg/l in Raklish (hand pump 1) to maximum 697 mg/l at Topolnica (hand pump 1) and with median 29.2 mg/l. Only the concentration of sulphate anions in water Topolnica (hand pump 1) exceeding the MPC for drinking water. Probably because it is near to the copper mine "Bucim."

**$\text{PO}_4^{3-}$ .** The results from the measurements of the concentrations of dissolved phosphorus expressed in form of phosphate) ranging from minimum 0.02 mg/l (Raklish B1 and Radovish P2) to the extremely high value of 4.75 mg/l (G. Zleovo B1), with a median 0.18 mg/l (Fig. 11). Only 9 of the tested samples exceed the content of phosphates from MPC for drinking water (0.91 mg/l). The higher values from MPC, are unusual for the presence of phosphate in natural waters, and their increased concentration indicates possible contamination of water with fertilizers and pesticides.

**Nitrates  $\text{NO}_3^-$ .** Concentrations of nitrates in the water indicate biological contamination of water. The range of concentrations of certain nitrate anions (Fig. 12) is from the minimum value of 0.361 mg/l in Radovish P4 to maximum 461 mg/l in Podares B5 with median 31 mg/l. In 19 of the 45 tested samples measured values for nitrate anions exceed the limit value of 50 mg/l according to the MPC.

Obtained values in the tested samples indicate a greater saturation of groundwater with organic matter as a result of pollution with municipal wastewater, wastewater from farms or pollution by fertilizers which contain nitrate anions.

**Nitrite  $\text{NO}_2^-$ .** Nitrite ions (Fig. 13) were detected at concentrations higher than MPC in 28 of 45 examined samples of groundwater, with a maximum concentration from 0,069 mg/l in Raklish B3.

**$\text{NH}_4^+$ .** Ammonium ions are indicators of the dynamics of self-purification of contaminated waters. Ammonium ions are detected in the 25 tested samples (Fig. 14), with a maximum concentration from 0.202 mg/l in G. Zleovo B6. Only two trials (G. Zleovo B6 and Raklish B3) are determined content for ammonium ions higher than the MPC value in drinking



water 0.1 mg/l. According to the classification of Alekin most of the tested waters by anion fall into hydrocarbons-chloride class, according cation in calcite-magnesium group.

### Conclusion

Based on the obtained values for the content of TDS,  $K^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $NO_3^-$ ,  $NH_4^+$  and  $NO_2^-$  in samples from groundwater in the area between the villages Topolnica and Gorno Zleovo in Radovis valley can be concluded that in the most of the tested samples were observed higher concentrations from MPC for drinking water.

Increased concentrations of these components indicate anthropogenic pollution of these waters from fertilization of agricultural land, livestock farms, copper mine "Bucim" as well as communal wastewater.

It is necessary to do additional research to determine the quality of groundwater in this area by expanding the analyzed parameters, and based on it, to take appropriate measures to prevent further contamination.

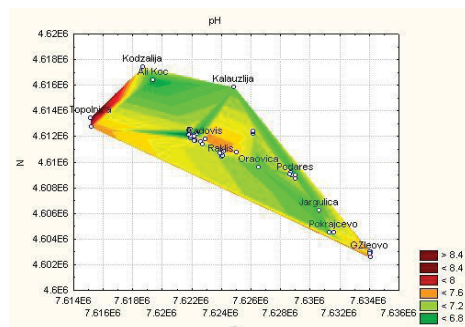


Figure 2.  
 Spatial distribution of pH

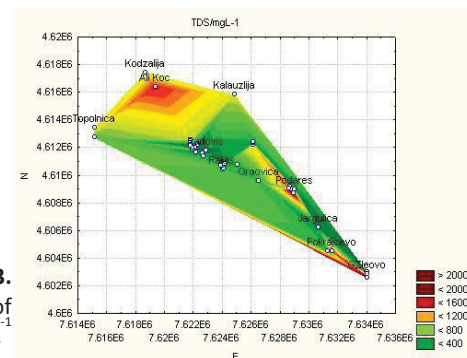


Figure 3.  
 Spatial distribution of TDS/mg/L

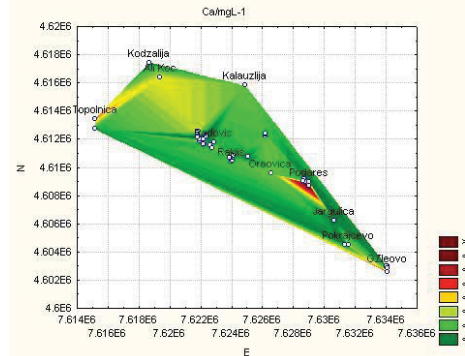


Figure 4.  
 Spatial distribution of  $Ca^{2+}$ /mg/L

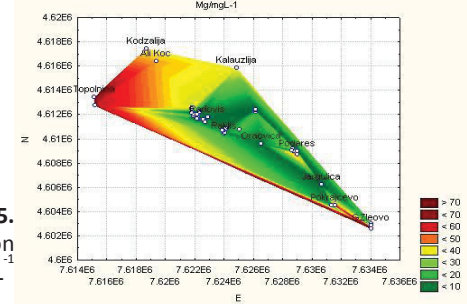


Figure 5.  
 Spatial distribution of  $Mg^{2+}$ /mg/L

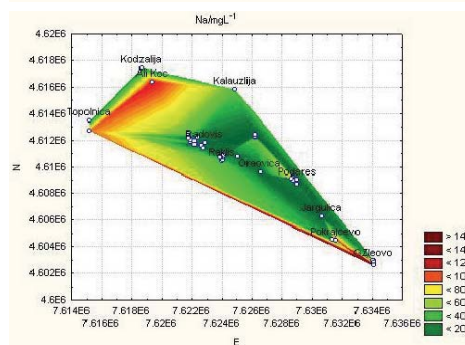


Figure 6.  
 Spatial distribution of  $Na^+$ /mg/L

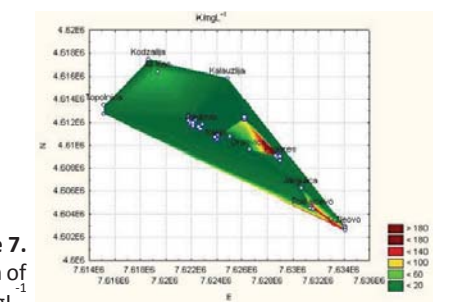


Figure 7.  
 Spatial distribution of  $K^+$ /mg/L

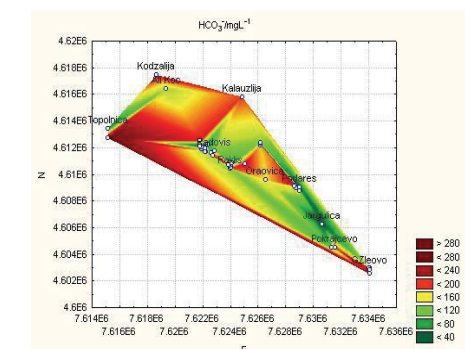


Figure 8.  
 Spatial distribution of  $HCO_3^-$ /mg/L

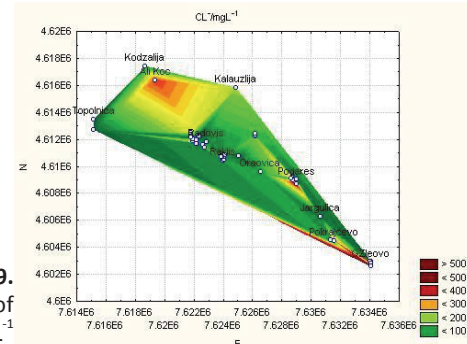
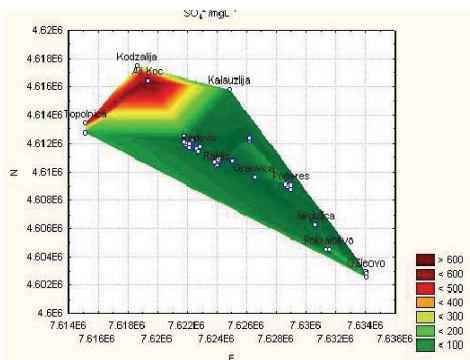
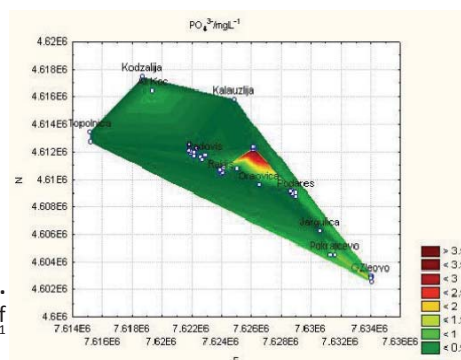


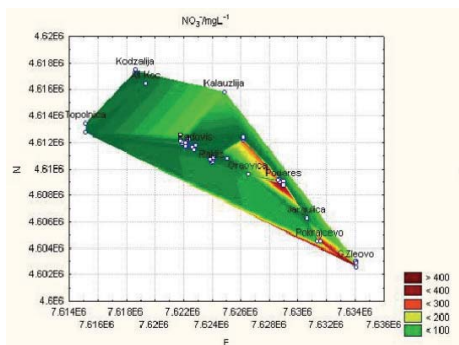
Figure 9.  
 Spatial distribution of  $Cl^-$ /mg/L



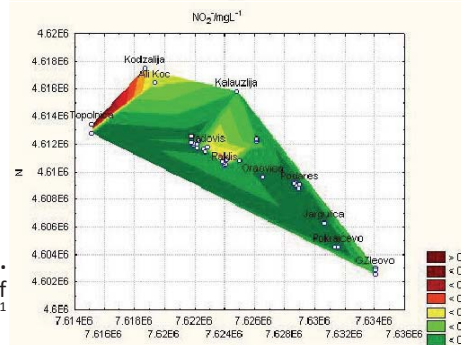
**Figure 10.**  
 Spatial distribution of  
 $\text{SO}_4^{2-} / \text{mgL}^{-1}$



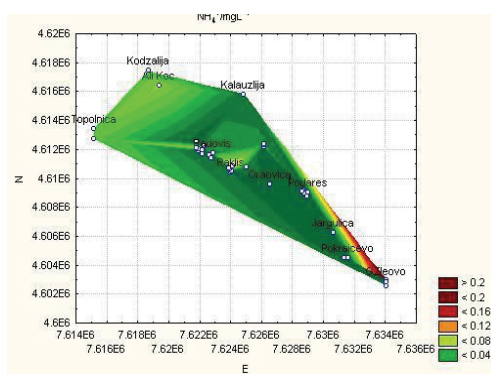
**Figure 11.**  
 Spatial distribution of  
 $\text{PO}_4^{3-} / \text{mgL}^{-1}$



**Figure 12.**  
 Spatial distribution of  
 $\text{NO}_3^- / \text{mgL}^{-1}$



**Figure 13.**  
 Spatial distribution of  
 $\text{NO}_2^- / \text{mgL}^{-1}$



**Figure 14.** Spatial distribution of  $\text{NH}_4^+ / \text{mgL}^{-1}$

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## LIQUEFACTION-INDUCED SETTLEMENT EVALUATION BASED ON IN-SITU TEST DATA AT SEMANI SITE IN ALBANIA

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### Abstract

Earthquakes are among the most severe natural disasters. Liquefaction in saturated sand deposits is one of the most dramatic causes of damage to structures during earthquakes. Loose sand tends to contract under the cyclic loading imposed by earthquake shaking. If the soil is saturated and unable to drain, normal stress can be transferred from the sand matrix onto the pore water. This causes a reduction in the effective confining stress within the soil and a loss of strength and stiffness that contributes to deformations of the soil. This process is called soil liquefaction. The consequences of soil liquefaction can be enormous. Generally, liquefaction-induced ground failures include flow slides, lateral spreads, ground settlements, ground oscillation, and sands boils. This work focuses on the estimation of the liquefaction-induced settlement. For saturated sand, excess pore water pressure builds up during the earthquake. After the shaking, excess pore water pressure dissipates toward the ground surface, where water pressure is relatively lower. The dissipation usually is accompanied by a reconsolidation of the sand. The reconsolidation manifested at the ground surface as vertical settlement, is termed liquefaction-induced settlement or seismic settlement. Its evaluation becomes very important for the design of structures located in areas susceptible to liquefaction. Ground surface settlement for one-dimensional reconsolidation can be computed by equating the vertical strains to the volumetric strain and integrating the vertical strains over the depth interval of concern. Post-Liquefaction Volumetric Strain can be computed by different methods based on SPT, CPT and  $V_s$  data. This work evaluates the liquefaction-induced settlement at Semani site in Albania using SPT and CPT data.

A subsurface investigation that include 12 SPT borings and 12 CPT soundings were performed in the site. According to Shkodrani et al. 2010, the soil conditions are classified as type D and Category III according to Eurocode 8 and to Albanian Earthquake-Resistant Design Regulation KTP-N.2-89, respectively. The PGA (Peak Ground Acceleration) for soil category III at Semani site according to maximum expected intensity is 0.26g and the moment magnitude of earthquake is

$$M_w = 4.5 - 6.$$

Liquefaction-induced settlements were evaluated based on the SPT and CPT data (Idriss & Boulanger, 2008). The input data for the methods include: SPT borings and CPT sounding with depth, moment magnitude of the earthquake, maximum surface acceleration during earthquake, depth to ground water table, and the unit weights of the soils. Liquefaction-induced settlement evaluation includes the following steps:

1. Assess the liquefaction potential based on the SPT and CPT data.
2. Calculate the maximum shear strain based on Ishihara and Yoshimine 1992 extended for the application of SPT and CPT data (relationships  $CRR - (N_1)_{60CS}$  and  $CRR - q_{c1Ncs}$ ).
3. Calculate the post liquefaction strain by using relationships expressed in terms of SPT and CPT penetration resistances.
4. Calculate the post liquefaction reconsolidation settlement.

Finally, some conclusions regarding the liquefaction-induced settlement in this site are highlighted.



## ISOTOPIC TECHNIQUES USED FOR UNDERGROUND WATERS CHARACTERIZATION IN QUATERNARY AREA OF MYZEQEA

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### Abstract

In Albania, Quaternary formations are the most important aquifers for drinking water supply and agriculture. The study area bounded between Shkumbini River to Semani River, is characterized mainly by alluvial deposits that overly the Neogene conglomerates. In order to precisely determine the groundwater origin and its features, isotopic techniques based on environmental isotopes as O<sub>18</sub> and H<sup>++</sup> were used.

In the study area, 14 pluviometers were placed in different altitudes, in various distances from the Adriatic Sea and also in different morphological shapes.

During the field work in 2009, 37 and 27 samples for chemical - physical and isotopic analysis, respectively, were collected. Similarly in 2010 42 and 45 samples, respectively, were collected. Lastly, in 2011 42 samples were collected for chemical - physical analysis. During a period of two years, the boreholes used for drinking and agriculture waters were monitored. The purpose was to determine the origin of underground waters, their hydraulic connection with surface and marine waters. Stable isotopes such as Deuterium and Oxygen 18O in 55 water samples were measured in Quaternary and Neogene formations in Lushnja area. The measurement's interval varies from -48.00‰ in three locations of bridges to -28.79‰ near Semani River location, for δ<sup>2</sup>H; and for δ<sup>18</sup>O -7.11‰ in three locations to -4.37‰, again in Semani River location.

Filtering properties of the layer and consequently specific debits change along the extension from north to south. In the Çërma area, filtration coefficients vary from 10 to 59 m/day, but more predominant are the values from 30 to 50 m/day.

In the Tërbufi area, the exploration wells have values from 34 to 92 m/day, while in the yield wells 62 to 165m/day. In southern Tërbuf up to Këmishtaj area, the filtration coefficients have values 8-34 m/day where the predominant values are those of 20 m/day and finally, in Krutja area, this coefficient varies from 14 to 33 m/day and values of 25 m/day predominate.

All the samples are characterized by a standard deviation. Standard deviation for δ<sup>2</sup>H must not be over 2 ‰. In the samples, this value varies from a minimum of 0.14 ‰ to a maximum of 0.93‰. Standard deviation for δ<sup>18</sup>O must be not higher than the value of 0.3 ‰. The samples show standard deviation from 0.03‰ to 0.23‰. One of the main problems has been the water salinity origin in the center of the study area, in the section from Savra - Këmishtaj - Bubullima villages.

For this reason, based on international meteoric line, we designed the local meteoric line as a base for Albania.

The isotopic analyses are conducted at the "Institute of Applied Nuclear Physics, University of Tirana" and at the "Laboratoire d'Hydrologie Isotopique", Université Paris-Sud, France, for comparison and standardization of analyses performed at the two laboratories. The results of this study are dependable since they portray the clear spectrum of the waters origin and their chemical - physical features.

We determined the zones with high salinity and the geometry of aquifers in three dimensions, and as a result, the Authorities from the area of water drinking supplies and agricultures have the possibility for better knowledge of how to use the waters, where investments can be made and how to better manage them in the future. These results are summarized in one authentic report deposited in the Central Archive of Albanian Geological Survey.



## THE WATER STATUS OF THE MAIN LAKES IN ALBANIA: OHRID, PRESPA AND SHKODRA LAKES

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<sup>1</sup>*Albanian Geological Survey, Albania*

### Abstract

Albania has three main lakes: Prespa, Ohrid and Shkodra bordering with Greece, FYR of Macedonia and Montenegro. Based on Water Framework Directive 2000/60 EC for the surface water, some observations were made for determining the lake's status. In order to evaluate the water quality for the lakes of Prespa, Ohrid and Shkodra, a number of samples taken at different locations and depths for every season during the years 2013-2014, were used. The data obtained were compared to older data. The physical-chemical analyses were computed in Albanian Geological Survey and Shkodra University Laboratories. The main parameters analyzed, belong to the main anions and cations, BOD, DO, total nitrogen, total phosphorous, transparency and total solid suspends, etc. The analyzed microelements were cadmium and lead. The used standards for the determination of oligotrophic, mesotrophic and eutrophic status have been those of transparency, where the main values in Ohrid Lake, in Lini station were 4.5-5 m, in Guri i Kuq, 5m, and in Tushemishti station 4.3 m. In Prespa Lake, the transparency in the Pusteci station reached a mean value of 2.5 m and in Gorica station, the mean value was 3.5 m. In Shkodra

Lake, the transparency values measured in three stations were the following: in Zogaj station 3.0 m, in Shiroka station 3.5m and in Kalldrini station 2.0 m. Regarding the values of PO<sub>4</sub> that vary from 4.67 µg/l in Ohrid Lake, 8.50µg/l in Prespa Lake and 4.33 µg/l in Shkodra Lake. We observed the oligotrophic status of the waters. pH measurements gave mean values of 8.28 in Ohrid Lake, 8.11 in Prespa Lake and 8.24 in Shkodra Lake. Finally, in order to determine the water status, we have taken in consideration many physical-chemical parameters and standards suggested by the WFD and in comparison with biological measurements we found some interesting results.

The used equipment were two boats equipped with necessary instruments, field laboratory, Routner bottle sampling, Secchi disk multi parametric probe-Quanda D, GPS, water thermometers. Samples preservation, transportation and their field treatment have been made in respect to scientific standards. The analyzing process had begun within 24 hours. The results were compared with those of Hydro-biological Institute of FYR of Macedonia and hydro-meteorological station in Montenegro respectively for Prespa and Ohrid lakes, also for Shkodra Lake.

## OCCURRENCES AND CHEMISTRY OF CARBONATED WATERS IN THE POLISH CARPATHIANS

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### Abstract

Therapeutic carbonated waters (free CO<sub>2</sub> above 1 g/dm<sup>3</sup>) and the waters containing carbon dioxide (free CO<sub>2</sub> in the range 0.250-0.999 g/dm<sup>3</sup>) have been reported in 226 sites of the Polish Carpathians. They are accessible in 73 springs and 153 drilled wells in 25 localities, and out of the latter eight have a rank of statutory spas. Six regions of water occurrences have been distinguished: the Szczawa, Krościenko-Szczawnica, the Poprad River valley, Wysowa, Iwonicz-Rymanów and Rabe ones.

**The Szczawa region:** the waters are accessible in 4 springs and 5 wells with depths 8.2-100 m. Their TDS ranges from 1.2 to 22.3 g/dm<sup>3</sup> and their main hydrochemical type is HCO<sub>3</sub>-Cl-Na+CO<sub>2</sub>+(I)+(H<sub>2</sub>S).

**The Krościenko-Szczawnica region:** the waters are accessible in 8 springs and 6 wells with depths from 7.0 to 32.78 m. Their TDS ranges from 1.2 to 21.9 g/dm<sup>3</sup> and their type is HCO<sub>3</sub>-Cl-Na+CO<sub>2</sub>+(I).

**The Poprad River Valley region** is the largest „balneological basin” in Poland with the waters in question occurring in 18 localities. The waters are accessible in 54 springs and 116 wells with depths from 8.0 to 948 m. Their TDS ranges from 0.3 to 29 g/dm<sup>3</sup> and their type is HCO<sub>3</sub>-(Ca)-(Mg)-(Na)+CO<sub>2</sub>+(I)+(Fe)+(H<sub>2</sub>SiO<sub>3</sub>).

**The Wysowa region:** the waters are accessible in 14 wells with depths from 14.5 to 100 m. The TDS ranges from 2.1 to 24.7 g/dm<sup>3</sup> and their three types are Cl-HCO<sub>3</sub>-Na+CO<sub>2</sub>; HCO<sub>3</sub>-Na-Ca+CO<sub>2</sub>+Fe and HCO<sub>3</sub>-Cl-Na+CO<sub>2</sub>+I+Fe.

**The Iwonicz-Rymanów region:** the waters are accessible in 5 springs and 10 wells with depths from 250 to 1255 m. The TDS ranges from 3.0 to 17.6 g/dm<sup>3</sup> and their two types are Cl-HCO<sub>3</sub>-Na+CO<sub>2</sub>+(I)+(Fe) and HCO<sub>3</sub>-Cl-Na+CO<sub>2</sub>+I.

**The Rabe region:** the waters are accessible in 2 springs and 2 wells with depths from 70 to 77 m. The TDS ranges from 0.6 to 4.8 g/dm<sup>3</sup> and their type is HCO<sub>3</sub>-Cl-Na+CO<sub>2</sub>+(H<sub>2</sub>S).

There are three factors that control the formation of the Carpathian carbonated waters: the genesis of CO<sub>2</sub> (their main component), the origin of the waters themselves, and the processes developing their overall chemistry. The waters were formed under complex water-gaseous conditions, when circulating underground water was saturated with CO<sub>2</sub> migrating from the deep basement of the Slovak Tatra Mountains through many tectonic discontinuities. Due to the presence of CO<sub>2</sub> the waters become aggressive, dissolve flysch rocks and get enriched in mineral components. The Carpathian carbonated waters can be divided into two genetic groups. The first one includes ordinary carbonated waters of shallow circulation and the HCO<sub>3</sub>-(Ca)-(Mg) main type, with their TDS below 6 g/dm<sup>3</sup>. Their resources can be considered renewable due to a continuous inflow of CO<sub>2</sub> and meteoric waters but on the proviso that the gas and water conduits remain undisturbed. The other group includes chloride carbonated waters of deeper aquifers and the HCO<sub>3</sub>-(Cl)-Na-(Mg)-(Ca) type, with higher TDS values reaching about 28 g/dm<sup>3</sup>. They represent infiltration waters mixed in various proportions with diagenetic waters (syndimentary and/or dehydrating ones).

The HCO<sub>3</sub><sup>-</sup> is the major anion deciding on the type of the waters considered, and few of them contain also the Cl<sup>-</sup> ion, while the deciding classification cations include Ca<sup>++</sup> and Mg<sup>++</sup>, occasionally Na<sup>+</sup>. The TDS of the waters discussed ranges from 0.30 to 28 g/dm<sup>3</sup>, pH from 5.3 to 7.5, and the temperature from about 7.5 to about 23°C. The contents of selected components are as follows: 250-3600 mg/dm<sup>3</sup> of CO<sub>2</sub>; 60-19,000 mg/dm<sup>3</sup> of HCO<sub>3</sub><sup>-</sup>; 0.9-7500 mg/dm<sup>3</sup> of Cl<sup>-</sup>; 3.5-6800 mg/dm<sup>3</sup> of Na<sup>+</sup>; 0.2-130 mg/dm<sup>3</sup> of SO<sub>4</sub><sup>2-</sup>; 12.2-1750 mg/dm<sup>3</sup> of Mg<sup>2+</sup>; 21.1-1082 mg/dm<sup>3</sup> of Ca<sup>2+</sup>; 2.0-65 mg/dm<sup>3</sup> of Fe<sup>2+</sup>.

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## EFFECTIVENES OF ELECTRICAL RESISTANCE TOMOGRAPHY, TO THE DEDECTION OF MASSIF GNEISSES OF INDUSTRIAL IMPORTANCE

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### Abstract

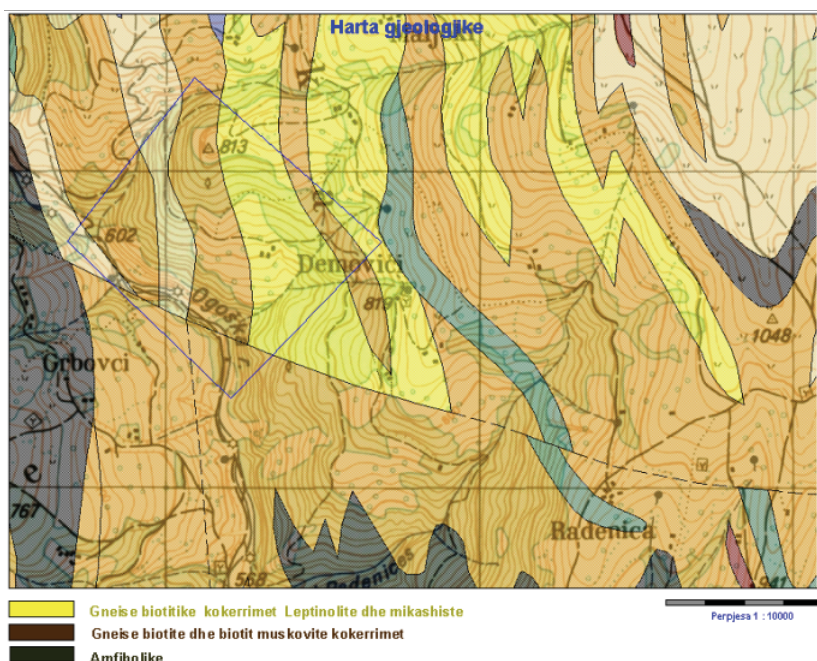
Parallel Electrical Resistance Tomography (ERT) profiles along the slope of the hill, in the Hogoste village, Kamenica municipality, in Kosovo have been conducted in order to detect the continuation of massif gneisses toward the east of the existing road (east of their outcrop). The length of ERT profiles was 295 m in four profiles (No 2-5), 235 m in one profile (No 1) and 145m in three profiles (No 6-8) with an investigation depth of 20-60 m. The surface of surveyed area is around 10 hectares. The high resolution geoelectrical ERT lines were surveyed using Wenner-gamma array. The spacing unit between electrodes is 5 m in 7 profiles and 4 m in one profile. The total number of electrodes used for each profile is 60 in 5 profiles and 30 in 3 profiles. The investigated depth using high resolution resistivity imaging system is up to 60m. With the use of ERT method, the lithology of the subsurface is well determined through the 2D true resistivity distribution along the lines. There are

delineated three anomalous belts related to the spatial extent of gneisses formation which are of industrial importance.

**Key words:** *Electrical Resistance Tomography, gneisses, inversion, apparent resistivity, true resistivity*

### Geological Settings and layout of geophysical surveys

The surveyed area is located in the eastern region of Kosovo Republic and is part of Dardanian Massif, which is a continuity of Rhodope Massif (Serbian-Macedonian) in Kosovo. From geographical administrative point of view, the surveyed area belongs to Kamenica Municipality (fig. 1). It is extended in the north-eastern part of Kamenica town, practically 3-5 km, north of Hogoshte village, towards the road to Dazhnica. The relief is hilly-mountainous with heights of 500-1070 m. The geological formations in the wider area are



**Figure 1.** The geological map of the wider area of the region under geophysical investigation.



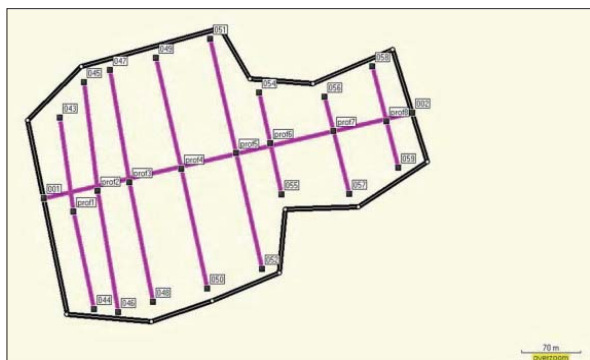
composed of gneisses, mica-schists, quartzites, amphibolites, migmatites and granites (Fig. 1). In the surveyed geophysical area, the geological formations are represented by gneisses.

#### *Lithostratigraphic characteristics*

Geological formations in the region under geophysical survey are composed of metamorphic rocks such as: gneisses, mica-schists, quartzites, migmatites and amphibolites; granitic rocks and quaternary deposits.

#### *Layout of Geophysical surveys and methodology*

The layout of geophysical surveys is shown in figure 2. The polygon with black outline represents the surveyed area, whereas the magenta line show the 2D Electrical Resistance Tomography (ERT) profiles. With abbreviations, profiles 1-8, are labeled the ERT profiles, whereas the line along the extension of the area (1-2 with direction 77 degrees from the true north) is used as a reference line during the interpretation of data. The direction of ERT lines is approximately north-south, with an azimuth angle of 167 degrees from the true north. The surveyed area is  $0.1\text{km}^2 = 10$  hectares.



**Figure 2.** Layout of ERT profiles in the surveyed area.

### **Methodology**

A series of electrodes is laid out on the ground and by using a multi-core cable and a multiplexing unit, a series of profiles with varying electrode spacing over the same area is automatically obtained. This type of data is difficult to be directly interpreted. In fact, the survey method falls into a class of approaches known as 'inverse imaging'. The aim is to extract information from the surface measurements about the structural variations at some distance below the surface. The treatment of the data-sets with the so-called 2-D non-linear inversion schemes is necessary.

Electrical Resistance Tomography (ERT) is an active geoelectrical prospecting technique used to obtain 2D, 3D and 4D (with time) images of the subsurface electrical resistivity distribution. It has been applied for investigating areas of complex geology, seismotectonic structures (Caputo et al. 2003), archaeological sites (Reci et al. 2009; Tsokas et al. 2007) and areas of hydrogeologic phenomena and environmental problems (Di Maio et al. 1998). Lately, ERT has been used to delineate the geometry of complex landslides (Bogoslovsky and Ogilvy 1977; Muceku and Reci 2006, 2008; Reci et al. 2013). Technically, the ERT is obtained by using different multi-electrode arrays, such as Dipole-Dipole, Wenner, Schlumberger, Wenner-Schlumberger, Gradient etc., the choice of which depends on the subsoil, the depth of investigation, the sensitivity to vertical and horizontal changes in the subsurface resistivity, the horizontal data coverage and the signal strength (Loke 1996, 1999). The current is injected into the ground through a couple of electrodes and the resulting potential differences are measured between another couple of electrodes at the surface.

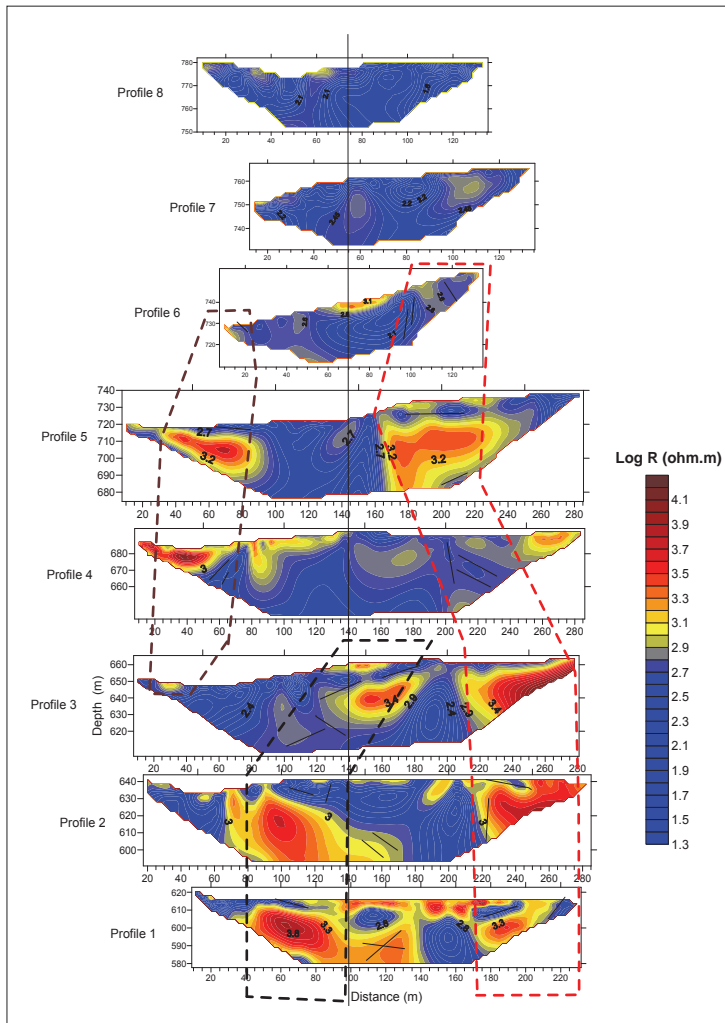
In this work, we conducted multi-electrode 2D resistivity imaging. To do a joint interpretation of resistivity data, experiments with different multi-electrode arrays as Wenner Alpha array (WENNER  $\alpha$ ) Wenner Beta array (Dipole-Dipole) and Wenner Gamma array were used. The final resistivity data are taken from Wenner Gamma array and Self Potential (measurements).

### **Results and discussion**

In figure 3 is shown the spatial distribution of logarithmic resistivity values of the surveyed area for each profile. From the resistivity distribution values of ERT profiles we distinguish three zones of their values. The low resistivity values (blue color) that normally is connected with mica-schists and quaternary deposits, another with mean resistivity values (yellow color) that is related with the interfaces (combination) between gneisses and mica-schists and the high resistivity values (red color) which normally are related with compact and massive gneisses.

After a detailed study and spatial interpretation of anomalous zones, we distinguish three anomalous belts directed in general extent almost west-east. In figure 4 are presented the layout of those belts on the surveyed area which represent interest for



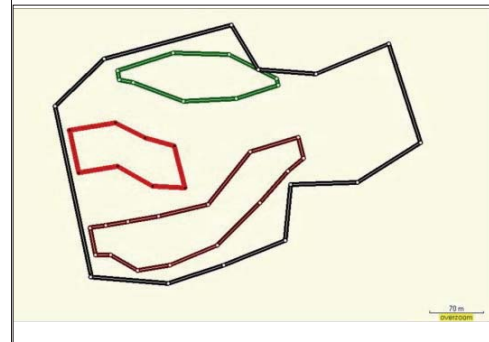


**Figure 3.** The resistivity anomalies along the depth, for each profile. With polygons are depicted the interesting areas for gneisses exploitation. The red color present compact body, yellow color fracture zones and blue color low resistivity formation which are not important.

gneisses exploitation of industrial use.

*The first anomalous belt (area 7799 m<sup>2</sup>).* According to geophysical interpretation is the most important in the surveyed area and extends from profile 1 in south-west and between the profiles 3 and 4, in north-east. It has an approximate length of 105 m with average width of 40-60 m, indicating that the manifestation of the compact gneisses body in surface in profile 1 continues towards east (Fig. 3 and 4). The anomaly continues towards east without interruption until beyond profile 3 and is limited towards depth. This polygon is presented with red color (Fig. 4)

*Second anomalous belt (area 16141 m<sup>2</sup>).* This anomalous belt is presented on the maps with coffee brown color. It is extended from profile 1 in south-west until beyond profile 5 in north-east, with interruption only in profile 4. The average



**Figure 4.** The interested areas where the compact gneisses are extended.

length of this anomalous belt is 250 m with a width that varies from 20-60 m. This shows that exists the possibility to reach another gneissic body, without surface manifestation interrupted in profile 4, which tends to be developed towards depth (profiles 2 and 3), with a thickness of 30-40m. According to geophysical interpretation, this body starts at profile 1 with limited dimensions, continues in profiles 2 and 3, is interrupted in profile 4 and starts again in profile 5.

*The Third anomalous belt (8896 m<sup>2</sup>).* It is shown on the maps with green color. It is located in the northern part of first anomalous belt and extends from profile 3 until profile 6 with average length of 175m and average width of 10-30 m. The depth of the anomaly is 5-30 m. The shape of the anomaly shows that the body is limited towards depth.

Inside compact gneisses there are shown some

low values of resistivity that could be related with fracture and fissure zones even though it is very difficult to be detected. The resistivity values distinguish very well the fractures and contacts between geological formations and facial variations as well. In accordance to economical value, the most important area is the belt 1, and after that the second and third ones.

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## OPEN EXCAVATIONS IN FLYSCH AND ASSOCIATED INSTABILITIES

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### Abstract

This study describes a range of excavation slope stability problems encountered during and after the completion of the earth works in the Banja Hydropower Plant Project, along Devoll River, Albania.

The geology of the project area is characterized by the presence of Tertiary flysch formed in connection with the Middle Eocene to Oligocene shallow water sedimentation. These sedimentary rocks were deformed throughout the Alpine orogeny. Failures in natural and excavated slopes with different slope angle occurred over a wide range of lithologies as alternating layers of sandstone, siltstone and shale, including slump sheets, all found within a localised area. The thickness of rock layers ranges from few centimetres to metres. Sandstone beds are generally thicker than siltstone ones. Furthermore, siltstone and shale layers vary from several centimetres to few millimetres in sheared zones.

Rock masses investigated all over Banja site, on both abutments of the dam as well as in the powerhouse and spillway locations were characterised by different degrees of strength, weathering and tectonic defects. Field estimates of uniaxial compressive strength of intact rock ranges from extremely weak to strong rock. The weathering degree changes from fresh to completely weathered within areas of only few square meters. The physical weathering rate is quite high especially in presence of water resulting in changes of the characteristics of the rock mass in a very short period of time. Siltstones and claystones are generally more sensitive to deterioration than the sandstone.

During the construction process it has been possible to adapt different slope geometry and protection measurements, to ensure the stability of permanent and temporary slopes. This was required owing to the flysch unexpectedly failing during excavations. When cutting into this flysch series the better part of the instabilities appeared mostly influenced by the complex structural geology of the site which governs the morphology of the area. These circumstances are aggravated due to the safety factor of the natural slope inclinations which is at the limit of stability. Circular, planar, wedge and combinations produced complex failure modes that included several cubic meters of failed material. Most of the failures occurred along pre-existing discontinuities characterised by low shear strength. Engineering geological mapping is fundamental in slope stability assessment. It has often been problematic due to mechanical excavations in weak rocks, which hide the traces of bedding and discontinuities

The most interesting events from a geological point of view are listed and described in this paper. A matrix has been developed in order to better understand the behaviour of flysch rock mass and to make a connection between the variety of lithology and different types of conditions and external factors that contribute to a possible failure mode, which failure mode is expected and how to deal with it in real time.

## POTENTIAL ANTHROPOGENIC IMPACTS ON THE VRAGOLI-KUZMIN GROUNDWATERS AND THE RISK OF WATER POLLUTION IN THE POTABLE WATER-SUPPLYING WELLS

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### Abstract

The drinking water wells of Vragoli-Kuzmin segment are located two kilometers west of Fushë Kosovë, between the localities of Vragoli and Kuzmin. The water supply station of Fushë Kosovë consists of 12 wells.

The studied terrain consists of alluvial deposits which belong to the upper coal-bearing basin of Kosovo. The thickness of the granular and intergranular medium of the alluvial aquifer ranges from 12 to 20m and consists of sandstone, gravel and gray sandstone covered by gray non permeable coral-bearing clay. The groundwater head occurs 2.6-7.7m below the earth surface and it is variable due to the extent of recharge from Sitnica and Drenica rivers and from rainfalls.

The Dupui's formula was applied to calculate the hydrogeological parameters like hydraulic permeability, the radius of influence and well productivity which range within the following intervals ( $K = 6.8-149 \text{ m / d}$ ), ( $R = 37-297 \text{ m}$ ) and ( $Q = 14-22 \text{ L / sec}$ ), respectively.

Considering both the geological and hydro-geological features of the region and in particular those of the narrower area where the water supply wells are placed, the possibility to enhance the water supply by extending the zone of groundwater pumping without any deterioration of the water quality represents a real challenge.

The vulnerability of the groundwater to contamination depends on hydro-geological factors like the depth of the groundwater, the vadose zone lithology or the permeability of the aquifer etc., but recently the anthropogenic activities have strongly influenced the deterioration of underground water quality.

The purpose of this study is to evaluate the role of the anthropogenic factors impacts and the extent they affect the quality of groundwater. This is very important because it allows to model the expected trends of the water quality evaluation in the future. The four rivers flowing in the collection pond of Sitnica River having low flow (2.5–2.7 m) potentially represent a great danger for the pollution of groundwater.

This study also tends to correlate the quality of groundwater with the quality of surface waters, which are directly under the stress of anthropogenic impacts.

The water of Sitnica, Prishtevka, Drenica and Granqanka rivers show different extent of its quality deterioration as it could be seen by the content of nitrates, nitrites and ammonia (0.9-22.6, 0.394-0.668, 0.364-10.89, respectively). Among the factors that influence such deterioration is the intensive pumping of groundwater from the public wells which extract about 12-20 L / sec fostering in this manner the hydraulic conductivity between groundwater and surface water.



## HYDROLOGICAL DATA OF BILISHTI-KORCA REGION

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### Abstract

The complex of unconsolidated rocks includes the Pliocene-Quaternary deposits located and in Korca and Devolli graben. These deposits are products of Devolli, Dishnica and Drenica rivers are represented by gravels, sands and clays. The city of Korca is supplied with water from drilling carried out near the village of Turan with a debit of 300 l / sec.

The compact rocks are represented by Triassic-Jurassic carbonate deposits. with cracks, karsts, caves that contain large water deposits. Here are the most important karst basins which feed the springs of Ventrok, Progerit, Mancurisht, Burimas etc. A part of groundwater flows in the area of Bilishti and Korca and could be used as drinking water. The spring that have big debit is Mançurishti spring with about 30 l / sec. Water is clean, tasteless, clear, with a temperature around -10 °C. Water of this spring is the type of calcium hydrocarbonate, magnesium, general mineralization 0.506 g / l, dry residue 310 mg / l, hardness 8.17 °G, and pH 7.19. Rocks with non-uniform medium water-bearing resources are represented by conglomeratic limestone, marls, conglomerates, sandstone conglomerate which are rocks with moderate to low deposits of water. These rocks are characterized by cracks, karsts and little pore-crack. Interesting spring is so called "pollution water" found in Dardha zone at 1288m high. It is characterized by an important sulphur content and

is known for its curative value. This spring comes in contact between the Pg<sup>2</sup> deposits represented by clay, sand, coal and Pg<sup>3</sup> deposits represented by sands, clays and coal layers. The debit of this spring is 0.09 l/sec and the temperature is 6°C. The water of spring is cold, not very transparent, with strong smell of sulfur that is result of coal layers. Flora is developed in the area surrounding the spring. The chemical composition is Mp=394.41 mg/l, dry residue = 244 mg/l, H<sub>2</sub>SiO<sub>3</sub>=2.59 mg/l, hardness = 11.76(Germany scale), PH=7. The low water-bearing rocks are represented by clay marls, alevrolitic clays, carbonate clay mixed with sandstones, marly sandstones, thick layered sandstones and Lithothamnium limestones. They are spread in Arrez-Zemblak, Miras-Zicisht-Vidohove zones. The presence of waters in these rocks is generally low. The average debit of wells is lower than 0.5 l/sec. The groundwater are fresh with medium to high hardness. Non water-bearing rocks are represented by heterogeneous ophiolitic melange and consists mainly of ultrabasic rocks and small outcrops of Triassic limestones, cherts, amphibolite rocks formed by basic volcanogenic rocks (QafeZvezd, Shuec, Rakicke). The groundwater can be found in different layers in sandy or tectonic contacts. The region of Korca (Sheet 43Korca) is characterized by diverse rock types that have water great potential with surface water and groundwater, which are put into use for various needs of the community.

## SOIL PROFILING BY USING CPTU IN DIFFERENT SITES IN ALBANIA

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### Abstract

This study aims to deal with the soil type identification and soil stratigraphy description using the CPTU correlations. The used CPTU data belong to different sites located in the western and central parts of Albania, where the geological formation show complex variations. The considered CPTU records belong to T.A.P. Compressor Station and Landfall Area project, both located in Semani beach, the Durresi Quay No. 1 project located in the Port of Durresi, the “Ruzhdi Bizhuta” Stadium reconstruction project in Elabasan city and a private building construction project located near to “Dinamo” Stadium in Tirana.

The data are collected using different cones and also different pushing machineries. All the cones used in the geotechnical investigations considered in this paper are conforming to the requirements of Application Class 1 of ISO 22476-1 Geotechnical Investigation and Testing – Field Testing – Part 1 Electrical Cone and Piezocone Penetration Test (2012) and have a cross-sectional area equal to 10 cm<sup>2</sup>. Cone resistance ( $q_c$ ), sleeve friction ( $f_s$ ), measured pore pressure in the shoulder position ( $u_2$ ) and the inclination in X and Y planes were measured in site while the other parameters used for soil profiling were estimated using the well known correlations of CPTU. The used pushing machineries were of three different types, 1.5 tonne, 14 tonne and 20 tonne CPT truck mounted rigs. The rate of penetration was kept constant at 2 cm/s  $\pm$  10%, except when penetrating very dense

or hard layers.

Classification charts proposed by Robertson et al. (1986), Robertson (1990), Eslami Fellenius (1997) and Ramsey (2002) were used for soil profiling by CPTU data records. The estimation of soil behaviour type using measurements of cone resistance and friction is based upon the variation of the friction ratio in respect to the cone resistance. For each penetration test, the measured cone resistance,  $q_c$ , is corrected for the ‘unequal area effect’, due to the influence of the ambient pore water pressure acting on the cone. The density and stiffness descriptions are based on derived value of  $N_{60}$  (Robertson et. al. 1986) and undrained shear strength  $s_u$  (Lunne and Kleven 1981) values from the cone resistance in accordance to BS5930:1999, respectively.

In all the considered sites, boreholes and laboratory tests were used to make the investigation and identification of subsurface conditions in addition to CPTU records. The soil profiles produced by CPTU data processing were compared with the results of exploratory borings records and laboratory test results. Differences in soil profiling are reported, including the differences in soils identification and in the thickness of layers. Also, some differences between the strength parameters evaluated from laboratory tests and derived from CPTUs are shortly mentioned.

Some conclusions regarding the thickness and identification of different layers during the soil profiling by using both techniques, and regarding the misclassification of “intermediate soils” are also highlighted.

## ASSESSMENT OF INTRINSIC VULNERABILITY MAKING USE OF DRASTIC METHOD AND GIS IN THE SHKODRA AQUIFER, ALBANIA.

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### Abstract

In the last two decades, the majority of Albania's population is concentrated in the lowland areas of the country, where the porous aquifers of Quaternary lie. Consequently, the aquifers are under the influence of pollution and over exploitation. The Shkodra porous aquifer has large resources of water and it supplies drinking water to the city of Shkodra, the largest urban center in the northern part of the country, along with the surrounding areas. This work addresses a vulnerability assessment of groundwater in the Shkodra aquifer. This aquifer covers an area of 85 km<sup>2</sup> and is located in an average altitude of 20 m above sea level in the northwestern part of Albania, in the Mediterranean climate belt. The average volume of rainfall, which makes up the main source of supply for groundwater resources, is around 1700 mm per year. Groundwater is associated with Quaternary gravel deposits in the area of Shkodra, which have an average thickness of 40 m. The concept of groundwater vulnerability is based on the assumption that the physical environment can provide a degree of protection for groundwater against human activity.

The DRASTIC method used for the evaluation of groundwater vulnerability was developed by the Environmental Protection Agency of the United States of America (EPA) and is based on seven parameters: w [D] Depth [R] Recharge (net), [A] Aquifer media, [S] Soil media, [T] Topography, [I] Impact of vadose zone, and [C] Conductivity of the aquifer. The DRASTIC index is determined by the sum of the products of the weight and site ratings of all the factors. For the evaluation of groundwater vulnerability, the geometrization of the aquifer, the hydraulic parameters and the quality of groundwater were based on previous hydrogeological studies and those of the last two years, as part of the program of the Albanian Geological Service. The map of groundwater vulnerability is built based on the DI values and by using Geographical Information Systems (GIS). The highest values of vulnerability cover most of the aquifer area. This conclusion is very important, as it serves decision making bodies responsible for the integrated management of water resources and determination of groundwater hygiene protection zones.

**Key words:** Aquifer, Albania, DRASTIC Method, GIS technique, Shkoder, vulnerability

## A CASE STUDY ON USE OF FOAM CONCRETE LANDFILL ON LANDSLIDE HAZARDOUS AREA IN ŞIRNAK CITY PROVINCE

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### Abstract

Şırnak province and the surrounding areas on steeper slopes, sliding large land masses or rocks, water, and harsh climatic conditions contain high risk hazard areas of urban living with higher population density. In order to eliminate landslides and related events, significant precautions should be taken. The landslide risk mapping may ease to take precautions and application of landfill rock may reduce water content of soil. Fly ash and Mine Waste Claystone thrown as waste in Şırnak City were used with low density foam concrete. Waste mixture at certain proportions decreasing instead of cement used, fine aggregate instead of fly ash in specific proportions decreasing improved mechanical strength and porosity. Hence landslide hazardous area could be safer for urban living.

**Keywords:** *foam concrete, landslide, stability, lightweight aggregate*

### Introduction

Especially in developing countries, according to the topology of land use in mountainous areas and improper land use increases the likelihood of developing landslide. Landslide risk areas of the physical environment change and sustainability in terms of land use cannot be evaluated (Anbalagan, 1992).

Generally landslide hazardous area can be described as “present in a horizontal or land masses which make an angle with the surface” (Cernica, 1995; Das, 1994). Slope stability and landslide problem dealing with the ground have been closely worked for many years by geotechnical engineers. For the reason of this interest, the deep disorder of land masses and slope stability, flood, are known as natural disasters such as hurricanes, similar to lead to serious loss of life and property (Anderson and Richards, 1982).

Parallel to the increase of population growth there is a great need for the fields remaining in long natural slopes. In those fields people requires some excavation, drainage conditions change for

urban constructions, such as removing vegetation interventions, which can lose natural balance. In addition, the natural land mass stability can be disrupted for the reasons such as heavy rains or earthquakes (Hök 1970; Hök 2013; Hök and Brad 1977).

Regarding earth created by the nature land slope geometry and design of the structures built on those land slopes, civil engineers are very interested in those issues. Increasing population and stability, and security, the technological development parallel to the housing needs proliferating ways on the high embankment, dams, large and deep excavations along with stability problems. Each year, causing heavy loss of life, property damage they create the millions of pounds in the world as you find landslides in Turkey is one of the most important geotechnical hazards.

Şırnak city province and the surrounding area were studied by geological mapping at 1/1000 scale and outcropping units of engineering geology, the unit soil properties were determined. Landslide hazardous area of the large-scale topographic maps provisionally was concerned the region's first landslide study. Soil engineering works promotes of construction distributions in the future of Şırnak city promoting winter tourism, one of the popular southeastern Anatolian land. Landslides and importance of civil constructions under threat were intended to draw attention to the urbanization of the area.

In order to minimize the landslide hazard, geological and geotechnical analysis of the land slopes were need to be done. In this study, in the area of south Şırnak province (Figure 1) 2-4 km circled from the center of the slopes S2 the was determined as landslide hazardous area due to some mass sliding occurred in the district. Geotechnical properties soil of four different locations was determined for examining the stability analysis. This project was carried out for urban use, which will open workspace and environment covering 7 km<sup>2</sup> area 1/10.000 scale engineering geological mapping of field and laboratory studies prepared as a result also the polar coordinate system using a field study with four slopes of the topographic



maps have been created.

### Geology of the Province of Şırnak

Southeastern Anatolian Region has tectonic structures and stratigraphy as containing fault system and especially tension cracks along the ground to the depths of the waters, geothermal energy fluids flow the deep formations. North-south direction across the region with the effect of compression of the earth's crust has been subjected to a stretching east-west direction, and the resulting

pebbles are associated with soil. Alluvium soil, muddy shale occurs in wide urban living area of Şırnak city, at the south side of the city as seen in Figure 1 extends to the study area. Field observations of the Miocene limestone and altered limestone were determined. Thickness is highly variable. Decrease in the slope of the land where a relatively small outcrop.

Southwestern calcareous ridges of the rocks in moderately degraded due to the decomposition of the rock into the significant advances and large parts of the resistance is more rock ratio between



Figure 1. Satellite image of the study area and the slopes.

tension cracks along the asthenosphere have risen from the olivine basalt magma.

Alluvium, altered limestone in the recent study area of the province of Şırnak (Figure 2) is splitted due to the alluvial deposits of the neighborhood. With angular gravels in this area very well rounded

50-90% were different. The cracks on the surface of the rocks are dominated by brown and blackish color. In the study area section (Figure 2) extending along the valley portion moderately differentiated, highly dissociated and is seen as a gateway to cut completely dissociated. In those regions, the

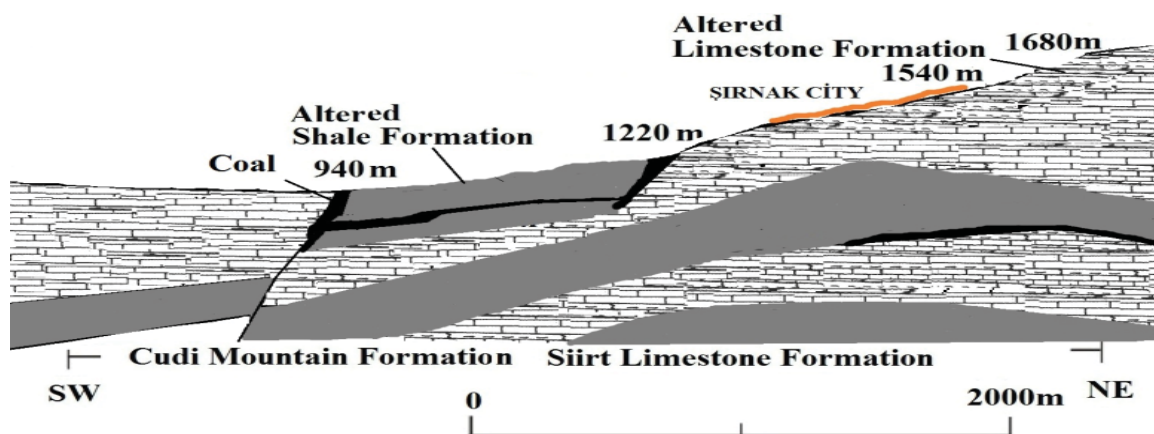


Figure 2. Geologic Cross-section of the Urban province of Şırnak.

separated segments of the shale are observed.

A high slope in the study area to the south of the city is basely urban located. Coarse sand with grain size varies from coarse gravel. Sorting and grading of unseen alluvial fill thickness varies between 10-35 m. In high slope massive fills, active and potential hazardous landslide areas were determined over a detailed examination.

### Geotechnical Properties

Landslide areas of outcropping ground experiments conducted to determine the geotechnical characteristics of the Turkish Standards (TS 1900) and American Standards (ASTM 3080) is based soils of landslide hazardous areas where the representative contents of drilling logs were taken in the rectangular field as seen from Figure 1. Regarding the logs of wells of D58m, D135m in 2003, D60m, D574m wells, mechanical properties of soils are given in Table 1.

In this zone in the area of fine-grained portions of alluvium samples were taken from slopes as undisturbed and disturbed. In the experiments conducted on samples disturbed grain distribution curve, unit weight and consistency limit grain sizes were obtained.

With the help of Shear tests on undisturbed samples the effective cohesion ( $c'$ ) and effective shear resistance angle ( $\phi^\circ$ ) belonging to was found. The Cutting box of undisturbed soil samples taken in the TS 1901 is used with respect to standards. Also when carrying out this experiment the bulk density of the material, and the void ratio was determined compression amount. Plastic and liquid limit of the results obtained in the experiments for each sample are given in Table 1. According to the classification of the soils in S1 and S2 landslide hazardous areas occurred in less plastic and non plastic group, The soils of S2 and S3 of the landslide hazardous areas was determined that the same assessment less plastic.

Prepared landfills compression strength for the slopes in the area is also shown in Figure 3. This S1 slope stability in terms of active and potential areas of landfill on the surface resulted landslide eliminated construction and structure life recognized.

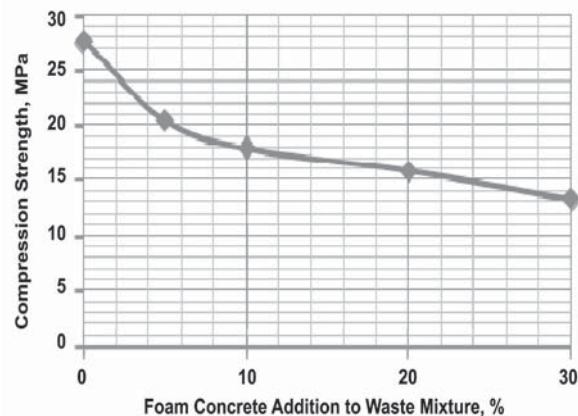
According to studies of landfill of landslide were deposited in and around the area in which there is relative movement is designated as the active landslide area.

**Table 1.** Properties Soil Formation in Şirnak City.

Spec No	S1	S2	S3	S4
level (m)	1225	1221	1233	1227
Wopt,%	15,9	13,7	10,8	11,4
$c'$ (kg/cm <sup>2</sup> )	0,12	0,49	0,53	0,25
$\phi'$	12,5	22,5	21	20
Li(%)	26	15	28	17
Pi(%)	19	11	18	22
Ip (%)	10	9	8	12
$\gamma_s$ g/cm <sup>3</sup>	2,4	2,5	2,4	2,3
$\gamma_n$ g/cm <sup>3</sup>	1,65	1,6	1,78	1,6
$\gamma_d$ g/cm <sup>3</sup>	1,82	1,76	1,9	1,7
$\gamma_s$ g/cm <sup>3</sup>	2,02	1,84	2,0	1,8
Spec. no	S11	S22	S31	S41
$\gamma_s$ max g/cm <sup>3</sup>	1,68	1,67	2,05	1,90
$w_{opt}$ %	15,9	15,8	12,3	13,0
Permeability (k) (cm/s)	$5,6 \cdot 10^{-4}$	$3,8 \cdot 10^{-4}$	$3,0 \cdot 10^{-4}$	$5,6 \cdot 10^{-4}$

Relative movements are determined by making use of tension cracks on the surface.

When potential landslide areas around the active site of where stress cracking moment of relative motion can be observed, but corresponds to the field . In the study area topographic cross-sections taken from four separate slopes.



**Figure 3.** Compression strength of Foam Concrete Landfill on hazardous landslide area.

Belonging to the limit equilibrium factor of safety of slopes drawn in accordance with different sliding surfaces for the Bishop in GEO5, with the circular shift diagram Janbu and Fellenius methods showed over 1.3 safety factors. When seen in the field of tension cracks are known to occur in movement. In the case of foam concrete landfill, the intrinsic parameters of the sliding surface will appear smaller than those found in

laboratories in other words; it is clear that lasting value closer to 1.5 and 1.8. From this point of view, landfill horizontal column improved water level under sliding surfaces and the safety factor values reached over 1.5 and 1.8.

### Conclusions

Soil samples performed on the laboratory test results in the slope material permeable that the cohesion value of 0.2-0.7 kN, angle of internal friction of the 17.5-22.4° varied between unified soil classification according to the slope of the material usually SP, SW and SC group than the floors are collected. Stability analysis performed in the light of this information, S1, S2 and S4 is unstable hillsides, The S3 slope was concluded that the stable.

As a result of the terrain views, especially in the months of May and June by the melting snow stream flow increase seen in the severe erosion of the slope formed on the heel and this effect was determined to have a negative impact on slope stability. Landfill material, or rock material or stream should be investigated and varied in water discharge effect.

Rocky slope stability analysis done for the ground, rocky land, which had been dissociated from the floor to act differently, next to the sliding movement of the rock fall incidents, such as being able to vary hazardous parameters. In the rocky terrain of slope stability analysis in order to solve problems with similar method of landfill may not be sufficient, however as a specially crafted construction works should be used.

For those reasons, geotechnical engineer can use virtual any classical slope stability programs, rock slope stability calculations in order to do construction safety.

Plants, rain water infiltration into the mass simplifies and reduces water runoff and cause land sliding. This is an obstacle to the erosion of the mass. Reaching deep into the roots of the plants roots improves the mechanical balance of the masses.

Landfill porosity thus reduces the retaining force which stabilizes the slopes. For this reason, the vegetation of landslide hazardous areas is preventive enrichment an important parameter in the region . However, up to 30 m depth to the sliding surfaces of vegetation stability effect will be minimal. Weathering of rocks varies greatly in to undergo, to the weakening of the bond between

grains and leads to total extinction. In the study area weakened by weathering rocks are easily eroded and slope angle of inclination of the slope is changing with height. Dissociation observed in rocks in the study area also offers a negative contribution to stability problems.

As a result of work performed in the field of geotechnical analysis, the future would not be expected of a very large landslide has been concluded. This result, however, urban areas and the urban development area for the possibility of landslide hazards.

### Symbols

$c'$  kg/cm<sup>2</sup> : Effective Cohesion

$c$  kg/cm<sup>2</sup> : Cohesion

$\phi'$  : Effective angle of internal friction

$\phi$  : angle of internal friction

$t$  kg/cm<sup>2</sup> : Shear stress

$\sigma$  kg/cm<sup>2</sup> : Normal stress

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## STABILITY ANALYSIS OF LANDSLIDE HAZARDOUS AREA IN WEST ŞIRNAK

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### Abstract

At West Şırnak urban area on alluvium and dissociated shale and marly limestone hazardly threat the plains settled common highly populated part of the city within the whole settlement area. Mass piles of waste in accordance with environmental design and reclamation are required. Therefore, the geotechnical properties of the current stack, static attributes are discussed in this study. Solid waste landfills earthquake, flood or other hazard according to static and dynamic stability analysis is required in the enterprise. Therefore, province of Şırnak, near the coal mine waste piles must be considered environmentally sensitive. Active and potential landslide areas were examined. Main aspects of geotechnical stability analyzes were performed. Effective angle of internal friction ( $\phi$  '°) 17-22.5°, effective cohesion ( $c'$ ) from 0.05 to 0.18 kg/cm<sup>2</sup> In cross-sections of the slope, the possibilities in the trial slip surfaces were examined. Bulk material designated geotechnical properties with the methods of Fellenius, Spencer, Bishop, Janbu and Hoek-Bray method through a safety factor determined and calculated. According to those values, at west Şırnak area the slopes under the stability analysis were unstable conditions and has been found to need soil stabilization.

**Key words:** *Stability Analysis, Landslide, Hazardous Area, West Şırnak*

### Introduction

The main factors that triggered mass movements as well as gravity, floating material, geology, rainfall, erosion, earthquakes and vegetation can be listed as deprivation. And determining the danger of slipping may occur in the future can be estimated limits of dynamic tension and equilibrium analysis gives accurate results (Hoek and Bray, 1977; Lamp and Whitman, 1969).

Heavy rainfall, seismic upheavals of underground water level, erosion, climate, decomposition

processes, topography, slope failures in critical areas of the trigger creates a natural parameters. These effects increase the shear stress or shear strength of the material decreases the slope (Bishop 1955; Hoek 1970). Growing urbanization brought on the slopes, housing, commerce, social areas, such as the creation and implementation of urban infrastructure operations use may impair the stability of the implementation.

Someone, landslides, as in the past the same geological, geomorphological, hydrological, climatic conditions are formed. Another is that, types and properties of landslides will be the same. Therefore, the mechanism of history and know the characteristics of landslides in the future, as in neighboring areas or similar areas of geotechnical may develop information constitutes an important basis for assessing landslide. Especially in developing countries, according to the topology of land use in mountainous areas and improper land use increases the likelihood of developing landslide. For this reason, the physical environment related fields, change and sustainability in terms of efficiency cannot be provided (Bishop 1955; Hoek 1970).

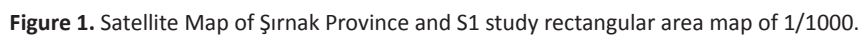
Şırnak province and surrounding areas by making geological maps, surface engineering, geotechnical properties of the units have been identified (Anonymous 2012). The slope of the large-scale geological map of topographic maps on the processing work in the region has been one of the first landslides. Determining the engineering properties of the slopes, the future importance in the construction of municipal development plans and geotechnical field is intended to draw attention to critical.

Possible difficulty in static piles for slope stability criteria were examined in landfills. Mass of the examined parameters affecting slope stability, possible anomalous situations and risk analysis are indicated on the map. Shale piles of coal waste will not threaten the environment and will not embarrass the company built in size is recommended. Static characterization of material properties and seismic

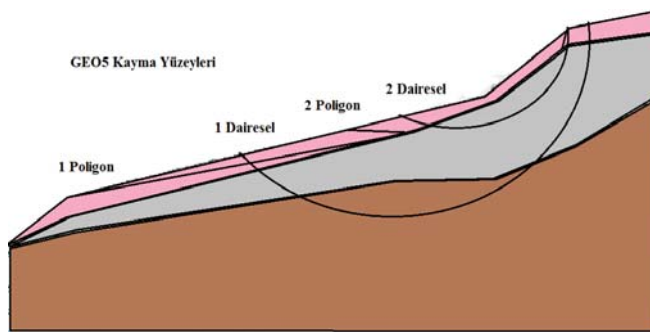


region's geological maps. Lithostratigraphic units in the study area from older to younger Mardin Volcanics (Upper Miocene), Old Alluvium (Quaternary), New Alluvium (Quaternary) and talus (Quaternary) have been recognized as. Volcanics, tuff, agglomerate consists of basaltic and andesitic. Spilitic make up a large portion of the study area basalt lavas in the study area show a cropped up.

In the study area (Fig. 1) to the south of the observed recent alluvial deposits shale outcrops



are gray marl. This section is generally covered by silty soil while some segments are composed of sandy and clayey zones. By the Province Bureau of Şırnak upto 35 m in the drilling alluvium is determined to continue. Rubble slopes are viewed in the area. S1 and S2 mass creeping to the south is hazardly located in the urban living site. Grain size varies from fine clay and coarse sand. Sorting and grading of unseen debris thickness varies between 10 to 35 cm.



**Figure 3.** S1 possible glide slope sections of the study area, representative slip surfaces.

Samples outcropping in the area to determine the geotechnical properties of soils in the experiments tested in 2012 with Turkish Standards (TSE, 1987) and American Standards (ASTM 3080) are considered. The presentation of the sliding content is illustrated in Fig. 3, S1, S2 of the field-study were conducted in the standards of 2013 (ASTM, 1990).

In the study area (Fig. 3) fine-grained parts of this zone of the talus in undisturbed and disturbed samples were taken. In experiments conducted on samples disturbed grain distribution curve, unit weight and consistency limits grain was obtained.

Undisturbed shear tests on samples with the help of the examples belonging to the effective cohesion ( $c'$ ) and effective shear resistance angle ( $\phi^\circ$ ) was found.

Cutting Box Undisturbed soil samples used in experiments according to TS has been 1900.1901.

Also when carrying out this experiment the bulk density of the material, and the void ratio was determined compression amount.

Soil water content ratio of the clay will be affected significantly. When evaluated according to the percentage of clay in the ground floor of the property shows examples non cohesive or less cohesive.

Partially water-saturated soils in undrained conditions as determined by testing the breaking strength envelope after a point is not parallel to the axis normal voltage and ground and acts as cohesive as well as internal friction. Total voltage analysis method, and the criterion to cover the floating mass is divided into a certain number of vertical slices to investigate stability. Bishop method, as in all these methods the problem of stability of  $t'$  as the initial shift have a posture as if they were received and accepted

and limit equilibrium balance equations taper is removed. Bishop is the total stress analysis with effective stress instead. This method of Taylor and brought Fellenius of the methods are older (Anonymous 2013, Anonymous 2009). Method JanBe; this method, whether or not circular can be used for any type of sliding surface (Vaneckov et al. 2011, Prusiner 2009). Slope stability analysis in the homogeneous excavation and filling that occurring in the landslide, with non-circular more general types of shifts stability analysis for the inter-slice forces, which takes into consideration is a method (Prusa 2009, Anbalag, 1992).

### S1W-Soil Slope Analysis

Sliding mass thickness varies from 11 to 20 m. Regarding the investigation of the slope the ground water level was observed at the base of 15 m. The S1W on the slope stability calculations made in the  $c' = 0.09 \text{ kg/cm}^2$ ,  $\phi' = 22^\circ$ ,  $\gamma_{\text{nat}} = 1.97 \text{ g/cm}^3$ ,  $\gamma_{\text{sat}} = 2.27 \text{ g/cm}^3$  and slip safety factor on the surface as shown in figure 5. According to the pore parameter analysis, the value of the safety factor is taken as 1.5. Even risk analyzing in figure 5 for hazard limit coefficient is taken as 1.5. Polygon 1 and 2 of the sliding surface can be easily seen to be unstable. If the sliding surfaces 3 and 4 are made according to  $\gamma_{\text{dry}}$  or is stable above the limit values, according to  $\gamma_{\text{nat}}$  analyzed appears to be unstable.

During field studies in the observations on this slope on the edge of the creek water flow and

### Results and Discussions

As a result of the terrain views, especially in the months of May and June by the melting snow in the heel of the slope of the hill also seen an increase in flow that create severe erosion and this effect was determined to have an adverse effect on slope stability. S1W, S2W and S3W cross-section slopes are effectively stabilized in order to prevent this situation so that ground water cannot move the heel size of the stream or creek in the accumulation of rock material has to be the flowing mass.

West Şırnak City urban area also offers a negative contribution to stability problems.

As a result of work performed in the field of geotechnical analysis, the future should be considered a danger to very large heaps and the field should be determined according to the method

of reclamation. Also within the project study area will be opened due to urban use preventive methods to investigate the instability in the region and it is important to develop a separate.

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## HYDROGEOCHEMICAL DEVELOPMENT OF TIRANË-ISHËM GRAVELLY BASIN

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### Abstract

This paper presents the results of the hydrochemical study of 25 monitoring points located in Tiranë-Ishëm catchment basin. These monitoring points consist of 16 groundwater wells, 1 natural spring and a few other monitoring points “set” in the rivers of the study zone, such as Lana, Tirana, Terkuza, Zeza, Gjola and Ishmi Rivers. Water sampling is carried out during wet and dry periods. Groundwater of Tiranë-Ishëm gravelly basin represents a rich water-bearing layer with a flowing direction from southeast to northwest. In general, the water-bearing layer is overlain by an impermeable clayey layer. A good hydraulic connection exists between groundwater and surface waters. This connection is distinguished by the gravel outcrop at the lower and middle part of Tirana, Tërkuza, Zeza and Droja Rivers. Groundwater comes in direct contact with surface water in specific locations so-called “hydrogeological windows” that supply the river, especially during the dry period.

The chemical composition of groundwater is developed from recharge zone towards the drainage zone, near the Adriatic Sea. The hydro-chemical parameters such as Total Mineralization, Total Dissolved Solid and Total Hardness increase and decrease periodically along the flowing direction. The general trends of Total Mineralization and Total Dissolved Solid parameters have the tendency to increase, reaching values above 1000 mg/l.

Furthermore, the phenomenon of the natural softening of groundwater occurs. Thus, the values of Total Hardness vary from 30dH in the recharge zone to less than 10dH in the drainage zone of the water-bearing layer. The water types are classified as bicarbonate-calcium, bicarbonate-calcium-magnesium, bicarbonate-magnesium-calcium, bicarbonate-chlorine-sodium and chlorine-sodium. The formation of water-types depends on the origin, source of feeding, the relationship between groundwater and surface water and water-rock interaction. The latter is expressed by chemical reactions which have occurred in the saturated zone. So, the main responsible reactions are the dissolution and precipitation of calcite, dolomite and gypsum minerals in the water. This is reflected in the features of hydro-geochemical parameters of the groundwater. Hence, the content of dissolved minerals and calcite, dolomite, gypsum saturation indices of the groundwater (calculated by AquaChem and PhreeqC softwares) are the main indexes of the geochemical processes which affect the natural groundwater development.

**Key words:** *hydro-geochemical development, water-type species, water-rock interaction, geochemical processes, saturation indexes*



## ARSENIC IN GROUNDWATER AND GEOTHERMAL WATER IN THE GREAT PLAIN, HUNGARY

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### Abstract

Environmental issues related to arsenic have been recognized and documented in numerous countries across the world, intensifying the related geochemical researches. Many authors have reported the presence of arsenic in the porewater of lacustrine sediments, in estuarine, coastal, as well as geothermal and groundwaters. Hydrogeochemical investigations worldwide are mainly focused on the processes controlling the arsenic mobility in subsurface water. The behaviour of dissolved arsenic is closely tied to that of iron and organic matter. During the weathering of As-containing minerals, the arsenic enters the surficial cycle mainly as soluble arsenate in which arsenic is present in pentavalent state. This form is quite mobile: although it coprecipitates with ferric oxide, in a reducing environment arsenic is released. In the present work, chemistry of the subsurface water is evaluated with special attention to the arsenic content from the near-surface down to 2500 m in the Great Plain, Hungary. The main objective is to describe the spatial distribution of arsenic and to reveal the relevant factors controlling its distribution.

The study area (about 22,000 km<sup>2</sup>) is the Great Plain in Hungary, the central part of the Pannonian Basin filled with Neogene sediments. The Lake Pannon was formed at the beginning of the Late Miocene. Sedimentation occurred initially in deep and brackish, later in freshening and shoaling water. The subsidence over the entire region was accompanied by rapid sedimentation leading to a complete filling-up by the end of the Pliocene. The thickness of the basin infill varies from several hundred to several thousand (up to 7000) meters. In the Pliocene, tectonic inversion and uplift became significant establishing conditions for meteoric infiltration.

During the Quaternary, the subsidence rate, however, still increased in the central part of the basin while uplift continued in the flanks. The Pliocene and the Quaternary are represented by variegated lacustrine, fluvial and terrestrial sequences.

Spatial variability of the dissolved components suggests that subsurface water in the study area consists of distinct water bodies (coherent units of water with specific origin and/or evolution), a few of them being flow systems (water bodies with recharge and discharge areas). Within the water bodies the chemical and isotopic composition of water is influenced by its origin, by the type of rocks accommodating the water, and by the hydrogeological feature of the area. Correlations between the concentrations of arsenic and other chemical parameters were studied within the water bodies. It was established that lithologic source, geochemical processes and mixing of different water flow systems are the main factors controlling the arsenic in subsurface water. The highest concentrations of arsenic are found in the groundwater originating from alluvial sediments. In geothermal water, independently of its origin, the maximum concentrations of arsenic are much lower. The adsorption model on ferric hydroxides seems to be consistent with the arsenic distribution.

## AN IMPACT OF VOLCANISM ON ACCUMULATION OF BROWN COALS IN THE TRANS-CARPATHIAN COAL SUB-BASIN

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### Abstract

The Trans-Carpathian coal basin is located in a southern and southwestern part of Zakarpattya Oblast, within the Trans-Carpathian sub-basin (Chop-Mukacheve and Solotvino depressions). The sediments of the Middle Sarmatian, Pannonian and Levantian stages are coal-bearing. The majority of coal deposits and manifestations are confined to sediments of the Upper Pliocene Ilnitska suite which is extended along southern and western flanks of the Vygorlat-Guta volcanic ridge. Brown coal of the Trans-Carpathian coal basin is of low thermal transformation rank.

The onset of coal rock massifs formation of the Trans-Carpathian region is closely connected with the formation of volcanic rocks composing the Beregovo hills and Kosino-Zapson heights. Volcanic processes in this area have begun at the end of the Tortonian or the beginning of Sarmatian.. It is not excluded that the accumulation of volcanic products occurred in several stages and has ended in Early Sarmatian. During Middle Sarmatian active epochs in the post-volcanic activity along with insignificant incidental volcanic activity were signaled. The sediments contain small coal lenses of low quality coal occurring mainly in the marly sequence and is enriched by rare metals. Tuff and tuffite beds are characteristic for this formation.

At the end of Middle Sarmatian, the volcanic activity was slightly intensified, fact proved by the occurrence of tuffaceous rocks on the bottom of coal seams. The alternation of volcanic events and relative quiescence epochs is evidenced by the presences of tuffs and marls in the coal rock massifs. It is necessary to notice that the coal members which occur within the clays do not contain rare earth elements or contain them in insignificant quantities. The volcanic activity has stopped at the end Middle Sarmatian. The minor subsidence of the Trans-Carpathian sub-basin has started in Pannonian.

The composition of the Pannonian sediments is rather monotonous and represented by alternation of clays, sandstones and tuffs. Thick coal lenses within the Pannonian sequence have limited spatial development. The total thickness of the Pannonian sequence in the Chop-Mukacheve depression does not exceed 150 m.

In the Trans-Carpathian sub-basin, the Pliocene sedimentary rocks of the Levantian stage occur with unconformity only in the Chop-Mukacheve depression. The even-aged Gutinska and Ilnitska suites are recognized here.

The Gutinska suite is represented by liparites and tuffs, andesitic basalts and basalts. These rocks compose the Vygorlat-Guta volcanic ridge. Various metasomatic, igneous and intrusive rocks are widely developed within the ridge. The Ilnitsky suite consists of sandy-argillaceous formations containing seams and layers of brown coal. Almost all commercial brown coal fields and numerous coal manifestations in the Trans-Carpathian region are confined to this suite. Among the rocks of the Ilnitska suite there are tuff beds and lava flows as well as alternation of sedimentary and volcanic formations in the vicinity of the Vygorlat-Guta ridge.

It is necessary to notice that volcanic and post-volcanic processes had a great influence on the formation and accumulation of coals in the Trans-Carpathian sub-basin. The influence of tectonomagmatic activation onto processes of biogenic sedimentation and lithogenesis is emphasized in this region.

Processes of peat sedimentation and coal formation occurring in different geological structures are characterized by specific modes of the tectonosphere and biosphere which control the pace, intensity and power of these processes. Presence of contemporaneous carbonate formations spatially close to volcanic (tectonomagmatic) areas points out on their paragenetic relationships.

## ENHANCED OIL RECOVERY AND CO<sub>2</sub> SEQUESTRATION IN THE GEOLOGICAL PAST – A CASE HISTORY FROM THE DANUBE BASIN, HUNGARY

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### Abstract

The well Mihályi-1, drilled in 1933 in the southern Hungarian part of the Danube Basin, produced almost pure CO<sub>2</sub>, accompanied by some percents of HC-gas and N<sub>2</sub> and traces of oil. In spite of the presence of mature oil-prone source rocks and promising structures, commercial oil accumulations have not been discovered in the basin during the 80 years of further exploration. On the other hand, several CO<sub>2</sub> fields and some HC-gas fields rich in N<sub>2</sub> have been found in the basin, in Hungary as well as in Slovakia.

Here we intend to explain this intriguing discrepancy by a multidisciplinary study of the neighbouring Mihályi and Répcelak multi-stacked fields, containing 7 and 5.5 Bm<sup>3</sup> of CO<sub>2</sub>, respectively.

The bulk of the reserves is contained by clastic reservoirs deposited in the Pannonian Lake between 10 to 8 Ma. The isotopic composition of the accompanying helium (R/Ra ranges between 1.7 to 4) shows that the CO<sub>2</sub> was sourced by degassing of mantle-derived magmas. These latters likely are the products of the basaltic magmatism active in the basin between 5 to 4.2 Ma. Basin modelling suggests that the Middle Miocene source rocks entered the oil window 9-8 Ma ago. Hence the oil expelled was able to enter the reservoirs before the liberation of the magmatic CO<sub>2</sub>.

We think the later arriving CO<sub>2</sub> replaced the bulk of the oil; the traces accompanying the CO<sub>2</sub> production from several reservoirs are considered as remnants of the naturally “recovered” oil. According to the methane  $\delta^{13}\text{C}$  (-41.5 to -46.1 ‰) and the wetness index (0.04 to 0.1), the HC-gases present in small amounts represent oil-associated gases partitioned into the CO<sub>2</sub> during replacement of the oil. On the basis of biomarkers, the oils have been generated by two distinct source rocks, deposited in normal marine and in anoxic settings, respectively. They have been generated during early maturation.

The CO<sub>2</sub> reacted with the mineral matrix of the reservoirs resulting in the breakdown of certain mineral phases (i.e., plagioclase) and their replacement by crystallizing dawsonite.

The absence of commercial oil fields in the Danube Basin is at least partly explained by the replacement of the oil by the later arriving CO<sub>2</sub>, produced by the basin wide basaltic magmatism.

## ALTERATION OF ZIRCON FROM IGRALISHTE GRANITE PLUTON, SOUTHWESTERN BULGARIA: PRELIMINARY INVESTIGATION

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### Abstract

At least four types of alteration were identified for zircon from the Igralishte granite pluton (~243 Ma), Ograzhden Mountain: (i) dissolution and replacement by other minerals (apatite, potassium feldspar, allanite, quartz); (ii) recrystallization; (iii) metamictization; (iv) chemical alteration of radiation-damaged parts of the crystal accompanied by depletion in Si and Zr and enrichment in U, Th, Y, Ca, Al, Fe. It is suggested that the processes (i) and (ii) are caused by high-temperature postmagmatic potassium and sodium metasomatism, while the process (iv) is induced by later tectonic and hydrothermal overprint (~36 Ma) related to Paleogene volcanism in the region.

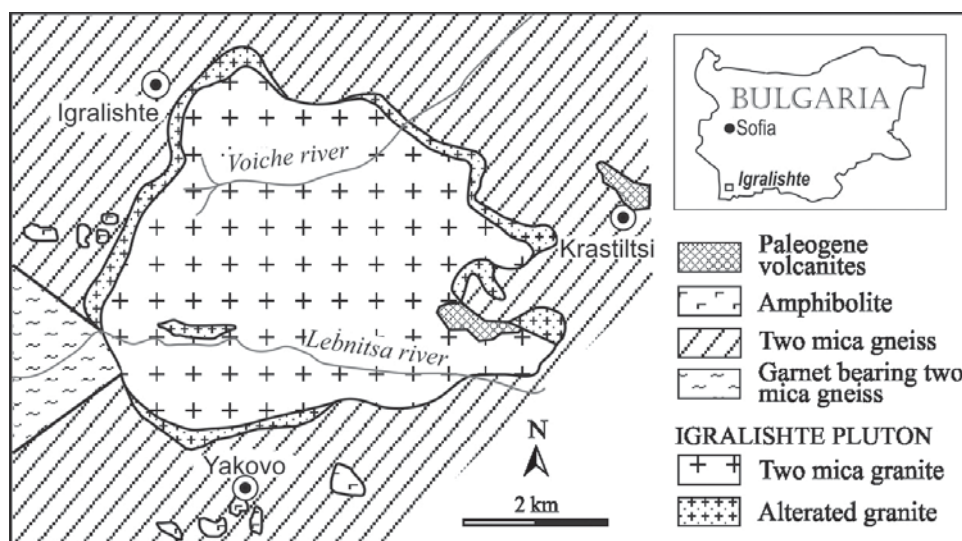
**Key words:** zircon, metamictization, hydrothermal alteration

### Introduction

Metamictization and fluid mediated alteration of zircon ( $\text{ZrSiO}_4$ ) was an extensively discussed problem over the past 25 years, mainly in view of (i) wide application of the mineral in geochronology and geochemistry, and (ii) high potential of its structure for waste actinides immobilization (Murakami et al. 1991; Geisler et al. 2007; Nasdala

et al. 2009). It is generally accepted that the metamictization of zircon causes essential change in its chemical and physical properties and makes it more prone to alteration, and the final state of the mineral is resulted from a complex combination/competition of accumulation of radioactively-induced damage, its thermal annealing and re-equilibration of the mineral in fluid media.

In the present preliminary work, the authors set a goal to establish the types of alteration of zircon in the Igralishte granite (Southwestern Bulgaria) and to make an attempt to correlate them with definite geological events and conditions. The Igralishte pluton is intruded in the Ograzhden block of the Serbo-Macedonian massif (Fig. 1). It is composed of two-mica granites belonging to the calcium-alkaline and high-calcium-alkaline series. The granite is dated at  $243.28 \pm 0.84$  Ma by concordant zircons (ID-TIMS data) and by the “*in-situ*” LA-ICP-MS and EPMA monazite analyses (Peytcheva et al. 2009). The most significant alterations of the pluton rocks are caused by postmagmatic high-temperature alkaline (K and Na) metasomatism. Besides a tectonic and hydrothermal overprint at  $36.36 \pm 0.56$  Ma is recognized using Rb-Sr analysis of whole rock and biotite (Peytcheva et al. 2009).



**Figure 1.** Schematic geological map of the region of Igralishte granite pluton in Ograzhden Mountain (according to Ignatovski (1970) with corrections by the authors).



## Material and methods

Crystals of zircon manually picked from the heavy fraction of granite samples of the Igralishte pluton, incorporated into epoxy resin pellet and polished according to a preparation protocol for EBSD (Nowell et al., 2005) were used for the present study. Optical microscopy, scanning electron microscopy-SEM (imaging in backscattered electrons - BSE, secondary electrons - SE, cathode luminescence-CL), energy dispersive X-ray (EDX) microanalyses were used for characterization of chemical and phase inhomogeneity of zircon crystals. The degree of metamictization of the crystals was examined by electron backscatter diffraction (EBSD) technique (Tarasov et al. 2013). All analytical investigations were carried out on a scanning electron microscope ZEISS SEM EVO 25LS with EDAX Trident analysis system operated at 20 kV for SEM investigation and EBSD examination and at 15 kV – for EDX microanalyses with standards. The samples for investigation were carefully coated with thin layer of carbon.

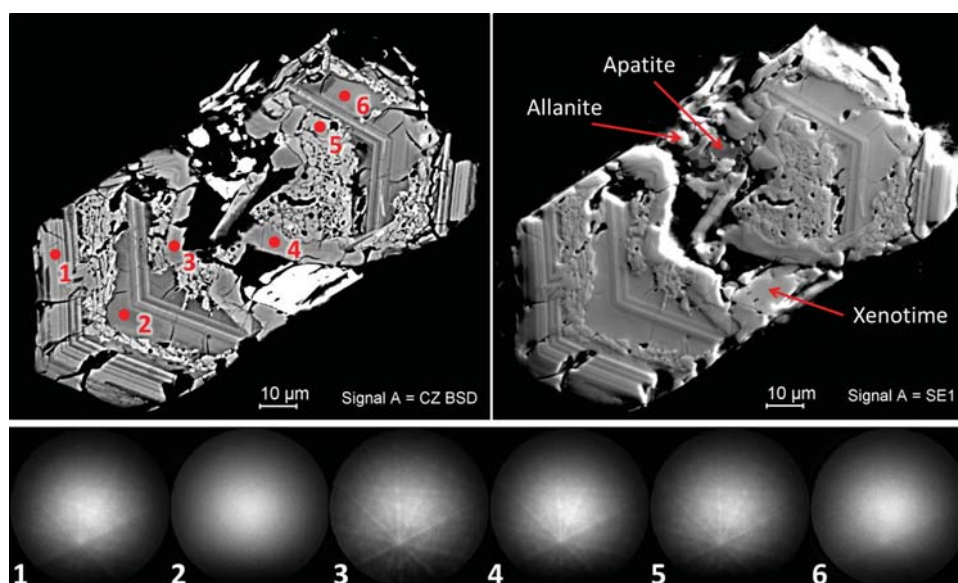
## Results and discussion

The studied zircons are represented by elongated crystals with well-developed prismatic and pyramid faces and size ranged from 100 to 150  $\mu\text{m}$ , rarely to 200  $\mu\text{m}$  (Fig. 2). Following features of internal anatomy of zircon crystals were established during the present investigation.

– All crystals show well pronounced growth zoning partially disturbed by secondary alteration and the presented mineral inclusions.

– The mineral inclusions are of several types: (a) primary magmatic inclusions formed slightly earlier or simultaneously with the zircon and presented mainly by apatite and rarely xenotime; some of the xenotime inclusions, as that shown in figure 2a and b, forms oriented intergrowths with zircon; (b) postmagmatic inclusions presented by quartz, potassium feldspar, apatite, biotite, allanite, iron oxide mineral; these minerals in fact occupy cavities in zircon formed due to partial dissolution of the mineral; (3) inclusions of uraninite and thorite formed due to recrystallization of primary U- and Th- rich zircon.

– The matrix of zircon crystals is presented by growth zones with variable brightness in BSE images (from light-grey to dark-grey signal) and different topography in SE images (Fig. 2a, b). Besides, there are a lot of swelling induced cracks typical for radiation damaged regions of zircon crystals. The observed picture is complicated by the presence of recrystallized zircon zones which look like as grained aggregates metasomatically replacing the region with radiation damaged structure. The recrystallized zircon zones have a distinct positive relief (Fig. 2b). All these data are indication for wide variation in chemical composition, physical properties and structural state of the studied zircon resulted from diverse processes suffered by the mineral.



**Figure 2.** Zircon crystal suffered (i) replacement by other minerals dissolution (allanite, apatite), (ii) recrystallization; (iii) metamictization; (iv) diffusion-controlled (?) chemical alteration of radiation-damaged parts of the crystal. (a) BSE image with indicated places examined by EDS and EBSD; (b) SE image; (c) EBSD patterns of the specified areas.

EDX analysis and EBSD examination of the all aforementioned zones of the mineral on example of a representative zircon crystal in figure 2a and b (light-grey zones - point 1, dark-grey zones - points 2 and 6, recrystallized zones - points 3, 4 and 5) show the following (Table 1 and Fig. 2c):

from the chemical alteration. The area with point 1 seems to be suitable for our calculation as this zone looks intact, there are no any clear indications for its hydrothermal alteration and the EDX analysis is appropriate. The accumulated alpha-decay dose calculated using equation of Holland

**Table 1.** EDS microanalysis of different parts of zircon (wt.%) (see figure 2).

Area	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	ThO <sub>2</sub>	UO <sub>2</sub>	CaO	FeO	Yb <sub>2</sub> O <sub>3</sub>	HfO <sub>2</sub>	Total
1	n.d.	32.80	n.d.	65.39	n.d.	1.03	n.d.	n.d.	n.d.	2.46	<b>101.68</b>
2	1.41	25.32	5.72	40.82*	0.48	6.76	1.41	0.83	0.96	2.43	<b>86.14</b>
3	n.d.	32.85	n.d.	65.72	n.d.	n.d.	n.d.	n.d.	n.d.	2.38	<b>100.95</b>
4	n.d.	32.77	n.d.	65.39	n.d.	0.50	n.d.	n.d.	n.d.	1.99	<b>100.65</b>
5	n.d.	32.57	n.d.	64.02	n.d.	0.54	n.d.	n.d.	n.d.	3.87	<b>101.01</b>
6	1.58	21.99	6.29	35.00*	0.43	6.30	1.08	1.03	n.d.	3.20	<b>76.89</b>

– EDX and EBSD data are well correlated with each other: the quality of the recorded EBSD patterns strongly depends on the content of U and Th, namely, the higher quality EBSD pattern evidencing good crystallinity of the mineral is recorded for U- and Th-poor zircon zones (points 3, 4, 5), and the low-quality pattern or even the pattern without any Kikuchi bands, evidencing strong structural disorder, is established for U- and Th-rich zones (points 2 and 6). The area with point 1 is characterized by intermediate characteristics.

– The dark-grey zones (points 2 and 6 –“dark BSE zircon”) seem to be the most altered part of the studied crystal being simultaneously strongly metamictized and chemically modified. The analyses of these zones show sum significantly below 100 wt.%. Besides this and the increased content of U, Th and Y, these zones contain such “non-formula elements” as Ca, Al, Fe which are considered as indicative for chemical alteration of metamictized zircon (Geisler et al. 2007; Nasdala et al. 2009). The chemical alteration of the studied zircon could be connected with the tectonic and hydrothermal overprint (to  $300 \pm 50^{\circ}\text{C}$ ) at  $36.36 \pm 0.56$  Ma according to Rb-Sr analysis of whole rock and biotite (Peytcheva et al. 2009). This thermal overprint can be related to the Paleogene volcanism in the region (Zagorchev and Dinkova 1991). To evaluate the readiness of the zircon for chemical alteration 36 Ma ago, we have to calculate the alpha-decay dose accumulated by the mineral between 243 and 36 Ma. The contents of U and Th found in the dark-light regions of zircon are not acceptable for this purpose as they significantly higher the contents of these elements in magmatic and metamorphic zircon, and are clearly resulted

and Gottfried (1955) (according to Murakami et al. 1991) is  $6.2 \cdot 10^{18}$  events/g. The obtained value corresponds at least to 60% amorphous component in the zircon (Nasdala et al. 2001). This means that the state of metamictization of zircon 36 Ma ago was sufficient the mineral to be sensitive to hydrothermal alteration and our suggestion on the connection of chemical alteration of zircon (dark-grey zones) with the Paleogene volcanism seems to be true. The reasons why the light-grey zone with point 1 in the studied zircon is preserved chemically unaltered can be seen in the position of recrystallized zircon (Fig. 2a, b) – the recrystallized zircon aggregates play role of screen preventing penetration of solution to the light-grey zone. The recrystallized zircon is poor in U and Th and therefore is stable during the hydrothermal event. These findings as well as the frequent association of the recrystallized zircon with potassium feldspar allow one to assume that the observed zircon recrystallization is caused by high-temperature postamagmatic alkaline metasomatism.

## Conclusion

During the present study we obtained preliminary data on alteration of zircon from the the Igralishte granite ~243 Ma, Ograzhden mountain, Southwestern Bulgaria. At least four types of alteration were identified in the studied zircon crystals: (i) dissolution and replacement by other minerals (apatite, potassium feldspar, allanite, quartz); (ii) recrystallization; (iii) metamictization; (iv) chemical alteration of radiation-damaged zones accompanied by depletion in Si and Zr and enrichment in U, Th, Y, Ca, Al, Fe. It is suggested

that the processes (i) and (ii) are caused by high-temperature postamagmatic potassium and sodium metasomatism, while the process (iv) is induced by later tectonic and hydrothermal overprint (~36 Ma) related to Paleogene volcanism in the region.

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## GEOCHEMISTRY AND TECTONIC SIGNIFICANCE OF THE KÖSEDAĞ METAVOLCANIC ROCKS FROM THE SAKARYA ZONE, NORTHERN TURKEY

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### Abstract

A series of a variety of metamorphosed and deformed volcanic rocks crop out in the Central Pontides of Northern Turkey. These low-grade metavolcanic lithologies appear to be unconformably overlain by the Jurassic to Cretaceous limestones of the Sakarya microcontinent and overthrust by the metamorphic mélanges of the Intra Pontide Suture Belt. The metavolcanics have widely varying chemical compositions including basalts, andesites and dacites. The studied rocks are subdivided into two groups named Type 1 and Type 2 based on immobile trace element systematics. Both groups have subalkaline character and display variable enrichment in Th and LREE with respect to HFSE on N-MORB normalized diagrams. The REE patterns of the two groups are also similar. Some differences exist, however. While Type 2 samples exhibit depletion in Zr and Hf, Type 1 samples have strong negative P anomalies. Overall trace element systematics signal to arc-related magmatism.

**Key words:** Arc, Köseadağ metavolcanics, Northern Turkey, Sakarya Zone, Subduction

### Introduction

In Northern Turkey, a series of variably metamorphosed and deformed volcanic rocks are exposed in the central part of the Pontides between the Istanbul and Sakarya Terranes. These low-grade metavolcanic rocks are associated with metasediments along an east-west trending belt of approximately 100 km long and 10 km wide, parallel to the North Anatolian Fault. Preliminary observations demonstrate that these metamorphics are disconformably overlain by the Jurassic to Cretaceous limestones of the Sakarya microcontinent and overthrust by the metamorphic mélanges of the Intra Pontide Suture Belt. In this study we present for the first time the geochemical characteristics of the metavolcanic assemblage and try to shed light on their petrogenetic history.

### Petrography

On the basis of petrography, the studied metavolcanic rocks can be classified as meta-basalts, meta-andesites and meta-dacites. Meta-basalts are weakly foliated. Plagioclase, pyroxene and olivine make up the primary mineralogy and

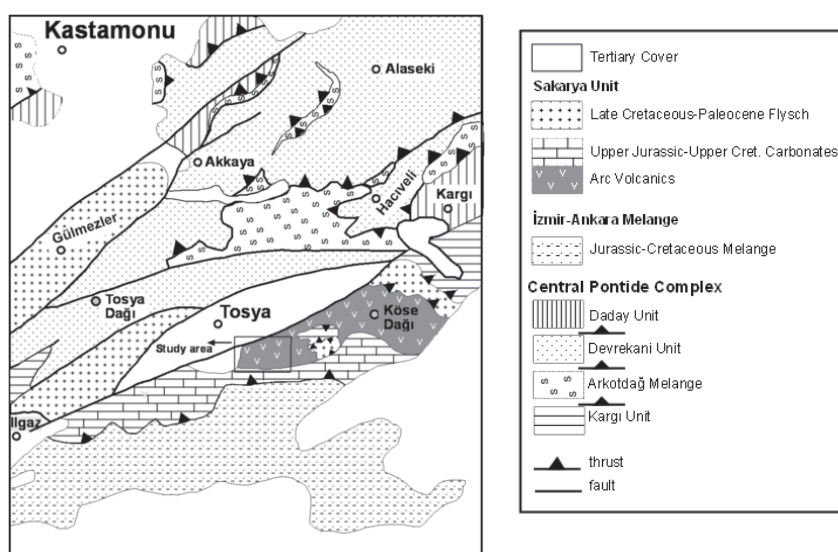
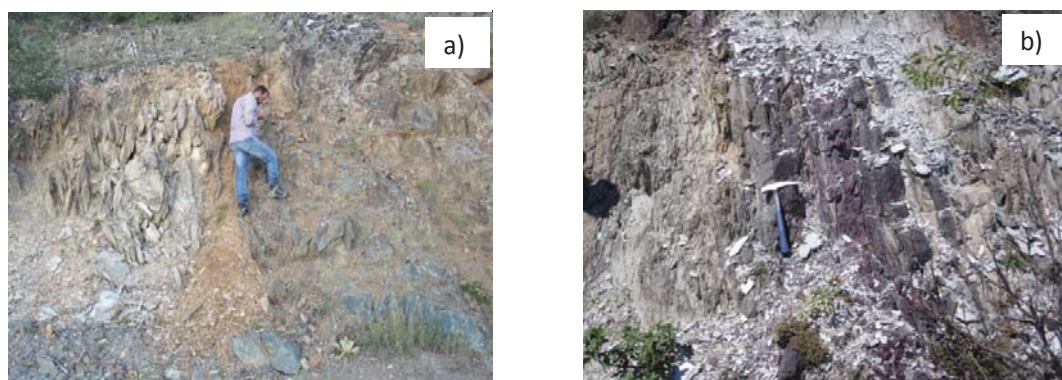


Figure 1. Simplified geological map showing the major structural units in the study area and its surroundings (modified from 1/1.250.000 scale geological map of MTA, 2012).



represent the major phenocryst phases which are embedded in a chloritized matrix. Epidote, chlorite and muscovite characterize the secondary mineral assemblage in this group. Meta-andesites contain corroded quartz and plagioclase phenocrysts and show glomeroporphyritic texture. Secondary minerals, such as muscovite, epidote and chlorite are found parallel to the foliation. Meta-dacites are also foliated and display blastomylonitic texture. Quartz, K-feldspar and plagioclase make up the phenocryst phases of meta-dacite. Furthermore, lenses and bands of meta-siltstone can be observed within the volcanic rocks.

heavy REE (HREE) on normal mid-ocean ridge basalt (N-MORB) normalized multi-element patterns ( $La/Nb=2.19-4.7$ ,  $Th/Yb=0.47-1.79$  for Type 1;  $La/Nb=2.92-5.93$ ,  $Th/Yb=0.07-1.45$  for Type 2). The presence of negative Nb anomaly is marked on both groups. REE patterns of the two groups are also similar. Despite these similarities, however, there appear to be some differences between the two groups. While Type 2 displays some degree of depletion in Zr and Hf, Type 1 is characterized by depletion in P. In addition, Type 1 displays greater enrichment in Th relative to Nb. ( $Th/Nb=0.66-1.44$  for Type 1;  $Th/Yb=0.17-1.93$  for Type 2).



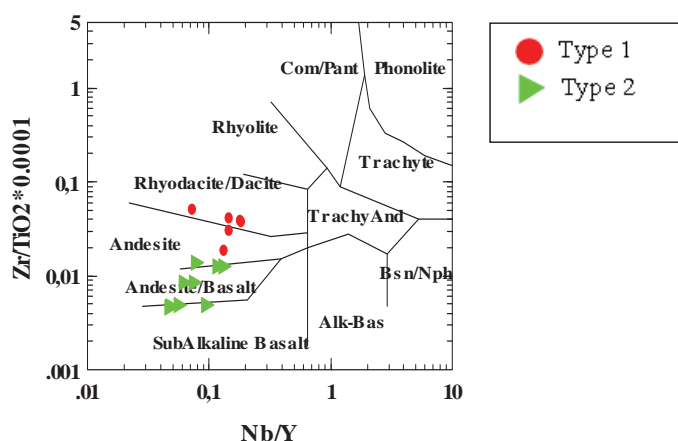
**Figure 2.** Field photographs of (a) felsic and mafic metavolcanics, (b) chert band interbedded with metavolcanic layers.

## Geochemistry

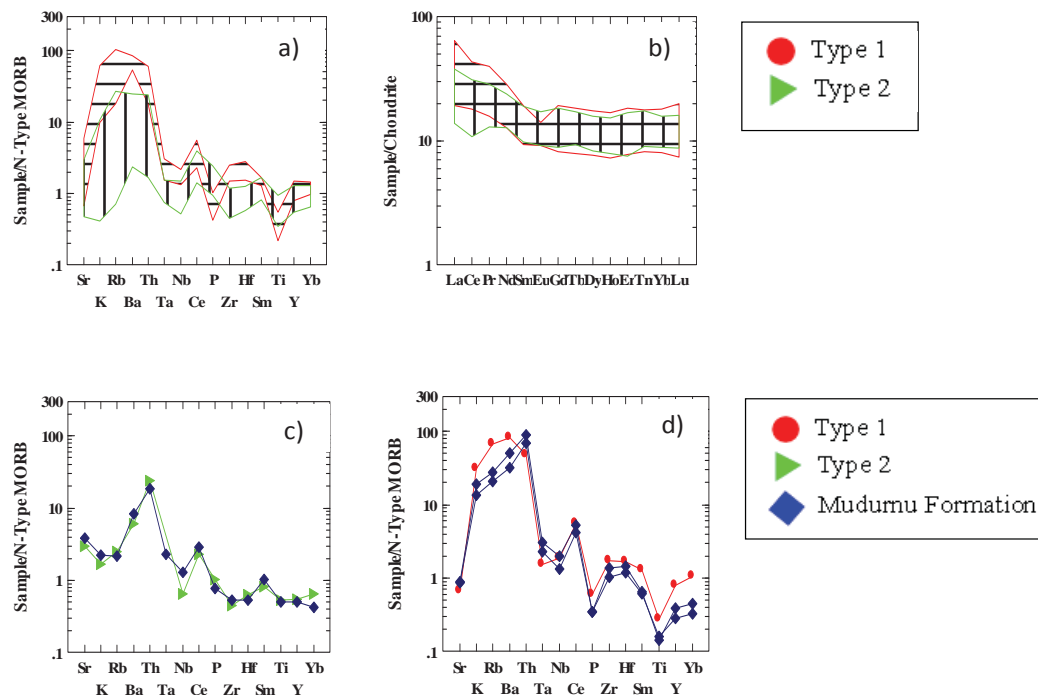
The studied samples display a wide range of chemical compositions, from mafic to felsic, including basalts, andesites, dacites. Based on immobile trace element systematics, two main groups are identified as Type 1 and Type 2. Both groups are of subalkaline affinity ( $Nb/Y=0.07-0.19$  for Type 1;  $Nb/Y=0.05-0.13$  for Type 2) and exhibit enrichment in Th and light rare earth elements (LREE) relative to high field strength elements (HFSE) (e.g. Nb, Zr, Hf and Ti) and

## Conclusion

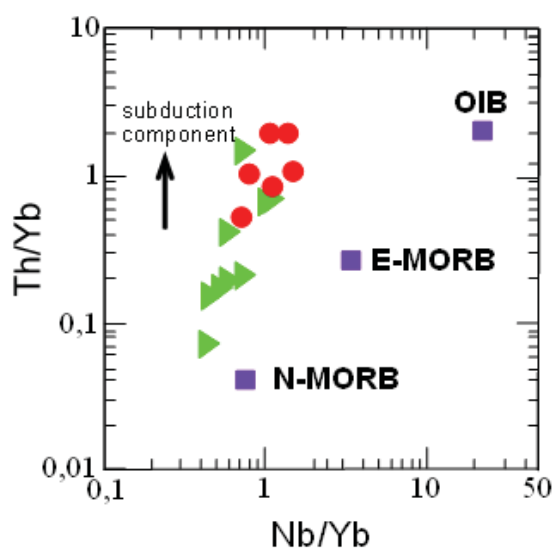
The trace element systematics of metavolcanics reveal arc-like characteristics, indicating involvement of subduction components in their petrogenesis. We therefore suggest that the metavolcanic rocks have formed above a subduction zone, possibly of oceanic origin. It is also noteworthy that although the studied samples differ from the Lower-Middle Jurassic Mudurnu volcanics in the Sakarya terrane in terms of



**Figure 3.** Chemical classification of the Kösedag Metavolcanics on the basis of immobile elements (after Winchester and Floyd, 1977).



**Figure 4.** *a)* Comparison of Type 1 and Type 2 metavolcanics based on N-MORB normalized trace element patterns *b)* Chondrite normalized REE patterns of Type 1 and Type 2 samples. *c)* Trace element patterns of the volcanics from the Mudurnu Formation (Genç and Tüysüz, 2010) and Type 2 metavolcanics. *d)* Trace element patterns of the felsic hypabyssal rocks from the Mudurnu Formation and Type 1 metavolcanics (Normalization values from Sun and Mc Donough 1989).



**Figure 5.** Variation of Nb/Yb against Th/Yb on the Köseadağ Metavolcanics (after Pearce and Peat, 1995). Compositions of N-MORB, E-MORB and OIB are from Sun and Mc Donough (1989).

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metamorphism, they exhibit similar geochemical features. If the age of the metavolcanics is confirmed by radiometric age data, the presence of a Jurassic subduction-related volcanism will be validated for the North Sakarya terrane.

## ZEOLITE BEARING TUFF IN THE VETUNICA DEPOSIT NORTHERN MARGINAL PART OF THE FAMOUS KRATOVO-ZLETOVO VOLCANIC AREA, EASTERN FYR OF MACEDONIA

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### Abstract

Studied zeolite-bearing tuff from the Vetunica deposit is localized in northern marginal parts of the well known Kratovo-Zletovo volcanic area (Republic of Macedonia). Zeolite bearing tuff occupies the shallowest parts of the Tertiary volcanic rocks complex in this area. The stilbite ( $\text{NaCa}_2\text{Al}_5\text{Si}_{13}\text{O}_{36} \cdot 14\text{H}_2\text{O}$ ) was determined within the aforementioned zeolite bearing tuff. In our detailed study we found out that in the Vetunica deposit stilbite is present with 27%. Also, cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for samples from the Vetunica deposits are in the range of 94–102 meq/100 g for CECs and 109–114 meq/100 g for AECs. All the values show that these tuffs could be very effective in a wide range of applications such as waste water ammonium removal, in animal nutritions, fertilizers, fish farming, additives to cement and others. Geochemical data illustrates high concentrations >30 ppm As, 1 g/t Ag, 70 g/t Pb, 17 g/t B etc., as representative elements for this volcanic area.

**Keywords:** *volcanic tuff, zeolite bearing tuff, stilbite, clay minerals.*

### Introduction

In several known volcanic area in the Balkan Peninsula has been determined the presence of natural zeolites within the Tertiary volcanic basins. In Serbia zeolites occur in the Tertiary basin around the Vranjska Banja (Trgo et al. 2012). In several localities in Greece were determined occurrences of natural zeolites related to volcanic tuff, such are those from the island Santorini (Tsolis-Katagas and Katagas 1989), as well as in Northern Greece within the area of Thrace where zeolites occur, also (Tsolis-Katagas and Katagas 1990, Voudouris et al. 2010). Vein-type zeolites in Kizari area, (western Thrace) are found within fresh to zeolite altered volcanic rocks of andesitic to dacitic composition.

In the Republic of Macedonia, natural zeolites were not found, but zeolite-bearing tuff were

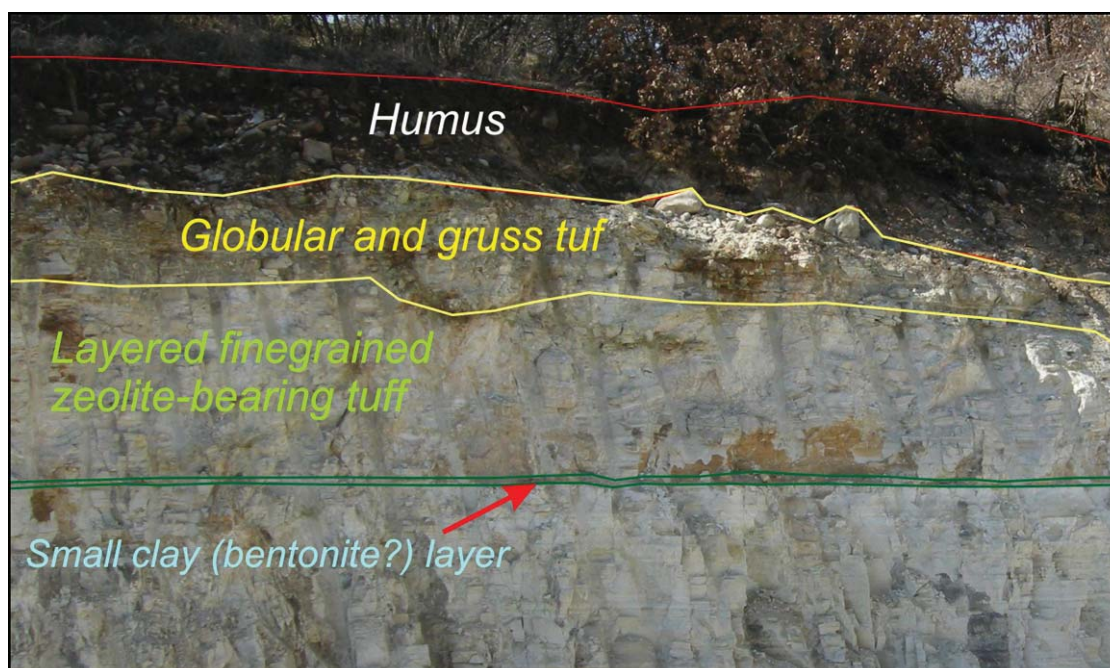
presented for the first time in Hristov et al., 1969 and some preliminary results of the stilbite occurrences in the volcanic tuffs in the southern part of the Kratovo-Zletovo volcanic area were given in Blazev et al. 2012. Our present study defined some mineralogical, geochemical and morphological features of zeolite-bearing tuffs in the Vetunica deposit, northern part of the Kratovo-Zletovo volcanic area. There were calculated geological ore reserves of zeolite-bearing tuffs of 11 000 000 m<sup>3</sup> (Bagasov 2007). Vetunica Mine started with exploitation in 2011.

### Geology

The geological framework of the studied area is completely represented by the Tertiary volcanic rocks of Kratovo-Zletovo volcanic area. The basic rocks are Precambrian gneiss, Riphean-Cambrian schist, Upper Eocene sediments (flysch) and Tertiary-Quaternary volcanic complex. Tuffs are the most common in the area and represent the basis of the younger effusive complex of Kratovo-Zletovo area. They lie above the Miocene sediments and below the volcanic breccia present in the Pliocene sediments and other volcanic rocks. Somewhere they lie directly above the Eocene sediments and crystalline schist or above the ignimbrite of dacitic composition. In general they are well stratified (Fig. 1). These stratified tuffs occur very close to the surface and their thickness ranges 15 to 30 m with certain discontinuities (Fig. 1). Discontinuities are represented by thin layers of clay (probably montmorillonite) or illite clays enriched with Fe-oxides.

Analyzing the open cross section (Fig. 1) clearly can be seen that almost sub-horizontal zeolite tuffs are covered with a thin layer of humus (0.7-1 m), while beneath were located globular tuffs (partly weathered, with thickness of 0.5-1 m), below are located characteristic zeolite tuffs, which are compact, finegrained, layered and kaolinized in some places (Fig. 1). The hiatus is found in the middle of the cross section (5-10 cm thick), while below it continue fine layered compact tuff.





**Figure 1.** Panoramic view of the open cross section through the Vetunica volcanic tuff deposit

Their color varies from white, grey, pale yellow, pale pink to green. Very common occurrence, especially in the shallow parts, is the weathering of tuffs in form of regular concentric spheres, which dimensions are variable (5-50 cm). The spherical layers are composed of crystaloclastic andesite tuff with altered components. In the core of such spheres could be found completely fresh andesite with angular shapes. These tuffs are mainly composed of volcanic ashes, crushed grains of plagioclase and biotite while rarely occur pyroxene, amphibole and magnetite accompanied with andesite pieces. They are the most common in the area of Stracin (village close to ours area of study). The hyaloandesite tuff lies under the hyaloandesite while above them were deposited pliocene sands. They have similar mineral composition with impurities of terrigenous material. In this particular horizon occurs a level of diatomite earth composed up to 90% of opalized substance, 2% of quartz, feldspar and biotite and 8% of other different hydrothermal silicates.

### Materials and Methods

The samples of fine grained layered volcanic tuff were taken from a small open pit in the Vetunica deposit near the city of Kratovo. Major and trace elements were determined by an ICP-AES method. The dissolution of the sample was made by procedures described in (Radojevic and Baskin 1999). Diffractometer PHILIPS Type PW 1051 in the region  $2\theta = 5^\circ$ ,  $60^\circ$  was used for X-

ray determination of mineral composition. Copper radiation was used  $\text{CuK}\alpha = 1.54178 \text{ \AA}$ , the voltage of the generator "NORELCO" was 40 kV and the current was 30 mA.  $2\theta = 2^\circ/\text{min}$ . The determination of clay minerals was made by two oriented thin sections (Blazev et al. 2012). One was taped untreated, then saturated with glycerine and taped, the other was annealed at  $480^\circ\text{C}$ . Identification of the type of clay minerals was made in the area  $2\theta = 3^\circ-14^\circ$ . The geochemical study was performed with an atomic emission spectrometry with inductively coupled plasma, ICP-AES, Varian 715-ES, at the Institute of Chemistry, Faculty of Science in Skopje, R. Macedonia.

### Results and discussion

Optical and X-ray investigations confirmed that feldspar, quartz, stilbite and clay minerals are present in these rocks. The X-ray diagrams (Fig. 2a and b) show that in the Vetunica samples the most common clay minerals and feldspar are present but there is also stilbite ( $4^\circ\text{A}$  and  $8.8^\circ\text{A}$ ). Based on the height of the peak it can be assumed that stilbite is represented by about 27%.

Results of the chemical analyses and cation exchange capacity (CEC) and ammonium exchange capacity (AEC) exchangeable cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) available for exchange in zeolite samples are given in Table 1.

The units are units milliequivalents per 1 g



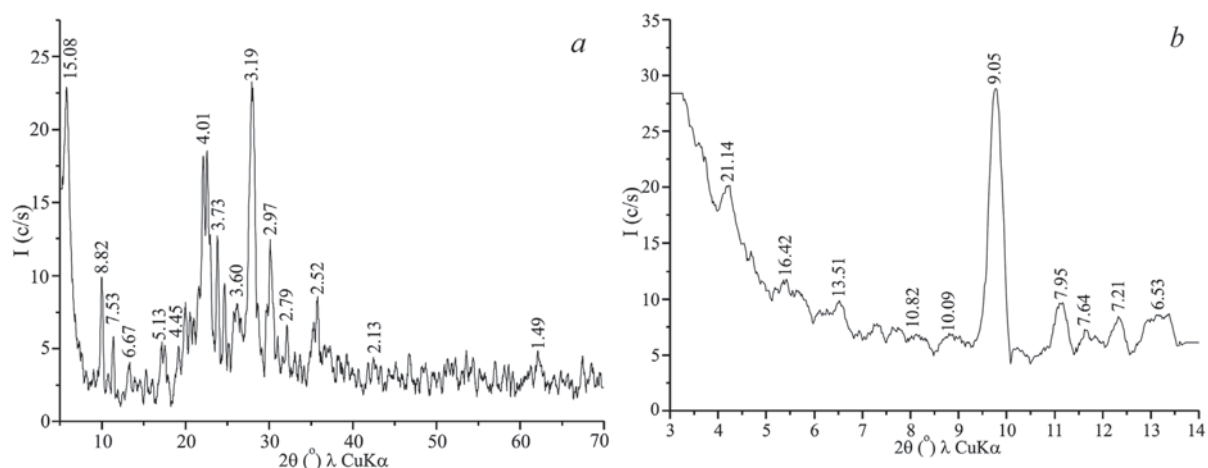


Figure 2. a) X-ray diagram of sample from Vetunica; d) X-ray diagram of sample from Vetunica annealed.

Table 1. Chemical and CEC/AEC values (a) and geochemical composition (b) of the Vetunica deposit tuffs.

a)					b)				
	K1	K2	K3	K4	(ppm)	S-1	S-2	S-3	S-4
SiO <sub>2</sub> (%)	57,27	54,84	52,82	53,73	Ag	1.02	1.04	0.9486	0.9672
Al <sub>2</sub> O <sub>3</sub> (%)	19,24	19,94	20,89	20,56	Al	41008.6	46464.5	40188.4	45070.6
FeO (%)	3,3	3,97	4,66	3,98	As	37.01	27.47	35.899	30.22
CaO (%)	4,23	4,85	4,94	5,4	B	17.89	-0.52 uv	16.638	17.21
MgO (%)	0,93	1,26	1,01	1,13	Ba	735.88	2194.53	706.445	1470.3
Na <sub>2</sub> O (%)	2,67	1,55	1,87	1,78	Ca	21224.3	18265.5	19844.72	21918.6
K <sub>2</sub> O (%)	2,23	2,39	2,55	2,41	Cd	1.17	-0.68 uv	1.1466	1.21
TiO <sub>2</sub> (%)	0,6	0,35	0,41	0,42	Co	-11.3 uv	-5.33 uv	-10.13 uv	-6.47 uv
MnO (%)	0,06	0,05	0,06	0,06	Cr	11.19	13.04	10.4067	11.86
P <sub>2</sub> O <sub>5</sub> (%)	0,2	0,22	0,25	0,27	Cu	62.31	19.33	57.948	27.062
LOI	9,15	11,32	10,51	10,01	Fe	25808.9	10388.8	25034.63	11666.6
Sum	99,88	99,93	99,97	99,75	K	12799.3	6261.11	11903.35	5822.83
Sr (ppm)	1367	1088	1128	1302	Li	6.17	18.8	5.7381	16.36
Ba (ppm)	1876	1531	1534	1756	Mg	4393.02	7194.25	3997.65	6690.65
Zn (ppm)	87,6	106	119	116	Mn	215.44	149.21	200.359	138.76
Pb (ppm)	171,2	87	104,3	132,3	Mo	0.08 uv	-0.07 uv	-0.09 uv	-0.07 uv
Ni (ppm)	7,7	6	8,1	7,8	Na	6611.48	2869.28	6148.68	4590.85
Cu (ppm)	44,6	33,8	39,9	39,4	Ni	8.16	10.67	7.589	9.923
Co (ppm)	15,4	10	12,3	11,5	P	709.29	365.97	659.6397	512.358
Cd (ppm)	0,7	0,9	1	0,9	Pb	52.4	671.98	49.78	624.941
As (ppm)	1,03	2,6	1,08	1,3	Sr	570.01	959.07	701.1123	891.94
Data on CEC /AEC values of Vetunica samples					Tl	-6.78 uv	-7.51 uv	-6.93 uv	-7.22 uv
Ca	0,21	0,21	0,22	0,22	V	127.7	25.72	123.869	29.06
Mg	0,08	0,09	0,09	0,08	Zn	70.86	35.52	69.4428	60.38
Na	0,04	0,03	0,04	0,03					
K	0,73	0,61	0,67	0,65					
CEC- meq/100 g	107	94	102	104					
CEC NH <sub>4</sub> <sup>+</sup> meq/100 g	112	109	114	111					

zeolite meq/g (Helfferrich 1962). Chemical composition, CEC and AEC values in tuffs from Rajcani and Kriva Krusa are shown on Table 1. Cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for samples from Rajcani deposit are 69–82 meq/g for CECs and 71–87 meq/100 g for AECs. From the Vetunica deposit they 94–107 meq/g for CECs and 109–114 meq/g for AECs. These values are very similar to the values from Mangatate and Ngakuru zeolitic tuffs (Blazev et al. 2012). Stilbite rich tuffs from the Vetunica are potential economic deposits of natural zeolite owing to their average contents of stilbite Rajcani 57% and Kriva Krusa 27% and the cation exchange capacity values 0.69–1.07 meq/g.

The latest geochemical study of the Vetunica tuff (Table 1b) displayed standard values for most of the analyzed elements, followed with increased concentrations of the representative geochemical association for this type of volcanic rocks primarily strontium, barium and especially boron, silver, zinc and phosphorus, which is representative for water environments. Among the major elements, the highest values displayed calcium, magnesium, iron, manganese as well as alumina and silica.

The values show that these tuffs can be very effective in a wide range of applications such as waste water ammonium removal in animal nutritions, fertilizers, fish farming, additives to cement, ideal host for loading with beneficial organic or inorganic liquids and as pelitization on ferronickel ore.

## Conclusion

Within the Vetunica deposit were calculated geological ore reserves of zeolite-bearing tuff of 11 000 000 m<sup>3</sup>. Zeolite-bearing tuff are of shallow type and regularly, at depth of approximately 10 meters below the surface are characterized by clay hiatus (probably bentonite or Fe-enriched illite). The present study confirmed presence of stilbite and light enrichment with B, Pb, Ag, Sr, As etc., and high concentration of Ca in studied tuffs. Also, in zeolite-bearing tuff was determined potassium enrichment within the finely stratified white to white-gray tuff.

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## GEOCHEMICAL AND SR-ND ISOTOPIC COMPOSITIONS OF GRANITOIDS FROM ALBANIA AND GENETIC SIGNIFICANCE

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### Abstract

Major- and trace-element contents, radiometric K/Ar ages and Sr-Nd isotope ratios of several granitoid samples from the most important outcrops of Albania have been determined.

These rocks, which are calc-alkaline, mainly allochthonous, and compositionally similar to A-type granites, show multi-element abundance patterns normalized against Ocean Ridge Granite suggestive of a hybrid origin between rocks of within-plate and volcanic arc geodynamic settings. The chondrite-normalized REE patterns of the most of the rocks show moderately high LREE/HREE and low (La/Ce)<sub>N</sub> ratios, except for the rocks from Levrushko displaying a pattern characterized by similar LREE and MREE normalized abundances.

The radiometric K/Ar ages range from 170 to 100 Ma and are lower than the "Concordia" ages determined on the samples, likely reflecting the different rock alteration rate. This latter is significantly lower for the samples from the autochthonous Trokuzi massif. The Sr isotopic ratios range from 0.706110 to 0.766141 and do not fit any isochron. The rocks from the Radomira massif display distinctly lower Sr isotopic ratios than the other samples, among which those from Trokuzi exhibit intermediate values. All the granitoids fit a regression line, to which it is associated an age of about 200 Ma, close to the "Concordia" ages of the samples, and a Sr initial ratio of 0.70935. However, the regression line can also be interpreted as a mixing line between mantle and crust materials, supporting the genetic setting unveiled by the multi-element abundance patterns.

The measured Nd isotopic ratios of the rocks show a very narrow range from 0.512421 to 0.512462, indicating a common source of mixed (mantle+crust) characteristics for all the granitoids and no significant mobilization of the REE despite different rock alteration rates.

Lastly, the Albanian granitoids display several geochemical and Sr isotopic characteristics similar to the Triassic meta-granites from the Serbo-Macedonian massif in northern Greece. This suggests their relation to rifting of the south European continental margin and formation of one of the numerous Tethyan sea basins. Moreover, the Albanian granitoids are close for chemical composition but for Al<sub>2</sub>O<sub>3</sub>, to low-volume western-Serbia granitoids associated with Jurassic ophiolites, of similar initial Sr isotopic composition, inferred to have derived from partial melting of meta-sedimentary rocks.

## COMPOSITION AND MORPHOLOGY OF HYALOPHANES FROM BUSOVAČA, BOSNIA AND HERZEGOVINA

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### Abstract

Hyalophane is a barium-rich silicate belonging to the feldspar group and an intermediate member of the series orthoclase-celsian-albite with general formula  $(K, Ba, Na)[Al(Al, Si)_2Si_2O_8]$ . Few world localities with hyalophane as the main constituent have been described; one of them is Zagrlski creek near Busovača in Bosnia and Herzegovina. Hyalophane crystals, along with quartz, albite and carbonate crystals, are primary constituents of alpine veins cutting Paleozoic fillites. Crystals are up to decimeter sizes.

Crystal habit of hyalophane changes during the crystallization in order: adular type (single crystals-early crystals); adular type (Carlsbad twins); orthoclase and adular type (Mannebach- Bavenno twins); special type of habit dominated by vicinal faces (late crystals). Thus, hyalophane crystals from this locality can be divided in four groups according to their morpho-genetic characteristics:

1. – single crystals – early crystals
2. – Carlsbad twins
3. – Mannebach- Bavenno fourling twins
4. – late single crystals which grew parallel on the early crystals – two variances are noticed: with and without channels.

Microprobe analysis of studied hyalophanes yield following chemical composition:  $SiO_2 = 48,01-51,48$ ;  $Al_2O_3 = 21,57-22,74$ ;  $FeO = 0,00-0,08$ ;  $BaO = 17,38-19,62$ ;  $CaO = 0,00-0,04$ ;  $Na_2O = 1,06-1,59$ ;  $K_2O = 6,62-8,01$ ;  $TiO_2 = 0,00-0,08$ , which is in good agreement with literature. Data from this investigation as well as data from literature, show dual trend in Al/Si ratio. One trend (which most

crystals show) is the usual one, in agreement with substitution of alkaline metal for alkaline earth metal and Si for Al. The other trend corresponds to relative depletion in Al (or relative enrichment in Si) which causes depletion in other cations in order to maintain the neutrality, which is observed in minority of analyzed crystals.

Infra-red spectra of analyzed crystals show usual absorption bands. But, in all analyzed crystals absorption band at approximately  $3130\text{ cm}^{-1}$  appears which corresponds to absorption of  $NH_4^+$  ion.  $NH_4^+$  ion was already determined in hyalophane from Busovača, but its' position and role in hyalophane crystal structure was not determine. In order to determine mentioned parameters, polarized oriented spectra have been taken on differently oriented plates of hyalophanes from Zagrlski creek. It was determined that the position of ammonium ion is constant, that ion is oriented, but band intensities are different for differently oriented plates. This means that ammonium ion is bounded in crystal structure in the cation position rather than it is a constituent of a fluid inclusion. Quantitative IR measurements yielded 0,08-0,17 % of  $NH_4^+$ . Perceived contents of  $NH_4^+$  ion are meaningful from several points of view:

1. values are relatively high for natural feldspar minerals
2. it is determined with high certainty that  $NH_4^+$  ion is accommodated in crystal structure and is a constituent as any other cation
3. from genetical point of view, it is worth noting that  $NH_4^+$  ion implies highly basic conditions during crystallization of alpine veins.



## PETROLOGY OF LATE JURASSIC – ALBIAN CHERT FORMATIONS IN MEGANISSI ISLAND (W. GREECE).

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### Abstract

Cherts of Late Jurassic – Albian age, intercalated in pelagic limestones at Meganissi Island (Ionian Sea, western Greece) were studied. These SiO<sub>2</sub>-rich materials were deposited in the Ionian intra platform basin and their presence indicates that this basin was under the CCD level. In the field, the cherts occur as bedded and nodular, with red and greyish colours. The microscopic study showed that they are composed of cryptocrystalline quartz, microcrystalline quartz, chalcedony and mega-quartz. The powder X-ray diffraction and SEM-EDS studies verified the dominance of quartz, a fact proving that the cherts of Late Jurassic-Albian are of increased diagenetic grade. The chemical analyses by ICP-OES/MS showed that the investigated cherts have very high SO<sub>2</sub> content and significant amounts of CaO. Their biogenic origin is supported by the presence of characteristic fossils (radiolaria) and distinct bulk geochemical fingerprints. REE geochemical diagrams indicated that these cherts were clearly deposited in a marine environment. Moreover, paleo-redox marine conditions, in conjunction with further diagenetic and epigenetic processes, are most likely the factors caused enrichment in LREE and an evident Ce negative geochemical anomaly (Ce/Ce\* av. 0.52).

**Key words:** *Chert, Petrology, Meganissi, Greece*

### Introduction

Cherts are fine-grained, dense, commonly very hard sedimentary rocks. They are composed dominantly of SiO<sub>2</sub> minerals. They occur in the field as bedded or nodular shapes. Bedded cherts consist of primary silica concentration, of biogenic or hydrothermal origin. This type of chert can further be subdivided based on their interior content. Nodular cherts on the other hand, are subspheroidal masses, lenses or irregular layers or bodies that range in size. They originate mainly by diagenetic replacement of

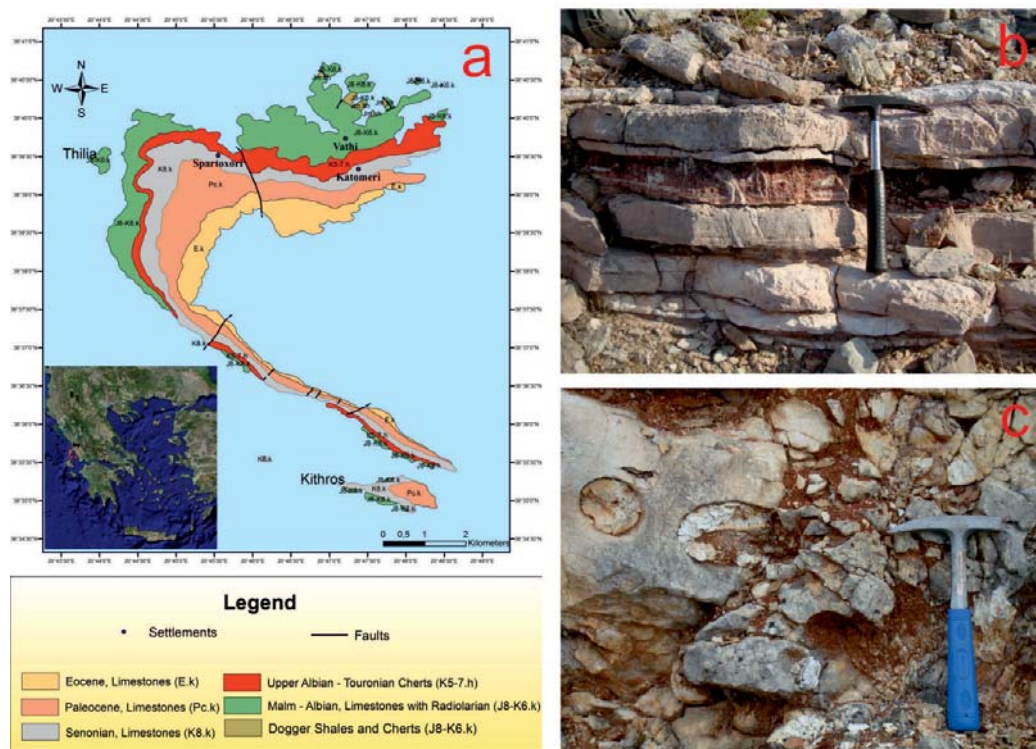
the host rocks. Cherts are volumetrically a minor component of sedimentary rocks, but they are associated to important economic deposits. They have been identified, in the geological scale, from Precambrian to Quaternary. This study brings for first time in the literature, data concerning the Late Jurassic-Albian cherts, in the Ionian intra-platform basin in External Hellenides. They are intercalated in pelagic limestones, known as Vigla formation (Karakitsios, 1995). In Meganissi Island, (Ionian Sea, western Greece) where our fieldwork took place, Vigla limestones have extended outcrop (Fig.1a).

### Materials and Methods

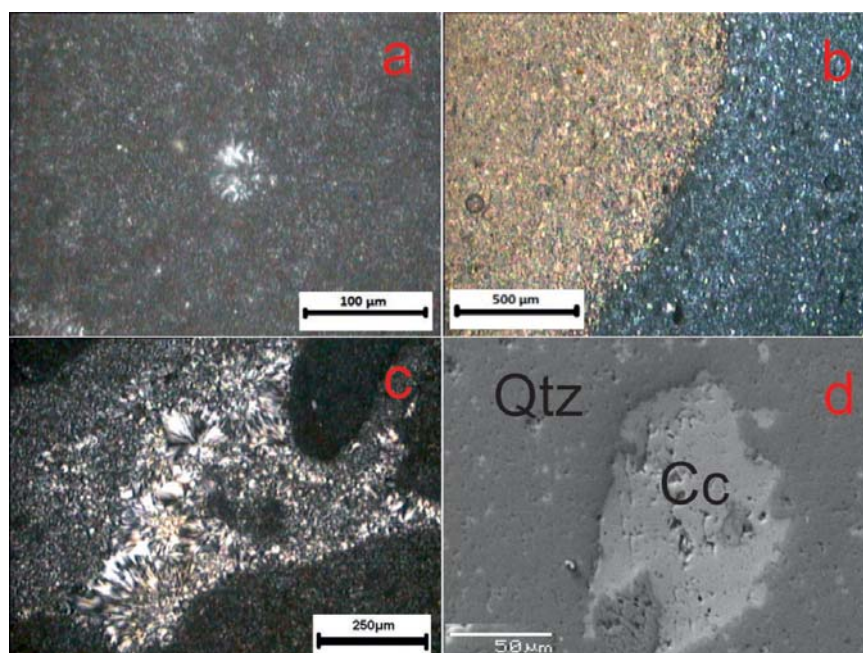
The extended fieldwork on the island included detailed mapping and macroscopic examination of the chert formations. Throughout this field campaign, 30 samples were collected for studying the mineralogy and the bulk geochemistry of the rocks. The laboratory work included preparation of rock slices for macroscopic evaluation and of thin and polished-thin sections for examination using an optical microscope and SEM-EDS (JEOL JSM-5600 SEM equipped with an Oxford EDS). Powder XRD patterns were obtained using a Siemens D5005 – now Bruker AXS - diffractometer. The data were processed by means of the EVA 10.0 software in conjunction with the DIFFRACplus software. Bulk geochemical analyses for major and trace elements were performed using ICP-OES/MS.

### Results and Discussion

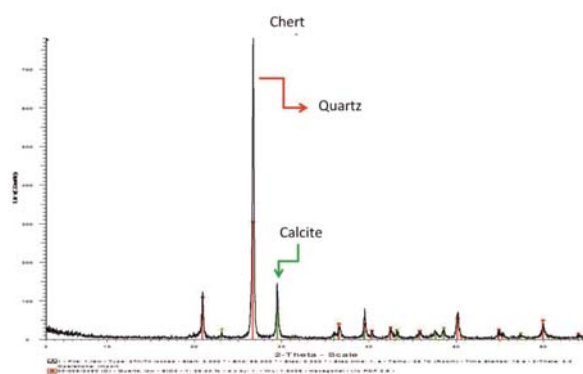
In Meganissi Island, Cherts of Late Jurassic-Albian occur as bedded and nodular. Bedded cherts constitute usually thin layers (5-10cm), cohesive or with many fractures (Fig.1b). Nodular cherts are well-formed with subspherical shapes (Fig.1c) and they vary in size (10-15cm in diameter). Bedded cherts appear at the lower parts of the Vigla formation, while the nodular ones at the upper parts. Their colour varies significantly from red to grey. The optical microscopic examination showed that



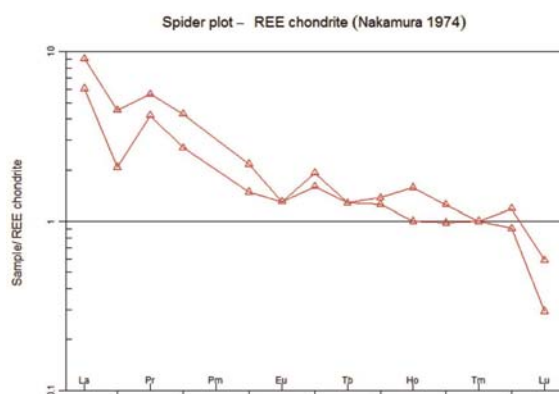
**Figure 1.**  
 a) Geological Map of Meganissi Island (modification form the I.G.M.E., 1994). b) Image of bedded chert and c) nodular cherts.



**Figure 2.** a) Microquartz with radiolaria filled by chalcedony. b) Microcrystalline calcite and microquartz. c) Chalcedony. d) SEM-EDS image of calcite (Cc) gain in quartz (Qtz).



**Figure 3.** Typical XRD pattern of Late Jurassic – Albian chert from Meganissi Island.



**Figure 4.** The REE pattern of the cherts in Meganissi Island compared to the Chondrite content (Nakamura 1974).

they are composed of crystalline quartz (crystal size smaller than  $5\mu\text{m}$ ), microcrystalline quartz ( $5-15\mu\text{m}$ ), chalcedony and mega-quartz ( $30-50\mu\text{m}$ ). Microfossils observed are mostly radiolarians filled with chalcedony microcrystalline quartz or both (Fig. 2). Cherts also contain small amounts of calcite as micritic layers. The dominance of quartz and the presence of calcite are also verified by the results of powder XRD (Fig. 3) and SEM-EDS (Fig. 2). The mineralogical texture (quartz and chalcedony) shows that the studied cherts exhibit increased diagenetic grade. Their sedimentation took place when the Ionian intra platform basin was under the CCD level. At the Late Jurassic-Albian, the Ionian intra-platform basin was submerged and the CCD was increased with not a

constant rate. In nodular cherts, the micritic calcite

**Table 1.** Geochemical analyses for major (% wt) and trace elements (ppm). The value of Ce anomaly is also demonstrated.

Sample	G1	G7
Rock	Chert	Chert
Age	Late Jurassic – Albian	Late Jurassic–Albian
Form	Bedded	Nodular
SiO <sub>2</sub>	79,44	80,84
Al <sub>2</sub> O <sub>3</sub>	0,19	0,84
Fe <sub>2</sub> O <sub>3</sub>	0,10	0,19
MgO	0,11	0,13
CaO	10,41	9,14
Na <sub>2</sub> O	0,06	0,05
K <sub>2</sub> O	0,06	0,23
TiO <sub>2</sub>	<0,01	0,03
P <sub>2</sub> O <sub>5</sub>	0,04	0,04
MnO	0,01	<0,01
Cr <sub>2</sub> O <sub>3</sub>	0,00	<0,002
La	2,00	3,00
Ce	1,80	3,90
Pr	0,47	0,63
Nd	1,70	2,70
Sm	0,30	0,44
Eu	0,10	0,10
Gd	0,44	0,53
Tb	0,06	0,06
Dy	0,43	0,47
Ho	0,07	0,11
Er	0,22	0,28
Tm	0,03	0,03
Yb	0,20	0,26
Lu	0,01	0,02
Ce/Ce*	0,40	0,61

zone is residue of the limestones, which means that they were formed by diagenetic replacement of the host rocks. The bulk chemical analyses have shown an average composition of 80% wt. SiO<sub>2</sub>, and of 10% wt. CaO, and low concentration in the other major elements (Table 1). Regarding trace elements (Table 1), there is a notable enrichment in REEs (normalized with chondrite) as well as a negative Ce anomaly with Ce/Ce\* av. 0.50 (Fig. 4), indicating, besides to characteristic silica microfossils, a marine depositional environment and specific paleo-redox marine conditions followed by diagenetic processes.

## Conclusions

This study brings for first time in the literature, data concerning the Late Jurassic- Albian cherts, from the Ionian intra platform basin in External Hellenides, intercalated in pelagic limestones of Meganissi Island (Ionian Sea, western Greece). They are characterized by high SiO<sub>2</sub> content and abundant quartz indicating an increased diagenetic grade. Trace element, and particularly REE data, showed a biogenic origin and deposition in a marine environment under the CCD.

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## PYRRHOTITE FROM MINERALIZATION RELATED TO ALBANIAN OPHIOLITIC COMPLEX

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### Abstract

Pyrrhotite is a common mineral related with Albanian ophiolitic complex, that in some sulfide mineralizations is the main component.

The geological setting of pyrrhotite-bearing mineralizations belong to restricted part of ophiolitic section from the uppermost ultramafic rocks, close to plutonic mafic sequence and layered gabbro-norite one.

Some mineralization-types and its pyrrhotite varieties are evidenced in relation with their geological setting. These features are characterized by different shapes of ore bodies, mineral associations and mineralogical properties of pyrrhotite itself. They are conditioned from both factors; by interaction between mineralizing fluids and wall rocks from which have been extracted some metallic elements and by medium to high temperature of these fluids that has conditioned the formation of rich Fe-sulfides.

The investigation of mineral associations and varieties of pyrrhotite concerning its composition belongs to Fe deficit towards the S contain and its  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio has been carried out to intend for evidence the active role of hosted rocks in hydrothermal plutonic mineral-forming.

**Key words:** *pyrrhotite, mineralization, associations, composition.*

### Introduction

The Albanian ophiolitic complex is distinguished for its complex metallogeny hosting different mineralization types. Particularly, some of them belong to Cu, Cu-Ni and Ni-sulfide, as well as arsenide types (Çina 1980, 1990; Shallo et al. 1995; Gjata et al. 1995).

The sulfide and arsenide mineralizations of hydrothermal origin hosted, by ultramafic and mafic rocks, have been investigated by several geoscientists (Garuti et al. 1984, 1986; Foose et al. 1985; Thalhammer et al. 1986). According to their mineralogical investigations, the hydrothermal activity linked with serpentinization processes is responsible for the liberation of metallic elements from silicates. The active role of hosted mafic and ultramafic rocks for enriching of fluids with some elements as Fe, Ni and Co, has been suggested by Çina (1990).

The pyrrhotite is the common mineral of these mineralization's that is distinguished by large mineral associations, and chemical variability belongs to insufficient content of Fe towards the S and consequently, the variable  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio.

The pyrrhotite-bearing mineralizations are hosted by serpentinized hartzburgites, supra-MOHO dunites, layered gabbro-norites and isotropic gabbro where the sheeted dike complex, plagiogranite-diorite intrusions, as well as the ultramafic ones, are widely present (Fig. 1) (Shallo et al. 1995; Gjata et al. 1995).

The geological and mineralogical investigations of pyrrhotite-bearing mineralization and pyrrhotite itself as concerns geological setting, shape of ore bodies, mineral associations and its composition have evidenced close relationships between these features and geological setting, due to common action of host rocks and mineralizing fluids.

### Geological setting and mineral associations

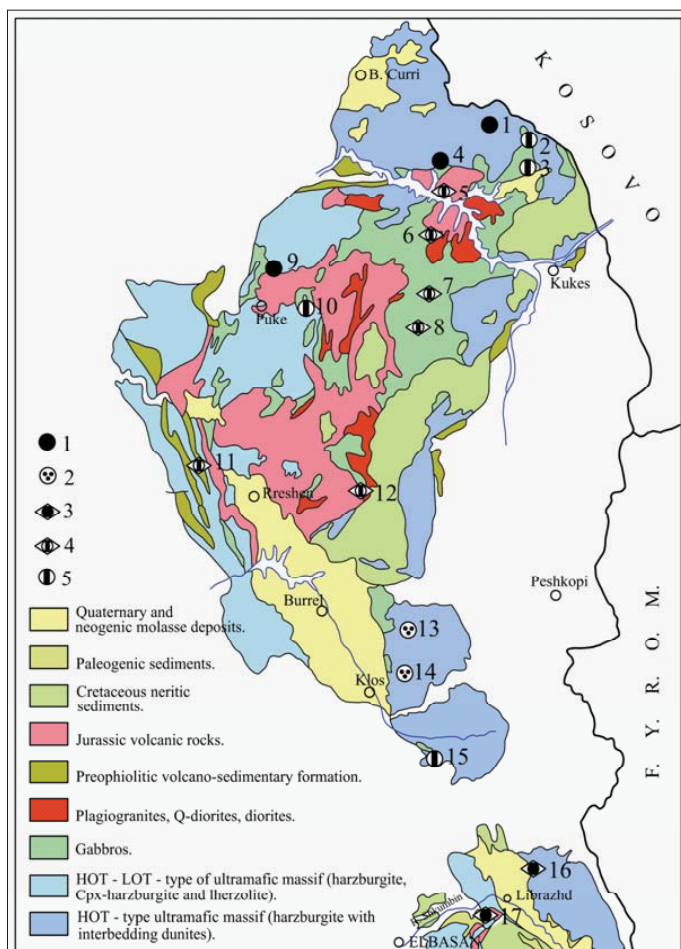
The pyrrhotite-bearing mineralizations are setting within restricted part of ophiolitic section, from uppermost ultramafic rocks up to plutonic mafic sequences.

The shape of ore bodies, presence and quantities of pyrrhotite, its mineral associations and their properties are in close relationship with this geological setting.

Within the uppermost ultramafic section, mainly serpentinized hartzburgites, are located the lens-like ore bodies composed by massive Cu-Ni sulfide mineralization-type. The predominant minerals are pyrrhotite, pentlandite, cubanite and chalcopyrite, associated by latter stage minerals as magnetite, native copper, mackinawite and valleriite. The characteristic texture is that exsolution of pyrrhotite-pentlandite and chalcopyrite-cubanite.

The mineralization-types hosted within the gabbro-norite sequence close to ultramafic part have also the lens-like shape ore bodies. Its mineral composition is variable. Two sub-types have been distinguished: Cu-As-Au mineralization composed by pyrrhotite, arsenopyrite, chalcopyrite and cubanite. The other sub-type belongs to Cu-Co-Au-mineralization and composed by pyrrhotite, chalcopyrite, Ni-cobaltite and native gold.

Two other mineralization-types are hosted within plutonic mafic cumulate sequences:



**Figure 1.** Geological map of North Eastern part and pyrrhotite-bearing mineralization-types related to Albanian ophiolitic complex.

- 1.** Lens-like ore bodies composed by massive Cu-Ni sulfides hosted with uppermost mantle harzburgites; **2.** Disseminated Ni-sulfide mineralization hosted with super-MOHO dunites; **3.** Lens-like ore bodies composed by massive Cu-As-Au minerals hosted with gabbro-norite rocks close to ultramafic ones; **4.** Vein ore bodies composed by Cu-Co-As-Au minerals hosted with gabbro-norite sequence; **5.** Vein quartz-Cu sulfide mineralization hosted with gabbro.

Vein quartz-Cu-Co-Au sulfide type, linked with layered gabbro-noritic sequence composed by pyrrhotite, pyrite, chalcopyrite and a few amount of cobaltite, arsenopyrite and native gold.

The second mineralization-type, vein ore body also, is related to the isotropic gabbro sequence, composed mainly by quartz, some parts by calcite as well as pyrite, chalcopyrite and less amount pyrrhotite. Its transformation into mixed pyrite+magnetite aggregate is an evident change due to augmentation of S contains in latter stage mineralizing fluids.

From the table 1 is clearly shown the close correlation between the pyrrhotite amount and associated minerals in one side, and the hosted wall rocks in other side:

The pyrrhotite-pentlandite association is situated from ultramafic rocks up to gabbro-norite ones. The pyrrhotite-cubanite association that has

**Table 1.** Geological setting of pyrrhotite-bearing mineralization and its mineral associations

Minerals some characteristics of pyrrhotite	Geological setting of mineralization				
	Ultramafic		Mafic / Gabbroic		Inter-med.-acid
	Close to mafic	Contact zone Ultra-mafic	Mafic	Close to ultra-mafic	
Pyrrhotite	—	—	—	—	—
Pentlandite	—	—	—	—	—
Cubanite	—	—	—	—	—
Chalcopyrite	—	—	—	—	—
Vallerite	—	—	—	—	—
Mackinawite	—	—	—	—	—
Bravoite	—	—	—	—	—
Nickeline	—	—	—	—	—
Arsenopyrite	—	—	—	—	—
Cobaltite	—	—	—	—	—
Sphalerite	—	—	—	—	—
Pyrite	—	—	—	—	—
Marcasite	—	—	—	—	—
Magnetite	—	—	—	—	—
Hematite	—	—	—	—	—
Quartz	—	—	—	—	—
Chlorite	—	—	—	—	—
Epidote	—	—	—	—	—
Calcite	—	—	—	—	—

moderate contains of Fe is characteristic for mineralization related to layered gabbro-norite sequence, close to ultramafic section. The pyrrhotite is associated with cobaltite, for mineralization hosted within gabbro-norite rocks due to highest content of Co for these rocks. The pyrite was appeared in restricted part of section, only in mineralization hosted within gabbro due to change of Fe: S ratio in favor of the latter. The presence of quartz, some times associated by calcite, is linked mainly to gabbro sequence due to augmentation of Si and Ca components for these mafic wall rocks.

This picture of distribution of pyrrhotite and associated minerals, signify the close relationships and active chemical influence of wallrocks into composition of mineralizing fluids penetrated, within them.

The mutual relationships of pyrrhotite and associated minerals are shown in several microphotografies.

### Chemical composition

Pyrrhotite has unstable composition expressed by variable deficit of Fe towards the S. In consequence of this deficit a part of  $Fe^{2+}$  has passed into  $Fe^{3+}$  (Tab. 2).

Pyrrhotite associated by pentlandite hosted within ultramafic rocks, is distinguished by smallest S-Fe deficit that has the composition like the troilite (Tab. 2, analysis 3 and 4).

Pyrrhotite associated with cubanite and chalcopyrite belongs to mineralization hosted to gabbro-norite rocks, close to those ultramafics is

**Table 2.** Chemical composition of pyrrhotite from hydrothermal plutonic Fe-Cu-Ni-Co-As±Au mineralizations.

	1 Qafe Shul	2 Perroi Bokes	3 Letaj	4 Stavec 60-1	5 Stavec 60-2	6 Stavec 60-3
<b>S</b>	38.7	39.1	36.8	36.5	38.0	38.4
<b>Fe</b>	61.7	59.36	63.6	63.4	61.8	61.7
<b>Ni</b>	0.05	0.21	0.02		0.04	0.02
<b>Co</b>	0.08		0.09	0.07	0.07	0.08
<b>Cu</b>		0.15	0.02			
<b>Tot.</b>	100.53	98.82	100.53	99.97	99.91	100.20
<b>S</b>	1.042	1.067	1.004	1.004	1.034	1.040
<b>Fe</b>	0.956	0.928	1.000	1.000	0.964	0.960
<b>Ni</b>	0.001	0.003			0.001	
<b>Co</b>	0.001		0.002	0.001	0.001	0.001
<b>Cu</b>		0.002			0.001	

Microprobe analysis are carried out by Ch. Gilles at BRGM, France and by D.Topa at Salzburg University, Austria.

1. (Fe 2+.754 Fe3+.162).916 S; 2. (Fe2+.616 Fe3+.256).872S;  
 3. (Fe2+.979 Fe3+.014).993S; 4. (Fe2+.991 Fe3+.006).997S;  
 5. (Fe2+.805 Fe3+.130).935S; 6. (Fe2+.772 Fe3+.152).924S.

characterized by moderate S-Fe deficit (analysis 1, 5 and 6).

By electronic microscopy investigation and electron microbeam analyses have been evidenced the presence of two polymorphic modifications of pyrrhotite, distinguished also by different S-Fe deficit (analysis 4 and 5).

The quartz-sulfide mineralization hosted within gabbro contains pyrrhotite in association with chalcopyrite and pyrite. This pyrrhotite is distinguished by higher S-Fe deficit (analyses 2) and the greater part of Fe<sup>2+</sup> is changed into Fe<sup>3+</sup>. This pyrrhotite is unstable, and partly transformed into pyrite and magnetite.

## Discussion

The formation of vein ore bodies is not only the result of the mineral deposition of the components transported by fluids from deep source, but also the result of some components extracted from wall rocks.. Some facts that support this suggestion as fellows: The particular minerals and their associations are closely related to specific rocks. The cobaltite from mineralization hosted within gabbro sequence close to ultramafic rocks, is distinguished by high content of Ni, 9,2%, that is Ni-cobaltite variety, in contrast with cobaltite related to gabbro sequence close to plagiogranite rocks, that is contains only 0,1% Ni (Çina, 2009, 2012).

The pentlandite component of Ni-sulfide mineralization hosted within super-MOHO dunites or serpentinites hartzburgites contains a

few Co, about 0,5%, while this mineral related to gabbro sequence is particularly rich in Co, 10 up to 23%, that is Co-pentlandite variety (Çina, 2010).

The trend of variation of pyrrhotite composition which in S-Fe deficit and Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio, reflects the influence of different hosted rocks into composition of fluids.

The mineralization related to ultramafic rocks and gabbro sequence ones close to the former, are composed only by sulfides without the quartz and calcite, but they are the main components for vein ore bodies hosted within gabbro rocks.

The Fe and Cu-Fe sulfides belong to minerals that have different S: Metals ratios which are higher for pyrrhotite (FeS) and become lower to cubanite-chalcopyrite direction up to pyrite, in conformity of hosted rocks from ultramafic up to gabbroic. The change of mineral associations from pyrrhotite-pentlandite up to pyrrhotite-chalcopyrite-pyrite is linked by augmentation of S concentration in fluids, due to decrease of its temperature.

## Conclusions

The different geological and mineralogical features of plutonic hydrothermal mineralization related to ophiolitic complex of Albanides, are in conformity with their hosted rocks.

This relationship is due to active role of wall rocks into composition of mineralizing fluids.

The mineral associations and the composition of pyrrhotite itself show an evolutionary trend which is closely linked with primary composition of fluids and hydrothermal activity, responsible for extraction the metallic elements from silicates.

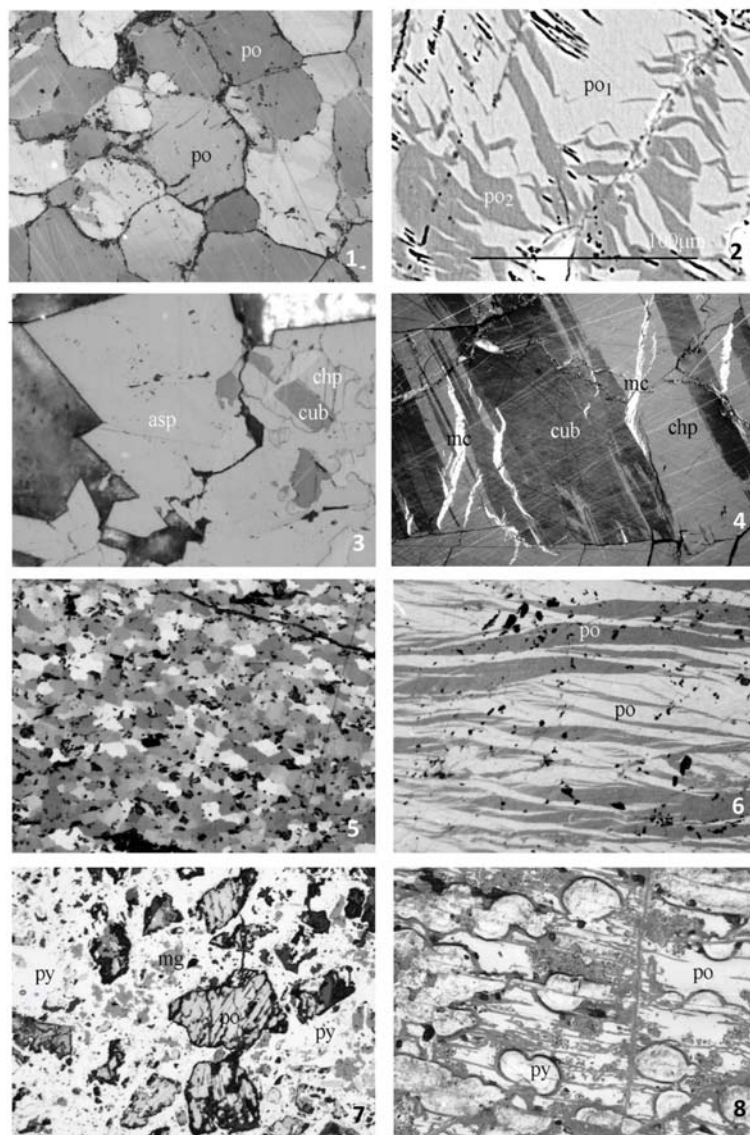
These mineralization-types have been the product of combined hydrothermal activity of plutonic origin, serpentinization processes and the different intrusions from ultramafic up to plagiogranite and sheeted dikes.

The mineral associations, mutual relationships of minerals and its exsolution textures suggest the temperatures of fluids from medium-high up to medium-low that have played the key role for augmentation of H<sub>2</sub>S dissociation.

The close relationships between mineralization-types and their hosted rocks may be used for effective geological exploration for definite mineralizations.

*Acknowledgments:* Thanks are due to Ch. Gilles from BRGM, France and D. Topa from Salzburg University, Austria for their assistance with regarding electro microprobe analysis of some minerals.





**Figure2.**

1. Euhedral pyrrhotite grains. Crossed nicols; 2. Two polymorphous modifications of pyrrhotite; 3. Arsenopyrite corroded by cubanite-chalcopyrite association with lamellar exsolution texture. Half crossed nicols; 4. Cubanite-chalcopyrite association with parquet-lamellar exsolution texture intersected by mackinawite-veils. Crossed nicols; 5. Lens-like elongated granoblastic texture of deformed pyrrhotite. Crossed nicols; 6. Lens-like twinned texture of deformed pyrrhotite. Crossed nicols; 7. Pyrrhotite remnants within pyrite+magnetite groundmass as product of its sulfurization; 8. The "bird eyes" aggregate of pyrite+marcasite by supergene alteration of pyrrhotite.

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## **BERYL ASSOCIATED WITH GRANITES TAOURIRTES, APLOPEGMATITES AND PEGMATITES OF THE LAOUNI REGION (CENTRAL HOGGER, ALGERIA)**

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### **Abstract**

The associated Taourites granites and pegmatitic formations of the Laouni area contain several indices of beryl, systematically associated with these aluminous post Pan-African granites belonging for some of them to a type of GMR low -P (Granites with rare metals, poor in phosphorus). These granites correspond to magmatism a topaz – albite that is expressed as small intersecting intrusions all surrounding formations implemented by accidents or intersection accidents.

This area is the only one in the Hoggar which has shown indexes of beryl (Alous Wan Rechla and Guerioun) as well as some occurrences of which some samples are treated here.

Chemical analyses with an electron microprobe and with the diffraction X rays (XRD), of a few individuals from the Laouni region show that there are two main types:

1 - The first type appears in the massif Alous Ouan Rechla linked to a spectacular zoned pegmatite formation corresponding to a stocksheider.

The beryl is associated with a mica rich with Lithium (Li) and manganese (Mn) (the masutomilite) and large crystals of quartz. The Beryl is greenish gray and is?? in the shape of spherulites ranging in size from 0.5 to 2.5 cm.

2 - The second variety of beryl was taken in a training aplopegmatite periphery of the granite massif TiT -N- Enir and stocksheider (pegmatite) of Tamazaror where it is associated with feldspar, zinnwaldites, topaz, quartz and albite. These beryls have the shape of well individualized crystals blue to greenish blue.

Chemically it is richer in iron (Fe) and beryllium (Be) but poorer in calcium (Ca), sodium (Na) and calcium (K).

The presence of beryl in this region is witnessing a very special feature singles out the Laouni S.S region.

The different mineralization arranges themselves from the inside to the outside of massifs:

-Mineralization Tantale (Ta) – Niobium (Nb) as disseminations

-Beryl associated with granites “Taourirtes”, aplopegmatites and pegmatites

This originality in Beryllium (Be) ads to the richness of Mn which is expressed in several minerals especially the manganotantalite the masutomilite and Hubnéríte.

**Key words:** *Beryl, Granites “Taourirtes”, Aplopegmatites, pegmatite, XRD, GMR and mineralization.*

## GEOCHEMISTRY AND AGE DATA ON GRANITOIDIC NUCLEI FROM THE GETIC BASEMENT OF THE SOUTH CARPATHIANS

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### Abstract

The Getic basement of the South Carpathians comprises two metamorphic complexes separated by a pre-Variscan overthrust plane. The lower complex, consisting by augen gneisses domes surrounded by micaceous gneisses, representing a continental crust with large granitoidic relics. The upper complex is very different, composed of quartzo-feldspathic gneisses, amphibolites, and micaschists with tectonic lenses of manganiferous rocks, metaperidotites and eclogites. Granitoid relict nuclei described by Stelea (2000) as occurring in the gneissic rocks of both complexes have been geochemically analyzed and dated. The lower granitoid nuclei (LGN), with coarse-grained texture and oligoclase, red biotite and garnet dominant mineralogy, are granodiorite-granites of peraluminous S-type with higher Al, Rb, Ba, Th, U, Cr and Ni contents, typical for granitoids with metasedimentary source from upper continental crust. The upper granitoid nuclei (UGN), with fine to medium-grained textures and oligoclase, brown-green biotite, magnetite and hornblende mineralogy, are of granodiorite-tonalite type. The UGN are peraluminous to metaluminous with both I- and S-type characteristics, lower contents of Rb, Th, U and heavy metals, which indicate a composite source of both oceanic and metasedimentary origin.

Over 60 zircon crystals from 4 granitoidic nuclei samples (2 from UGN - Sebes Mts. and 2 from LGN - Fagaras Mts.) were analyzed for in situ U/Pb dating by LA-ICP-MS. Age data on LGN zircons show protomagmatic crystallization at ~449.3 Ma (M1B?) belonging to the Ordovician-Silurian time-span of apparent ages between 485-410 Ma, related to tectono-thermal processes during a presumed the Caledonian collision in the South Carpathians area. The LGN zircons inherit corroded the Paleo-Proterozoic (2.4, 2.3 Ga) and Neo-Proterozoic (808, 655, 629, 551, 538 Ma) cores from the source rocks. Outer

zones with ages of 379-378 Ma show probably recrystallization effects of the Variscan orogeny (M2). Published age data on the Luncani LGN (Balica, 2007) showed crystallization age of 446 Ma, 642-464 Ma relicts' ages and recrystallization at 421 Ma. The main age data of UGN zircons indicate crystallization time at ~490.9 Ma (M1A?) obtained from the Cambrian-Ordovician apparent ages (529-432 Ma), which also relate to magmatic events of the Caledonian crustal building in the South Carpathians. The Cadomian ages between 571-543 Ma, contemporary to Tilisca granitoid (569 Ma) and Frumoasa UGN (569.6 Ma) obtained by Balica (2007) and Balintoni et al. (2009), are interpreted as ages of the composite source material. Recrystallization effects are noticed on a single zircon crystal margin at 390 Ma. The time elapsed between UGN and LGN formation is of ~40 Ma which may indicates the same tectono-thermal event affecting two different types of crust. Considering the insignificant gap between the recrystallization ages on LGN and UGN, the collisional event which superposed the two crusts could have acted during the Caledonian orogeny. The Variscan event, marked by thermal effects on zircons, is related to the post-collisional up-lift of the Getic crust.

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## CRYSTAL SIZE DISTRIBUTION (CSD) OF TITANITE INCLUSIONS IN GROSSULAR FROM THE CALC-SILICATE SKARN IN MALÉ KARPATY MTS., SLOVAKIA

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### Abstract

Titanite inclusions ( $L \approx 10\text{-}60\ \mu\text{m}$ ) regularly dispersed in garnet porphyroblast ( $V = 0.068\ \text{cm}^3$ ) from calc-silicate skarn have been studied using the X-ray high-resolution micro-tomography. This advanced methodical approach allowed the direct acquiring of the crystal size distribution (CSD) and its numerical assessment that forms a stereological basis for detailed analysis of the number, shape and size of a particular mineral in a given rock volume. In most petrological studies the random sections through minerals in thin sections are measured and the obtained data are then mathematically transformed in a 3D picture. This transformation requires a lot of geometrical crystal shape corrections though in many cases thin section data and 3D measurements provide a well consistent numerical data set (see e.g. Castro et al. 2003). Titanites, as tiny idioblastic inclusions are regularly distributed in garnet grains ( $L \approx 0.01\text{-}0.7\ \text{cm}$ ). Central parts of garnets contain larger titanite inclusions. However, in other calc-silicate rock matrix minerals (calcite + tremolite + quartz), titanite crystals have been only seldom identified microscopically. Idioblastic garnets have a tendency to occur in enriched quantity zones and their occurrence is obviously attributed by original lithology and chemical composition of the sedimentary protolith. It is presumed that protolith contained some detritic sedimentary Ti minerals as e.g. ilmenite, titanomagnetite, leucoxene, etc. that were during increase of metamorphic temperature transformed by metamorphic reactions into idioblastic shapes of titanite. After the decomposition of detritic sedimentary Ti minerals the tiny titanites may have been formed at their decomposition places and in further recrystallisation processes these places might have served for preferred heterogeneous garnet nucleation and growth. The mass balance progressive metamorphic reactions, however,

have not been identified on the basis of the modal appearance of the idioblastic titanite inclusions in garnet. Garnets are quasi homogeneous with low decrease of Ti and Fe from the core to the rim. They were growing under temperature increase as the stable part of the mineral assemblage attaining equilibrium in periplutonic zones at  $\sim 300\ \text{MPa}$  and  $\sim 500\ ^\circ\text{C}$ . This assemblage has been significantly determined by the adjacent intrusive magmatic body and metamorphic fluid composition, where high  $\text{H}_2\text{O}$  content ( $X_{\text{CO}_2} < 0.2$ ) expresses an intense influence of the deliberated magmatic fluids on the mineral assemblage. If these fluids were source of Ti, needed for titanite formation, the pervasive fluid front would have attributed the forming of titanite throughout the mineral assemblages of the calc-silicate periplutonic zone. As the titanite crystals occur in clusters, formed prior to the garnet nucleation and growth, the source of Ti is presumed to be in sedimentary protolith. CSD of tiny titanite inclusions in grossular present the normal, Gauss distribution patterns with a minimal log-normal distribution tendency indicating thus the conservation of number and shape of the formed CSD, after the crystallization has been completed. The nucleation and growth of titanite inclusions was swift and the data show that titanites have been grown within a very short time period. The calculated value obtained for average nucleation rate was as  $J' = 5.61 \times 10^{-6}\ \text{N}^\circ\ \text{cm}^3\ \text{s}^{-1}$ , and average growth rate  $Y' = 2.06 \times 10^{-12}\ \text{cm}\ \text{s}^{-1}$ , giving thus the crystallisation residence time for titanite inclusions in garnet at  $\tau = 40\text{-}80\ \text{yr.}$ , what is consistent with the other data on titanite nucleation and growth. The grossular garnets hosting tiny titanite inclusions grew, in comparison, in a much longer time span,  $\tau \approx 400 - 8000\ \text{yr.}$

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## FLUID REACTION BETWEEN CARBONATITE AND ALKALINE ROCKS FROM THE GULI MASSIF, NORTHERN SIBERIA

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### Abstract

The Guli massif is located in the Maimecha-Kotui Province, the northern part of the Siberian platform. The massif is composed of a giant dunite-clinopyroxenite complex, alkaline suite and carbonatite intrusion. This fluid inclusion in alkaline rocks study shows that many minerals contain melt inclusions (clinopyroxene, perovskite, nepheline, apatite) and fluid inclusions (nepheline, apatite and calcite). Fluid inclusions contain abundant phase H<sub>2</sub>O-NaCl, without any evidence of CO<sub>2</sub>, measuring below 15µm in diameter. The homogenization temperature of the trapped fluids are mostly in the range of 140°C to 406°C and salinities mainly 4.1% - 20 wt.% NaCl equivalent, in this case evidence of metasomatic reaction between intruding carbonatite and alkali-ultramafic sequence. Fluids can be distinguished into different types depending upon phase (L-liquid, V-vapour, S-solid) in nepheline (type I, Type II, type III, type IV), apatite (type I, type II) and calcite (type I), with respect to melting temperature.

**Key Words:** *Fluid inclusion, nepheline, apatite, calcite, Guli massif*

### 1. Introduction, geological settings

The Guli massif occupies an area of about 2,000 km<sup>2</sup> according to geophysical data (Malitch and Kostoyanov 1999) (Kogarko and Kononova 1995), (Yegorov 1989) (Vasilev and Zolotukhin 1995) within the Maimecha-Kotui province in the northern part of the Siberian platform (Taimyr Province, Russia). The massif, supposed to be the largest zoned Alaskan-Aldan-type complex (Thalhammer and Meisel 2005), is composed of the dunite core complex, an alkali-ultramafic sequence and carbonatite intrusions. The ultramafic complex is composed of dunite, wehrlite and clinopyroxenites, and is enveloped by dunites, showing a typical cumulate texture. The alkali-ultramafic sequence is composed of clinopyroxenite, ijolite, olivine melaphelinites, melilite, jacupirangite etc. Carbonatites are

represented in two intrusions composed of calcite, magnetite, perovskite etc. Highly disseminated to schlieren type chromitite are very common and have been found at the periphery of the dunite complex (Thalhammer et al., 2006). Furthermore, the Guli massif is characterised by occurrences of economic PGE and Au-placer deposits (Malitch & Lotapin 1997, Malitch et. al., 2002, Dvorani et al., 2005).

All rock types are characterised by an alkaline geochemical character, except for the dunites. A significant enrichment of the elements such as Fe, Na, Ca, Al, LREE, LIL and HFSE becomes obvious towards the carbonatite intrusion (Thalhammer and Meisel 2005), (Thalhammer et.al. 2006), (Dvorani 2009). Mckelsen and Thalhammer (2005) report that the Guli massif is strongly influenced by metasomatic mantle fluids and Dvorani (2009) report about metasomatic reaction between the intruding carbonatite and alkali-ultramafic-sequence. In this paper we treat the investigation of fluid inclusion as evidence of fluid reaction between carbonatite and alkali-ultramafic-sequence rocks.

### 2. Method

A detailed mineralogical petrological, geochemical and fluid inclusion investigation was carried out, on the basis of five selected drill cores (Z2, Z3, Z4, G28 and Z12). The drill core locations were selected from the periphery of the dunite core complex in the direction of the carbonatite intrusion. The rock suite investigated is composed of dunite at the periphery of the dunite core complex, showing a typical cumulate texture of the olivine melanephelinites, clinopyroxenite and carbonatite. Sample Preparation and investigation of fluid inclusion was conducted in the Laboratory of Raman spectroscopy at Montan University Leoben (Montanuni Leoben) Austria, also mineral chemistry composition was determined by electron microprobe techniques (ARL SEMQ 30;15 kV; 15 nA). Samples were prepared in polished thin sections for investigation with optimal thickness of 100µm (microns).



Analysis of inclusion fluid phases was carried out with a Jobin Yvon Raman LABRAM spectroscope equipped with a double-Nd-YAG laser (100 mW, 532.2 nm), He-laser (633 nm) and CCD detector matrix. Laser focusing and sample viewing was performed through an OLYMPUS BX 40 microscope with reflected and transmitted light.

The heating and freezing stages of fluid inclusions were performed at temperatures between -190°C and 600°C. The process was controlled through a LINKAM THMSG 600 equipped with an OLYMPUS BX 60 microscope and a PC. Sample images were acquired through a colour video camera and projected on a video monitor.

### 3. Microthermometry

Fluid and melt inclusions are very common in alkaline rocks of the Guli massif, we detected several melt inclusions in perovskite, clinopyroxene, nepheline and apatite, also Kogarko et al. (1991) report on melt inclusions in perovskite and calzirtite from carbonatite intrusion of the Guli massif. In this paper we only discuss investigations into fluid inclusions.

Fluid inclusions were detected in Nepheline, apatite and calcite. A large variability in the fluid

inclusions in terms of form and composition can be identified. Regarding the form spherical, elongated oval and irregular inclusions appear. The analysed inclusions can be divided into two groups. A group contains only two phases L + V and the second group includes L + V + S (L-liquid, V-vapor, S-solid). The inclusions with fluids phases L+V and those with solid phases (S) in the inclusion can be divided into different types with respect to the melting temperature ( $T_m$ ) (Fig.1). FI are below 15 microns in size, homogenization temperatures of fluid inclusion are mostly within a range of 140°C to 406°C. Under high salinity conditions (up to 20wt% NaCl equivalent), exclusively only two types of nephelines which show a positive melting temperature melt at temperatures in a range between (-14.8°C) and (-2.3°C), (Tab.1). Jinzhong (2000) report a very similar condition in fluid inclusion, homogenization temperature and salinity condition in alkaline rocks from Gold deposits in china.

The Fluid phase, salinity,  $T_f$  (freezing temperature),  $T_m$  (melting temperature) and  $T_h$  (homogenization) offer us a better overview of the chemical and physical state of the fluids system. Homogenization temperature can be considered a “minimum T” trapped temperature

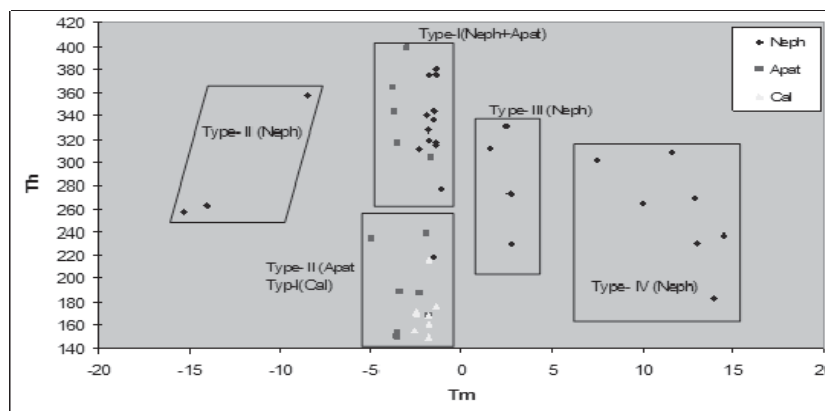


Figure 1. Fluid inclusion (FI) Type in nepheline, apatite, calcite, homogenization temperature ( $T_h$ ), melt temperature ( $T_m$ ).

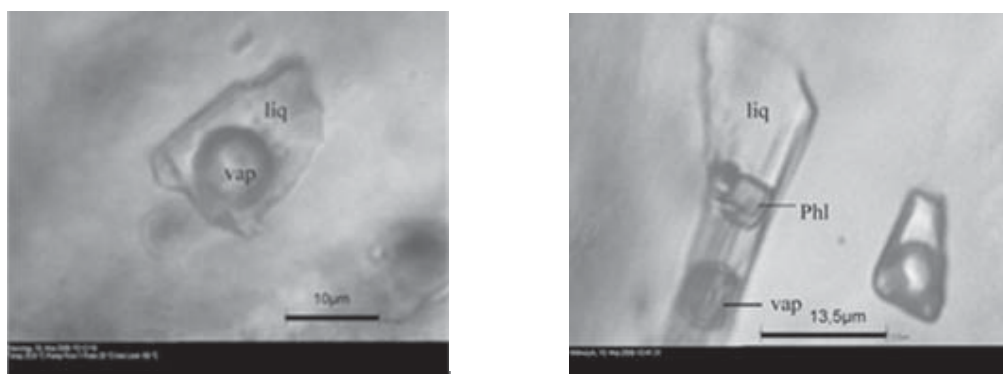


Figure 2. FI in nepheline type-I,  $T_f$  (-43,5°C),  $T_m$  (-2,3°C),  $T_h$  (311,5 °C), type II,  $T_f$  (-53,8 °C),  $T_m$  (-8,5 °C),  $T_h$  (357,3 °C). 3.2 FI in Apatite.

of FI or mineral formation. The fluid inclusions data constrains the geological environment or process of ore formation (Wilkinson 2002), in this case evidence of metasomatic reaction between intruding carbonatite and alkali-ultramafic sequence (Dvorani 2009).

### 3.1. FI in Nepheline

Large numbers of inclusions take place in Nepheline distributed on the whole part of the mineral phase. In this case, it is very difficult to distinguish the primary or secondary Fluid inclusion (FI), but we can conclude that we didn't see any evidence which proved a secondary FI. The inclusions surround L + V and additionally solid phases. The enclosed solid phase is mentioned as "Accidental inclusion", daughter mineral inclusion (Wilkinson 2000). Phlogopite, calcite, apatite and graphite (?) could be identified as solid phases in the FI on the basis of the Raman spectroscopy.

Multiphase FI can be subdivided based on the volumetric relationships at room temperature, the melting temperature and the number of phases (L,V,S) into the Following types:

**Type I**, two phase inclusions (L + V) in the system H<sub>2</sub>O-NaCl. Homogenization temperature (Th) range 218-406 °C, melting temperatures between -1.4 °C and -2.3 °C with salinities of 4.2 to 1.4 wt.% NaCl equivalent (Fig. 2).

**Type II**, FI with the phase composition (L + V + S), whereas phlogopite occurs in the solid phase. This FI has homogenization temperatures between 257.1 and 357.3 °C and melting temperatures (Tm) of -8.5 and

-14.8°C, which corresponds to a high salinity content of 3.12 to 9.19 wt.% NaCl equivalent (Fig. 2).

**Type III**, this type contains FI with or without solid phases (L + V ± S), but with a melting temperature (Tm) between 1.6 and 2.7 °C. The total homogenization temperature is 273-330 °C.

**Type IV**, this group contains inclusions in the system H<sub>2</sub>O-NaCl or (L + V ± S) with very high melting temperatures from 7.5 to 14.5 °C. The total homogenization temperature is between 237-308 °C. With the exclusion of a measured FI with a homogenization temperature (Th) of 183 °C, which is oriented transversely with respect to the examined inclusions (secondary FI)?

The trapped fluids in apatite usually occur elongated or spherical in shape, rarely irregular. The FI can be divided by the total homogenization temperature and the occurring phases (LVS) into two types. Both types have salinities of 2.7 to 7 wt.% NaCl equivalent, with the exclusion of a FI with a salinity of 20.9 wt.% NaCl equivalent.

**Type I**, in these inclusions there are only two phases in the system H<sub>2</sub>O-NaCl (L + V) with melting temperatures of -1.7 to -4.9 °C and total homogenization temperatures in a range between 234.9 °C to 398.6 °C. FI in this group are in principle very similar to fluids of type I in nepheline with significantly higher Salinity. The homogenization temperature corresponds to the range of FI in nepheline (Tab.1).

**Type II**, inclusions of this type H<sub>2</sub>O-salt (L + V ± S) have significantly lower homogenization

**Table 1.** Microthermometry of Fluid Inclusions in nepheline, apatite, calcite.

Mineral	Nephelien								
Typ	Typ-I		Typ-II		Typ-III		Typ-IV		
	<i>min</i>	<i>max</i>	<i>min</i>	<i>max</i>		<i>min</i>	<i>max</i>	<i>min</i>	<i>max</i>
Tf (-°C)	39,50	59,50	41,00	68,00	Tf (-°C)	40,20	57,00	50,00	68,00
Tm(-°C)	1,40	2,30	8,50	14,80	Tm(°C)	1,60	2,70	7,50	14,50
Th (°C)	218,00	406,00	257,10	357,30	Th (°C)	273,00	330,00	183,00	308,00
V vol %	14,30	46,00	1,50	12,50	V vol %	22,50	24,60	9,30	28,90
density	0,55	0,90	0,96	1,14	density	0,75	0,78	0,71	0,90
Salinity %	2,40	4,10	12,30	19,90	Salinity %	nn	nn	nn	nn
Mineral	Apatite				calcite				
Typ	Typ-I		Typ-II						
	<i>min</i>	<i>max</i>	<i>min</i>	<i>max</i>	<i>min</i>	<i>max</i>			
Tf (-°C)	30,10	69,50	50,70	51,50	42,30	44,60			
Tm(-°C)	1,70	4,90	2,30	3,60	1,40	2,60			
Th (°C)	234,90	398,60	149,80	188,90	140,00	216,00			
V vol %	16,90	36,70	8,70	16,90	7,00	26,70			
density	0,66	0,88	0,87	0,96	0,78	0,96			
Salinity %	2,80	7	3,80	5,80	2,70	4,10			

temperatures of 149.8 °C to 188.9 °C, as phlogopite occurs in the solid phase.

### 3.2. FI in calcite

In calcite inclusions are two-phase (L + V) with homogenization temperatures between 140-216 °C and melting temperatures between -1.4 and -2.6. The apatite fluid inclusions of type II confirm homogenization temperatures in the same range. The salinity is in the range of 7.2 to 1.4 wt.% NaCl equivalent (Table 1)

## 4. Conclusion

The geochemical enrichment trend, the significant increase of the mineral phase such as calcite, apatite, sodalite towards that of the carbonatite, as well as the existence of the melt and fluid inclusion etc, in the clinopyroxenites and olivine melaneophelinite in the vicinity of the carbonatite

indicate a metasomatic reaction between intruding carbonatite and the already existing alkali-ultramafic sequence.

This metasomatic reaction according to the investigation occurs in system H<sub>2</sub>O-NaCl under high salinity conditions at temperatures between 140 °C to 406 °C. Melting of two Types (III and IV) of FI in nepheline above 0 °C is uncommon and are unclear phenomena.

The exchange of the chemical element is very clear at this temperature between Fluid and host minerals, the reaction happened in the periphery of the host mineral, which means new zoned periphery are built as well as a different composition and distribution of chemical elements. Elements exchanged between fluid-rock reactions is a physical process invoked as possible control ore deposits.

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## FLUID INCLUSION STUDY AND RAMAN SPECTROSCOPY OF HYDROTHERMAL QUARTZ FROM THE CERTEJ EPITHERMAL ORE DEPOSIT, APUSENI MTS., ROMANIA

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### Abstract

The Certej low sulphidation type epithermal Au deposit, one of the most important in Romania, occurs in the southeastern part of the Apuseni Mts. within the well-known "Gold quadrangle". It is a small-scale ore deposit in the European Goldfields Ltd, 2010 classification, with estimated reserves of 47 million tons at 1.6 g/t average Au content (i.e. 2,41 million ounces Au) and 11.5 g/t average Ag content (i.e. 17.3 million ounces Ag). The licensed company will extract and process 32.8 million tons of primary ore and further 14.1 million tons of waste dump material during the 16 years of planned operation period. The disseminated Au mineralization with invisible gold is hosted in Miocene amphibole andesite and brecciated Cretaceous and Neogene sedimentary rocks (sandstone, microconglomerate and black claystone). The ore deposits are closely related to the calc-alkaline andesite-dominated volcanic and intrusive activity (14.7-7.4 Ma) in the Apuseni Mts., representing the "Internal segment" of the Carpathian-Pannonian Neogene-Quaternary igneous province. The characteristic mineral association of the studied ore deposit consists of pyrite, sphalerite, galena, chalcopyrite, tetraedrite-tennantite series minerals, bournonite, arsenopyrite, pyrrhotite and mackinawite accompanied by quartz, calcite and barite as gangue minerals. Pyritization, silicification, adularization, carbonatization and sericitization are the prevailing hydrothermal alteration types in relation to the main mineralization stage. Our research was focused on the study of fluid inclusions found mostly in hydrothermal quartz crystals of representative samples collected at various levels of the former subsurface mine and of the current open pit covering a vertical extent of

the ore deposit of 170 m. More than 500 individual fluid inclusion measurements have been conducted using a Chaixmeca-and USGS type heating/cooling stage at the Mineralogy and Petrology departments of Eötvös Loránd University in Budapest, Hungary. According to the results obtained, the primary and secondary fluid inclusions in quartz and sphalerite crystals were trapped from a heterogeneous (boiling) fluid. Measured homogenization temperatures range between 178.8–333.8°C, however, due to the occurrence of heterogeneous entrapment, the temperature of ore forming processes most probably occurred at around 180 – 230°C. We consider these values representative for the fluid inclusion entrapment temperatures. The determined eutectic temperatures of the fluid inclusion brines range between -19.3 and -24.4 °C, while freezing point depressions from -4.1 to -0.1°C. The final melting temperature mostly occurs between -0.1 and -3.3°C and thus fluid inclusion salinities are in the range 0.18–5.41 wt.% NaCl. These data allowed for pressure calculations and determination of the corresponding depths of the paleo-watertable (100–300 m) at the time of the mineralization processes. Vapor-rich fluid inclusion compositions in selected quartz crystals were determined using Raman spectroscopy through which the main chemical components, have been identified and their abundances ( $H_2O = 67.00-99.98\%$ ,  $N_2 = 0.00-7.24\%$ ,  $CO_2 = 0.00-29.75\%$ ) calculated. The quantitative data obtained, characteristic for hydrothermal fluids, allowed to better understand the paleoenvironment and the chemical and thermodynamic conditions in which the Certej Au deposit has formed.



## SOME GEOCHEMICAL FEATURES OF THE SULFUR MINERALIZATION IN THE GASHI ZONE

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### Abstract

In order to evaluate the geochemical features of the sulfur mineralization in the Gashi Zone, a considerable number of chemical and spectral-chemical analysis of the sulphur ores were statistically analyzed. The geochemical data of the ores were statistically analyzed for each the following ore deposits and ore occurrences: Kreshta, Çeremi, Livadhi i Katanes, Lluzhnica, Baliaj, Presh, Tringellime, Kersh i Kuq, Rreshkeza, Mollafci, Breu i Çobaneve, Doberdoli and Rupa. The results of the statistical analysis (correlation coefficients, factor analysis etc.) show that: (i) the highest values of geochemical factors were observed for the Rupa mineralization, where both factors have a value up to 5. In the other ore deposits and occurrences, the factors do not surpass the value of 1.5; (ii) it is not observed a strong correlation between the geochemical factors and the

spatial location of the samples. This is interpreted to show that there are not two independent Cu and polymetallic sulphur mineralizations, but two superimposed mineralizations in different spatial locations and sometimes in the same locality??. (iii) in the Rupa mineralization, the high values of each of the factors were observed in different samples, indicating that the two generations of Cu and polymetallic sulphur mineralization differ from each other in space and time; (iv) in the other sulphur mineralizations (with the exception of Rupa), the geochemical factors have lower weights and their spatial superposition is clearer. The geochemical factors show two different sulphur mineralization generations in the Gashi zone: a polymetallic sulphur mineralization and a copper rich sulphur mineralization. Based on the available geochemical data, it cannot be concluded if these two sulfur mineralization generations belong to the same hydrothermal solution or to two unrelated hydrothermal solutions.

## CORRELATIONS BETWEEN OUTDOOR GAMMA RADIATION LEVELS AND CONCENTRATION OF $^{232}\text{Th}$ , $^{238}\text{U}$ AND $^{40}\text{K}$ IN SOILS DEVELOPED ON ALKALINE ROCKS IN DITRĂU MASSIF AREA – EASTERN CARPATHIANS, ROMANIA

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### Abstract

This study assesses the level of terrestrial gamma radiation in air associated by the presence of the naturally occurring radionuclides  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{40}\text{K}$  in soils developed on alkaline rocks in an area of approximately 200 km<sup>2</sup> covering the Massif Alkaline Ditrău. This massif, unique by mineralogical and petrographical variety, is emplaced in metamorphic basement rocks belonging to the Tulghes Group, in the internal part of the Eastern Carpathians. The large variety of alkaline rocks (hornblendite, diorite, syenite, nepheline syenite, monzonite, monzodiorite, aplite, granitoides) is fairly rich in radioelement concentrations. Thorium and uranium are constituents of the accessory minerals as zircon, monazite, titanite, allanite, apatite, xenotime, rutile. Potassium is associated with feldspar mineral series, feldspathoids (nepheline) and micas (biotite and muscovite). The young soil developed on these rocks, has undeveloped a depth profile with a mineralogical composition dominated by the presence of unaltered primary minerals.

The outdoor gamma radiation levels-estimated as *gamma dose rate* was determined in air at 1 m above ground, in 70 measurement points, same points in which the soil samples were collected. The radiation levels above ground are controlled by types of rocks from which the soil originates, depth profile of soil, soil density, ground cover by grass. Also, the gamma dose rate in air varies somewhat with time being influenced by rainfall, soil moisture and snow cover.

The field radiometric measurements and sampling of soil have been performed in relation to the type of bedrock. A portable gamma monitor (BERTHOLD UMo LB-123) was using for field measurements of dose rate and were recorded values between 0.138  $\mu\text{Sv/h}$  and 0.585  $\mu\text{Sv/h}$  with an average of 0.261  $\mu\text{Sv/h}$ . The outdoor gamma radiation level frequently surpasses the threshold value of 0.200  $\mu\text{Sv/h}$ . The annual individual effective dose equivalent was calculated in the range between 1.2 mSv/yr to 5.21 mSv/yr, with an arithmetic mean of 2.28 mSv/yr. Although 2.28 mSv/yr is less than the recommended safe levels and for more than 50%

measurement locations were calculated higher values than the global average (2.44 mSv/yr). The concentration of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  determinate in soil samples are in good agreement with in-situ radiometric measurements.

The specific activity of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in 70 soil samples have been determined by low background gamma-ray spectroscopy using an n-type high purity germanium detector (relative efficiency of 27%, resolution of 1.80 at  $^{60}\text{Co}$  1.33 MeV and peak/Compton ratio of 56:1) connected with a MCA (ORTEC). The average of  $^{238}\text{U}$  specific activity in soil is 36.8 Bq/kg and 58.8 Bq/Kg for  $^{232}\text{Th}$ , whereas the  $^{40}\text{K}$  specific activity in soil has an average of 181 Bg/kg. These dates showed that the soils of the massif are enriched in radionuclides in according with rocks data. The spatial correlation between distribution of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in soil and the geological background of Ditrău massif indicated that the soil above the sienite and nephelin sienite, from the central part of the massif, is enriched in uranium. The distribution of  $^{232}\text{Th}$  and  $^{40}\text{K}$  concentrations shows some relationships with the petrography of the underlying rocks, especially with the porphyritic K-feldspar granitoides and contact rocks occurring in northern, eastern and southern parts of the massif. Unlike U, the average K and Th content of soils reflects the average K and Th content of the rocks from which they are derived. The higher values of annual individual effective dose equivalent was estimated only in the points from massif area which characterized by the highest value of  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{40}\text{K}$  in soil samples associate with presence of REE+ Th+ U mineralizations. Also, the correlation matrix between gamma dose rate values and  $^{238}\text{U}$  (0.37),  $^{232}\text{Th}$  (0.57) and  $^{40}\text{K}$  (0.21) specific activities from soil samples suggesting that the  $^{232}\text{Th}$  is the main contributor to outdoor gamma levels in Ditrău massif area, followed by  $^{238}\text{U}$  and  $^{40}\text{K}$ .

All these data, clearly indicate that the gamma dose rate in air depend on the types of bedrock which is the primary source of gamma radiation being possible a risk assessment given by radiation exposure in Ditrău massif inhabited area.

## SUSPENDED MINERALS IN THE GROUNDWATERS OF AMYNTEO BASIN (NW GREECE), AS DETECTED BY RAMAN AND ELECTRON MICROSCOPY

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### Abstract

The aim of the present study is the application of complementary, state of the art, analytical techniques for the identification of suspended particles in the groundwaters of the Amynteo hydrogeological basin (NW Greece). Ten groundwater samples were collected from several depths throughout this area, which were vacuum filtered. The suspended particles trapped in the filters were analysed by Raman microscopy and Scanning Electron Microscopy (SEM) coupled to Energy Dispersive System (EDS). These two techniques were combined in order to certify the analytical results. The identified main minerals were quartz, hematite, pyrite, microcline, along with the accessory minerals as actinolite, baryte, monazite, zircon and pyrrhotite. Coal particulates were also determined related to the Amynteo lignite deposit of the area. All minerals are obviously related to the lithostromatography of the region including metamorphic rocks (gneisses, amphibolitic schists, slates), carbonates and granites. Overall, the combined utilization of the Raman and Electron Microscopy provided precise determination of the mineralogical and geochemical features of the groundwater's suspended particles.

**Key words:** *suspended particles, groundwaters, ESEM-EDS, Raman, Amynteo*

### Introduction

Suspended particles in the groundwaters are directly related to the lithology of the aquifers. Therefore, their precise determination may provide useful information regarding hydrogeological (groundwater plumes, movement direction and dispersion etc.) and environmental (water quality) issues. Several state of the art analytical methodologies can be applied for the identification of morphological, mineralogical and chemical characteristics of suspended particles. Image

analysis, using the conventional Scanning Electron Microscopy (SEM), coupled to energy dispersive system (EDS) for the chemical analysis, is widely used for such analyses. Raman spectroscopy is also becoming increasingly important in a broad range of scientific disciplines. Raman spectroscopy combined with a con-focal microscope is a powerful technique for the identification of particles in micrometer scale. In the present study, the effectiveness and the advantages of Raman and SEM microscopy are examined, in an effort to identify suspended particulates in the groundwaters.

### Description of the study area

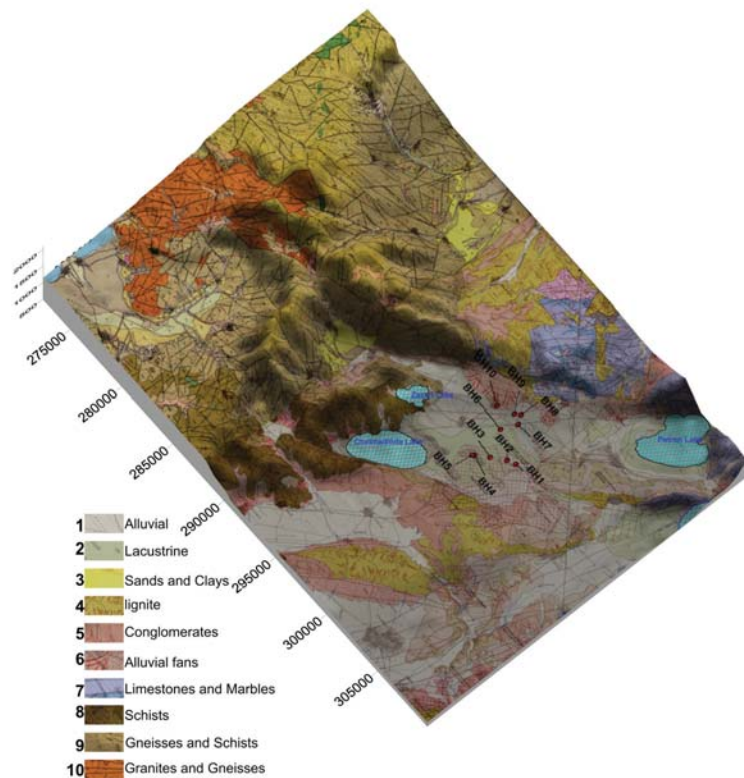
The elongated intermontaine Florina-Ptolemais-Kozani basin is a NNW-SSE trending graben, which extends over a distance of 250 km from Bitola, in the Former Yugoslavian Republic of Macedonia to Serbia, southeast of Kozani, Greece. Within this basin, Pliocene lignite beds alternate with marls, clays and sands. There is a great variance in the thickness of the overburden, intermediate and floor rocks as well as in the thickness of lignite seams (Iordanidis et al. 2014a). The bedrock formations are Mesozoic carbonates, metamorphic rocks (gneisses, amphibolites, and slates) and partial granite intrusions (IGME, 1997). The Amynteo hydrogeological basin, i.e. the study area, has a total surface of 228 km<sup>2</sup> and belongs to the aforementioned coal-bearing basin (Gudulas, 2012). Numerous wells are located in the area, some of them employed for the drainage of the Amynteo open-pit lignite mine (Fig. 1).

### Materials and Methods

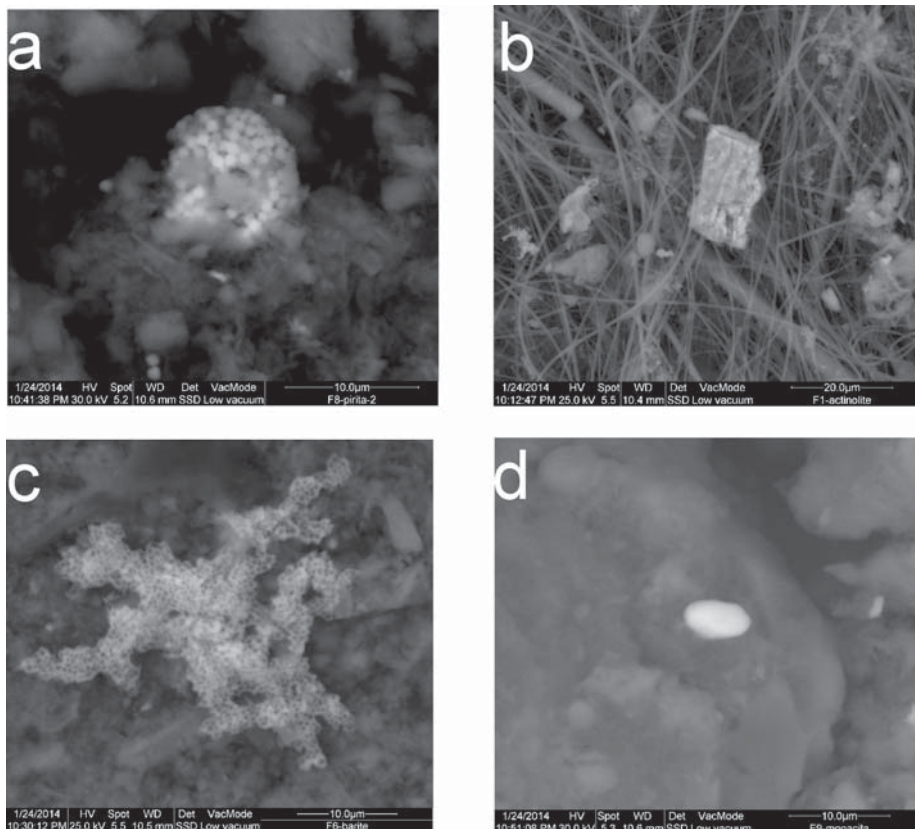
Ten groundwater samples were collected from the study area, which were vacuum filtered in order to remove suspended particulate matter from the aqueous phase. All filters were analysed by ESEM-EDS and Raman spectroscopy. A Philips

QUANTA 200 Environmental Scanning Electron Microscope (ESEM), coupled with an Oxford INCA Energy 200 Energy Dispersive System

(EDS) was used for the chemical analyses and the recording of pictures, under back-scattered electron (BSE) mode. A Thermo Scientific DXR



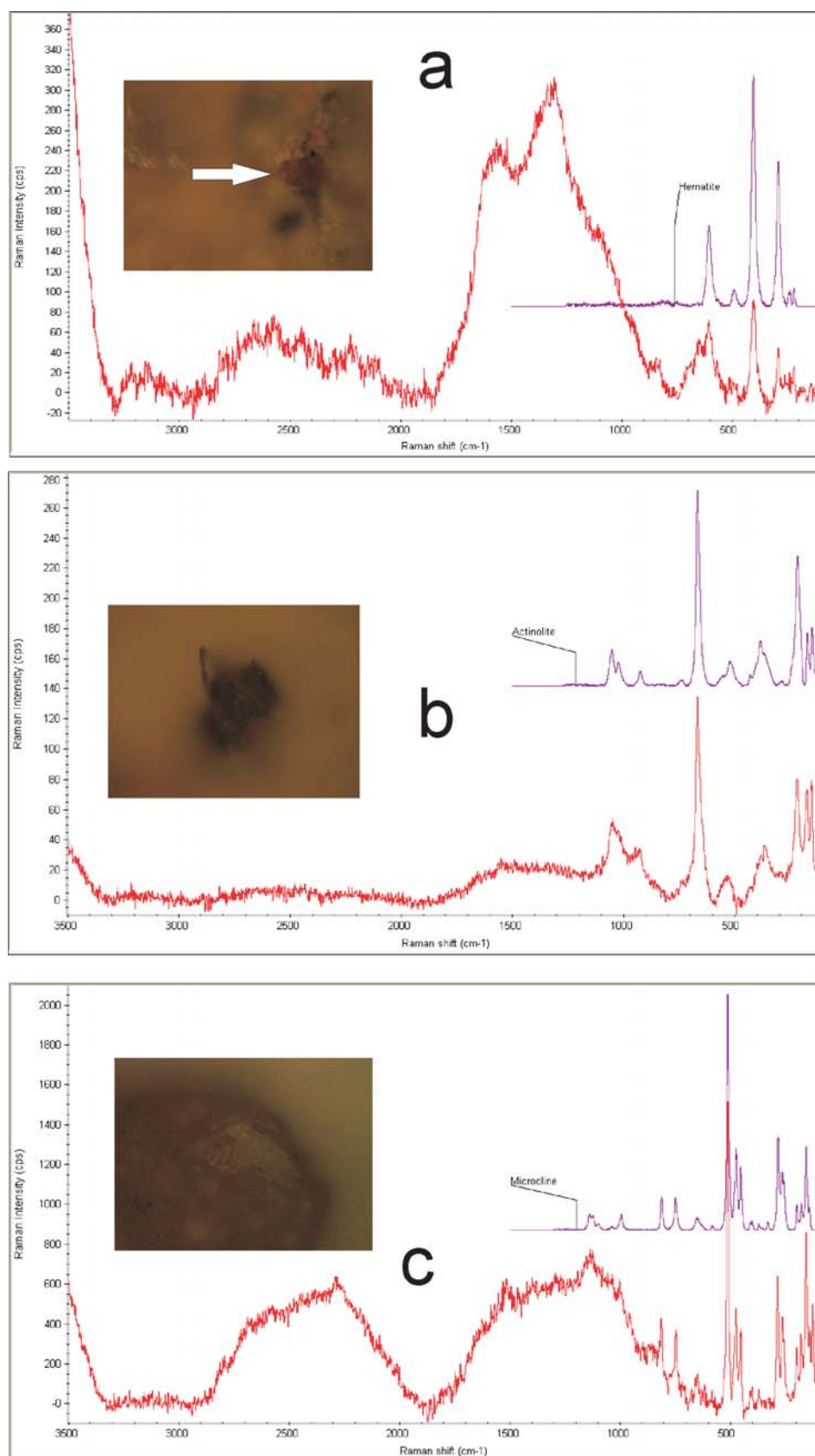
**Figure 1.** Geological map and sampling sites of ten groundwater samples from the Amynteo coal-bearing basin of northern Greece.



**Figure 2.**

ESEM photomicrographs of characteristic suspended minerals found in the groundwater samples of this study: a) framboid of pyrite ( $\text{FeS}_2$ ), b) actinolite [ $\text{Ca}_2(\text{Mg}, \text{Fe}^{++})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ], c) baryte ( $\text{BaSO}_4$ ), d) monazite [ $(\text{Ce}, \text{La})\text{PO}_4$ ].





**Figure 3.** Raman spectra and photomicrographs of characteristic suspended particles, along with their assignment to specific minerals: **a)** hematite ( $\text{Fe}_2\text{O}_3$ ) **b)** actinolite [ $\text{Ca}_2(\text{Mg}, \text{Fe}^{++})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ] **c)** microcline ( $\text{KAlSi}_3\text{O}_8$ ). The horizontal scale on each photomicrograph is approximately 50  $\mu\text{m}$ .

Raman Microscope with two laser beams, one at 780 nm and another at 532 nm, was also employed. The analytical parameters are described elsewhere (Iordanidis et al. 2014b).

## Results

ESEM/EDS and Raman spectroscopy yielded valuable information for the nature of the groundwater's suspended particulates. Micro-Raman microscopy provided a rapid and accurate identification of minute (down to 2  $\mu\text{m}$ ) suspended minerals. Several distinct mineral phases were effectively determined, such as the common minerals quartz, hematite, pyrite, microcline, along with minor minerals as actinolite, baryte, monazite, zircon and pyrrhotite (Figs 2 and 3). Coal particulates were also determined related to the Amynteo lignite deposit of the area. All minerals are related to the lithological units of the region, which includes metamorphic rocks (gneisses, amphibolitic schists, slates), carboantes and granites.

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## GRANITIC ROCKS – WINDOWS TO CRUSTAL EVOLUTION DURING THE PHANEROZOIC IN THE WESTERN CARPATHIANS

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### Abstract

The evolution of the continental crust is reflected by major magmatic events, which have been produced at both convergent margins and within plate tectonic environments. Granitic rocks – acid, felsic igneous rocks that crystallized from magma represent important constituent of continental crust and their origin is generally related to subduction and collisional processes, where melting process require middle- to lower crustal P-T condition. The genesis of the Paleozoic, Mesozoic and Cenozoic granitic rocks from the Western Carpathian is discussed in the frame of the European tectonic evolution from the Caledonian peri-Gondwanan margin to the Neo-Alpine back-arc extension within the Carpathians arc. Changing tectonic processes produced in the Western Carpathians following orogenic granitic suites: *i*) the Late Cambrian-Ordovician felsic magmatites/volcanites now – orthogneisses; *ii*) the Late Devonian subduction related (gabbro)dioritic mafic suite; *iii*) the Early Carboniferous calc-alkaline I-type and/or I/S hybrid tonalites and granodiorites; *iv*) the Middle Carboniferous (Visean) peraluminous S-type granites and subaluminous I/S-type granodiorites; *v*) the Early Permian post-orogenic subalkaline A-type granites; *vi*) the Middle Permian specialised ore-bearing S<sub>s</sub>-type granites; *vii*) the Late Cretaceous calc-alkaline “banatitic” granites, and *viii*) the Miocene calc-alkaline granites. Different granite types well mirrored changing tectonic processes from rifting, subduction and amalgamation of an oceanic/sub-continental lithosphere, through collision with lithospheric thickening, followed by delamination or break-off and finished in extensional tectonic during three orogenic cycles. The recycled continental crust with a contribution from lithospheric mantle plays crucial role at their genesis and compositions, as a matter of repeated intrusions of the Andean-type calc-alkaline and the Himalayan-type peraluminous and/or scarce A-type alkaline granitic magmas.

**Key words:** *Western Carpathians, granitic rocks, tectonics, petrology*

### Introduction

The Western Carpathians as a part of Stille's (1924) Neo-Europa form a piece of an extensive, equatorial, orogenic belt extending from the Atlas Mountains in Morocco, through the Alps, Dinarides, Pontides, Zagros, and Hindukush to the Himalayas and to China. They are the northernmost, E–W trending branch of this Alpine belt, linked to the Eastern Alps in the west and to the Eastern Carpathians in the east. The present-day structure of the Western Carpathians was derived from the Late Jurassic to Tertiary (Alpine) orogenic processes connected with the evolution of the Tethys Ocean, in a long mobile belt sandwiched between the stable North European Plate and continental fragments of the African origin. Albeit the Western Carpathians belong to Neo-Europa, their pre-Mesozoic basement rocks represent distinctive analogues of the basement ones known in the Meso- and Paleo-Europa (Stille 1924). A typical feature of the Carpathians mobile belt is the presence of huge reworked slices of the pre-Alpine crystalline basements within the Mesozoic and Cenozoic sedimentary successions that have been deformed into large-scale nappe structures. The polyorogenic history of a basement is characterised by juxtaposition of various terranes and/or blocks that in most cases originated at the Gondwana margin due to multistage tectonic evolution with large-scale nappe and strike-slip tectonics, what resulted in the European Variscan collisional orogeny. The pre-Alpine granite bearing crystalline basement crops out mainly in the Central Western Carpathians (CWC), heart of the Western Carpathians, consisting of three principal crustal-scale superunits from north to south – the Tatricum, Veporicum and Gemericum. However, besides the pre-Mesozoic granites, there are present the Alpine ones like the Late Cretaceous – Rochovce subsurface granite intrusion emplaced into the contact zone between the Veporicum and the Gemericum and the Miocene granitic rocks of the Central Slovakian Neovolcanic field (CSNF) within the Western Carpathians.

## Results and Discussion

The Cambrian-Ordovician felsic magmatites/volcanites that were sheared to orthogneisses are presented mainly within the polymetamorphosed basement in the Veporicum and Tatricum units. They are felsic coarse-grained and porphyritic to medium-grained rocks with K-feldspar, plagioclase, albite, quartz, biotite, phengitic white mica, minor monazite and garnet. Geochemical characteristics:  $\text{SiO}_2$  vary in 70~77 wt.%,  $\text{K}_2\text{O}/\text{Na}_2\text{O} = 0.54\sim 1.38$ ;  $\text{Rb}/\text{Sr} = 0.8\sim 2.3$ ; contents of Ga, Y, Th, U, and Co have slightly enriched, whereas Sr and Zr they have depleted. Generally, have peraluminous character ( $\text{ASI} = 1.0\sim 1.4$ ). REE's have moderate values and show typical fractionated pattern with distinct negative Eu anomaly, and partly elevated HREE contents controlled by presence of monazite and apatite. Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values range 0.709~0.725 and  $\epsilon\text{Nd}_{(i)}$  between -8.3~2.6 are suggesting rather for their crustal source alike their Pb/Pb isotopic characteristics ( $^{206}\text{Pb}/^{204}\text{Pb} = 19.58\sim 20.65$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.67\sim 15.76$  and  $^{208}\text{Pb}/^{204}\text{Pb} = 38.95\sim 40.10$ ) with hint of the lower crustal metaigneous source. The Early Palaeozoic zircon  $\epsilon\text{Hf}_{(i)} = -7.7\sim -2.8$  reflect their crustal character, whereas the Proterozoic restitic zircon cores having  $\epsilon\text{Hf}_{(i)} = +3.8\sim +13.0$  indicate former mantle character for part of the sedimentary protolith. The stable isotopes with  $\delta^{18}\text{O} = 11.0\sim 11.7\text{‰}$  and  $\delta^7\text{Li} = -4.5\sim +1.6\text{‰}$  call for crustal source. Protomagmatic ages of these orthogneisses were dated by SHRIMP at 515~460 Ma (Putiš et al. 2009), metamorphic conditions were partly masked by the Variscan migmatization reaching up to ca.  $P = 0.8\sim 1.0$  GPa and  $T = 700\sim 800^\circ\text{C}$ .

The Late Devonian subduction related (gabbro)dioritic mafic suite is represented by scarce plagiogabbros and more common diorites. The pyroxene gabbros are medium- to coarse-grained rocks with characteristic mineral assemblage consisting mainly of calcic plagioclase, pyroxene and ilmenite; hornblende and biotite commonly formed by late-magmatic pyroxene alteration, or rather during the Variscan metamorphism. Major- and trace-element distribution illustrates an E-MORB affinity. Gabbros have low HFSE abundances and elevated contents of REE as well as steep chondrite-normalized REE patterns ( $\text{La}_N/\text{Yb}_N = 5.3\sim 27.5$ ). Variable degrees of Eu depletion/enrichment ( $\text{Eu}/\text{Eu}^* = 0.8\sim 1.2$ ) were observed. Diorites are medium- to coarse-grained rocks dominated by plagioclase, quartz, biotite

and hornblende. Accessory minerals include allanite, epidote, titanite, magnetite, hematite, zircon, monazite, xenotime and apatite. Diorites are mainly metaluminous to peraluminous rocks ( $\text{ASI} = 0.8\sim 1.3$ ), showing enrichments in  $\text{MgO}$ ,  $\text{FeO}$  and  $\text{CaO}$  relative to other granitic rocks of the CWC. Typical features are high contents of REE ( $\Sigma\text{REE}$  up to 400 ppm) and slight LREE enrichments; Eu anomaly is comparable to reported gabbros ( $\text{Eu}/\text{Eu}^* = 0.8 \sim 1.1$ ). The radiogenic isotope data  $^{206}\text{Pb}/^{204}\text{Pb} = 18.63\sim 18.77$ ;  $^{207}\text{Pb}/^{204}\text{Pb} = 15.67\sim 15.74$ ;  $^{208}\text{Pb}/^{204}\text{Pb} = 38.43\sim 38.68$ ;  $^{87}\text{Sr}/^{86}\text{Sr}_{(i)} = 0.704\sim 0.707$ ;  $\epsilon\text{Nd}_{(i)} = +0.7\sim +2.1$ ; zircon  $\epsilon\text{Hf}_{(i)} = +2.6\sim +9.4$ , together with their stable isotopic characteristics  $\delta^{18}\text{O} = 7.8\sim 8.4\text{‰}$ ;  $\delta^{34}\text{S} = +0.4\sim +0.7\text{‰}$  and  $\delta^7\text{Li} = -2.9\sim -0.5$ ) correspond to a lower crustal mafic (basic meta-igneous) source with limited mantle-derived contribution. Recent SHRIMP zircon dating (Putiš et al. 2009) exhibits their ages between 385 and 370 Ma, whereas most of diorites display age close 350 Ma.

The Early Carboniferous (Early Mississippian) calc-alkaline I-type and/or I/S hybrid tonalites and granodiorites represent dominant granitic suite within CWC and are common in the Core Mountains of the Tatricum and within the Veporic composite batholith. Generally, they are rather metaluminous to subaluminous ( $\text{ASI} = 0.8\sim 1.1$ ), dominated by biotite tonalite to granodiorite with scarce hornblende. Muscovite-biotite granodiorite to granite are less frequent. The accessory mineral association magnetite + allanite, and the occurrence of mafic microgranular enclaves (MME), are characteristic of this group. Lower  $\text{SiO}_2$  concentrations 60~70 wt. %, coincide with higher trace elements Zr, Ba, Sr (up to 380, 1350 and 800 ppm), higher LREE and Fe group element contents. REE patterns are typically steeper, with higher LREE and without Eu anomaly. These rocks are clearly richer in  $\text{CaO}$ ,  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  than subsequent granites, whereas  $\text{K}_2\text{O}/\text{Na}_2\text{O} = 0.5\sim 0.9$ . The initial  $\text{Sr} = 0.704\sim 0.709$ ;  $\epsilon\text{Nd}_{(i)} = -2.8\sim +2.2$  clearly indicate interaction with a basic or intermediate (dioritic) lower crustal melt, what confirm their zircon  $\epsilon\text{Hf}_{(i)} = -0.3\sim +7.6$  as well. The  $^{206}\text{Pb}/^{204}\text{Pb} = 17.99\sim 18.85$ , and  $^{207}\text{Pb}/^{204}\text{Pb} = 15.53 \sim 15.70$  suggest heterogeneous continental crustal source with recycled oceanic crust. The stable isotopic ratios with  $\delta^{18}\text{O} = 7.8\sim 9.9\text{‰}$ ;  $\delta^{34}\text{S} = -2.9\sim +2.3\text{‰}$  and  $\delta^7\text{Li} = -1.2\sim +0.5\text{‰}$  support melting of a more basic lower crustal protolith. Magmatic intrusion ages of this I-type and/or I/S hybrid granitic group vary between 365~350 Ma



(Kohút et al. 2009; Kohút et al. 2010; Kohút et al. 2013a; Broska et al. 2013).

The Middle Carboniferous (Middle Mississippian) peraluminous S-type granites and subaluminous I/S-type granodiorites alike previous groups are common in the Core Mountains of Tatricum and the Veporicum composite batholith where made typical intrusion in intrusion. They are peraluminous ( $ASI = 1.1\sim1.5$ ), dominated by two-mica granodiorites and granites while biotite granodiorites to tonalites are less common. The accessory mineral association monazite + ilmenite, and the presence of metamorphic xenoliths are typical. Geochemically: Ba, Sr and Rb range widely (up to 1600, 600 and 200 ppm respectively) with  $Rb/Sr = 0.2\sim0.8$ ; rarely up to 1.8;  $SiO_2 = 65\sim77$  wt. % and  $K_2O/Na_2O = 0.7\sim1.4$ . The contents of CaO,  $TiO_2$  and  $P_2O_5$  are generally low ( $<2.5$ ;  $<0.7$  and  $<0.3$  wt. %). The REE content is moderate, with a fractionated pattern and a small negative Eu anomaly. Initial Sr ratios =  $0.706\sim0.714$ ;  $\epsilon Nd_{(i)} = -7.7\sim-1.3$ ;  $\epsilon Hf_{(i)} = -7.7\sim+2.5$ ; the  $^{206}Pb/^{204}Pb = 18.39\sim19.28$  and  $^{207}Pb/^{204}Pb = 15.59\sim15.74$ , and the stable isotope values  $\delta^{18}O = 8.8\sim11.3\text{‰}$ ;  $\delta^{34}S = -0.9\sim+5.7\text{‰}$  and  $\delta^7Li = -3.2\sim+7.0\text{‰}$  what indicate substantial crustal recycling at their genesis. New SHRIMP zircon ages of this S-type and I/S granitic suite are ranging between 343~332 Ma (Kohút et al. 2009; Kohút et al. 2010; Kohút et al. 2013a).

The Permian mildly alkalic A-type group of granites occurred within the Veporicum and its border zone with Gemericum. Various petrographic types like porphyritic, aplitic to microaplitic varieties and granite porphyries were observed. They exhibit: high Si, K, F, REE, Ga/Al, sometimes Na, Rb, Zr, Nb, Y and W; low Ti, Mg, Ca, P, Ba, Sr, and V contents;  $SiO_2 = 70\sim77$  wt. %, peraluminous character  $ASI = 1.0\sim1.3$ ,  $K_2O = 4\sim5$  wt. %, Rb =  $66\sim280$ , high Ga =  $17\sim35$ , F =  $350\sim500$ , Th =  $10\sim52$ ; low Sr =  $30\sim110$ , Ba =  $50\sim500$  rarely up to 1300 (all in ppm). Particularly distinct fractionated patterns REE's have pronounced negative Eu-anomaly.  $^{87}Sr/^{86}Sr_{(i)} = 0.705\sim0.709$ ;  $\epsilon Nd_{(i)} = -3.1\sim+1.9$ ; zircon  $\epsilon Hf_{(i)} = +0.2\sim+9.9$ . Depleted stable isotopes values  $\delta^{18}O = 7.8\sim8.0\text{‰}$ ,  $\delta^{34}S = -2.0\sim-0.7\text{‰}$  and  $\delta^7Li = +4.7\sim+6.6\text{‰}$  indicate a lower crustal meta-igneous protolith influenced by slab-derived fluids. Recent SHRIMP zircon data suggest for 283~262 Ma of their magmatic age (Uher et al. 2010).

The Middle Permian ore bearing  $S_s$ -type granites

are found only in Gemericum. They have elevated  $SiO_2 = 73\sim78$  wt.%, a strongly peraluminous character  $ASI = 1.2\sim1.6$ , high concentrations of F, B, Rb, Li, Cs, Sn, Mo, Be and low contents of Sr, Ba, Zr and V. Isotopic characteristics  $^{87}Sr/^{86}Sr_{(i)} = 0.707\sim0.725$ ; negative  $\epsilon Nd_{(i)} = -4.6\sim-0.3$ ; zircon  $\epsilon Hf_{(i)} = -5.3\sim-0.7$ , lead isotopes with high  $^{206}Pb/^{204}Pb$  above 18.6 and high  $^{207}Pb/^{204}Pb$  above 15.7; and/or elevated stable isotopes values  $\delta^{18}O = 10.0\sim10.4\text{‰}$ ,  $\delta^{34}S = 4.5\text{‰}$ ,  $\delta^7Li = -1.4\sim+1.2\text{‰}$  and tourmaline  $\delta^{11}B = -14.2\sim-10.3\text{‰}$  indicate a mature continental feldspar and muscovite-rich metasedimentary protolith with admixture of the lower crust that experienced sea-floor weathering. The Permian age ( $263 \pm 0.8$  Ma) was confirmed by recent Re-Os molybdenite dating from greisen endocontact (Kohút and Stein, 2005).

The Late Cretaceous – Rochovce hidden granitic body was discovered by geophysics in the contact zone between Veporicum and Gemericum. Two intrusive phases comprise: 1<sup>st</sup> coarse-grained biotite monzogranites with the pink K-feldspars phenocrysts, locally with mafic microgranular enclaves, and granite porphyries; 2<sup>nd</sup> more evolved type is representing by medium- to fine-grained biotite leucogranites and leuco-porphyries. They have normal to elevated  $SiO_2 = 66\sim77$  wt. %, typical calc-alkaline, subaluminous to peraluminous character  $ASI = 0.9\sim1.4$ , high concentrations of Ba, Rb, Li, Cs, Mo, Nb, Y, V, W, Cr, F, Th, U and low concentrations of Sr, Zr and Be. The low  $I_{Sr} = 0.708\sim0.713$ , together with negative  $\epsilon Nd_{(i)} = -3.0\sim-2.4$ , zircon  $\epsilon Hf_{(i)} = -5.2\sim+0.2$ , and stable isotopes  $\delta^{18}O = 8.0\sim8.3\text{‰}$ ;  $\delta^{34}S = -2.1\text{‰}$ ;  $\delta^7Li = 4.7\text{‰}$  suggest a lower crustal meta-igneous protolith. Their Cretaceous magmatic age 81.5 Ma was proved by SHRIMP zircon U-Th-Pb and Re-Os molybdenite dating (Kohút et al. 2013).

The Miocene calc-alkaline granitic rocks are presented only in the Central Slovakian Neovolcanic field (CSNF). The massive granodiorites consist of intermediate plagioclase, quartz, K-feldspar, biotite, amphibole, and accessory magnetite, titanite, pyroxene, apatite and zircon. The rock's texture is evengrained and porphyric in marginal parts, locally with mafic microgranular enclaves. The granitic rocks are often altered – sericitized, chloritized and propylitized. These granodiorites have standard values of  $SiO_2 = 59\sim66$  wt.%, higher contents of CaO, FeO, MgO and lower content of  $TiO_2$ . Generally, they have enriched Ba, Cr, V and F, whereas values of Sr, Rb and Zr are

standard compared to other CWC granites. The initial Sr values of 0.706–0.710 and/or isotopic characteristics of CSNF en bloc suggest a lower crustal source affected by lithospheric mantle and its I-type character. New SHRIMP zircon and ZHe dating proved their age at 13 Ma (Kohút and Danišík 2012).

## Conclusions

Presented review throughout the time show that granitic rocks mirrored orogenic evolution within the Western Carpathians since the Cambrian to the Miocene. Various types of granitic rocks and their composition document change of tectonic processes from rifting, subduction and amalgamation of an oceanic lithosphere, through collision with lithospheric thickening, followed by delamination or slab break-off and finished in extensional tectonic during three orogenic cycles. Many similarities in character of these granites indicate repeating origin of calc-alkaline I-types, peraluminous S-types and scarce alkaline A-type granites in our realm, while M-type granites were not proved yet, indeed some indications of plagiogranites exist there mainly within LAC complexes. Taking in account: granite typology, their ages, associated mafic and/or metamorphic host rocks and their P-T conditions, it is obvious that the Western Carpathians granites originated during several stages of convergent orogeny mainly at an active Andean-type arc, and Himalayan continental collisional processes within the Caledonian, Variscan and Alpine orogeny during the Phanerozoic times.

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## BI-MINERAL ASSOCIATION WITHIN THE SKARN ORE AT THE STAN TERG DEPOSIT (TREPÇA, KOSOVO)

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### Abstract

The Stan Terg deposit is described as a classic example of the Pb-Zn-Ag skarn-type deposit, however the majority of ore has hydrothermal origin. Two main paragenesis are known from the deposit: skarn one with silicates, magnetite, pyrrhotite and galena as well as hydrothermal one with sphalerite, galena, pyrite, pyrrhotite, boulangerite, Ag-minerals, stannite as well as numerous types of carbonates. The significant content of bismuth allowed the production of this metal in the past years. This is the new scientific report about form and distribution of bismuth in the deposit.

The investigated samples have been collected from X<sup>th</sup> and IX<sup>th</sup> horizons in the mine from the northern part of the deposit. The samples comprises massive galena intergrowth with pyrrhotite in association with skarn minerals. They were investigated by the mean of reflected light microscopy and the chemical composition of bismuth minerals as well as galena was examined by electron microprobe.

The skarn mineral paragenesis in the Stan Terg deposit comprises silicates (mainly hedenbergite and ilvaite) and sulphides pyrite, pyrrhotite, sphalerite and galena. Magnetite is very common. Small grains of native gold (up to few microns) have been found in association with Ti oxides and galena within silicates. Not all galena grains in association with skarn-silicates contain inclusions of Bi-bearing minerals.

The presence of investigated association of Bi minerals has been confirmed by microprobe analyses. The Bi-bearing sulphosalts, bismuthinite and native bismuth occur as fine inclusions within

Bi and Ag-bearing galena ( $\text{Pb}_{0.98}\text{Ag}_{0.01}\text{Bi}_{0.01}\text{S}_{1.00}$ ). Galena has higher content of silver and bismuth in amounts up to 0.45 wt.% Ag and up to 1.25 wt.% Bi, respectively. The size of Bi-sulphosalts inclusions do not exceed 20 microns in diameter. They are usually disseminated in galena, fill the fractures of the galena grains or overgrowth galena crystals. Sometimes they occur together with native bismuth. The Bi sulphosalts has been classified as members of the lillianite homologous series. The <sup>4</sup>L, Ag-bearing lillianite ( $\text{Pb}_{2.52}\text{Bi}_{2.24}\text{Ag}_{0.24}\text{S}_6$ ) with lillianite type of substitution ( $\text{Ag}+\text{Bi}=2\text{Pb}$ ) ranging from 18 up to 31 mol.% and <sup>7</sup>L, heyrovskýite ( $\text{Pb}_{5.53}\text{Bi}_{2.24}\text{Ag}_{0.24}\text{S}_9$ ) with 10 mol.% of AgBi end member substitution were identified. Lillianite is much more common and heyrovskýite is rare. Native bismuth precipitated as tiny crystals of various size, generally about 10 microns. Numerous very fine native bismuth blebs marks the external contours of galena grains. Bismuthinite ( $\text{Bi}_{1.9}\text{Fe}_{0.05}\text{Pb}_{0.03}\text{Cu}_{0.02}\text{S}_{2.79}$ ) was identified in several grains as intergrowths with lillianite or native bismuth. The degree of meneghinite type of substitution ( $\text{Cu}+\text{Pb}=\text{Bi}+\text{vac.}$ ) in bismuthinite is low.

The presence of Bi sulphosalts suggests possible higher temperature of precipitation in the hydrothermal system. The presence of elevated Bi and Ag content allows distinguishing studied galena from the other, younger galena generations, with no visible Bi-bearing mineral inclusions and lower grades of Bi and Ag.

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## PETROCHEMICAL TYPIIFICATION OF NEOVOLCANITES OF ALPINE OLDING BELT OF THE EASTERN EUROPE

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### Abstract

Magmatism of volcanic provinces has evolved from calcareous through calcareous-alkaline to subalkaline type in the direction: Carpathians - the Dinaric Mountains - the Large Caucasia and the Fore-Caucasia - Armenian Uplands. It was a supposition that basalts of Georgian Massif have previously post-orogenic origin.

**Keywords:** *petrochemical typification, neovolcanites, alpine belt, Eastern Europe*

### Introduction

To systematize magmatic rocks use different approaches including a classification of their chemics. There is an easy way to determine petrochemical peculiarities of magmatites when they are discriminated with proper diagrams (Zavaritsky, Kuno and the other). If we use any separate magmatic series with Kuno-diagram (1959) in coordinates  $(\text{Na}_2\text{O}+\text{K}_2\text{O})-\text{Al}_2\text{O}_3$  then basalts are divided on several group and most of points of aluminous basic rocks (excepting basalts of Central-Transcarpathian region) located in the alkaline field. While, on mineralogical criteria, only nepheline-bearing basalts of Western Carpathians and Pannon Massif belong to the group of the alkaline volcanites. From these considerations is reasonable to select a different alkaline series of volcanites of the Alpine belt of the East Europe and carry out their identification with the well-known Borodin diagram (1987).

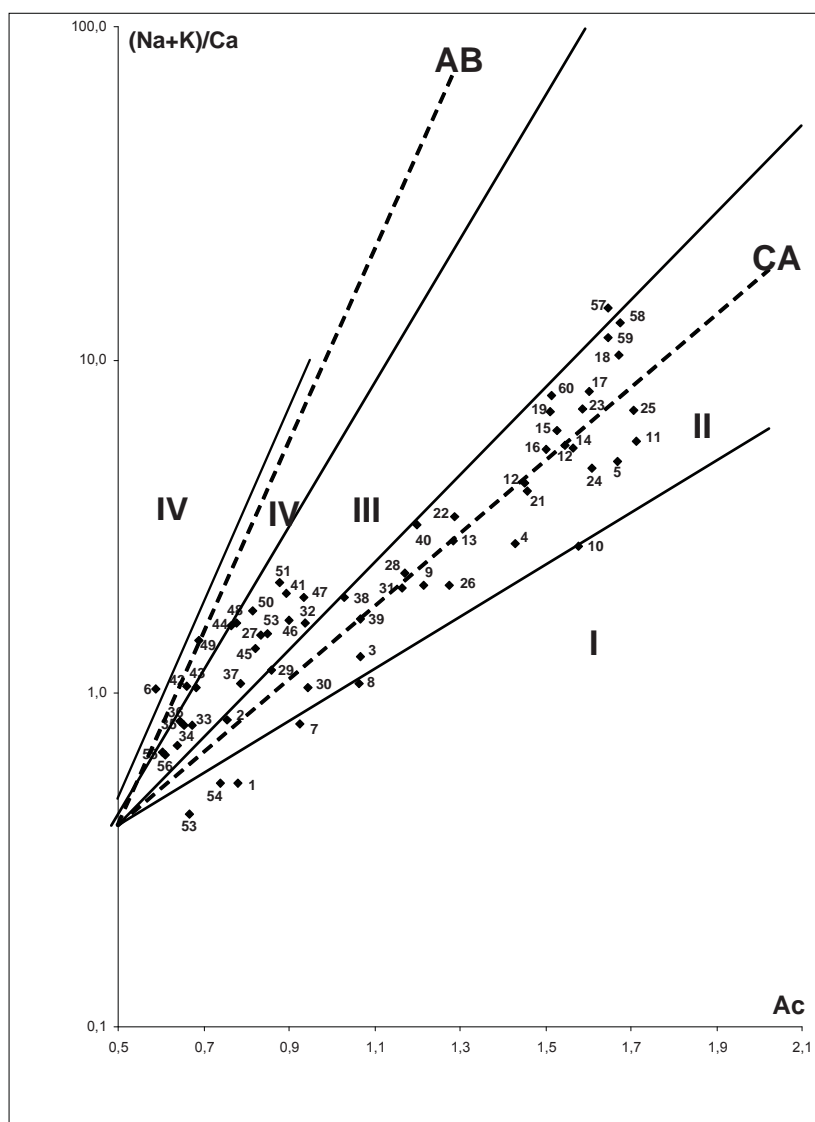
### Results.

There are data on chemical composition of neovolcanites of four different volcanic provinces: Carpathians, Dinaric Mountains, the Large Caucasia and the Fore-Caucasia, West Transcaucasia and Armenian Uplands (fig. 1). The points of rocks' chemics of the presented areas gather around selected Borodin trends of magmatic formations. All points have been localized in fields

of different alkalinity. In particular, volcanites of Transcarpathians and Pannon Massif are subjacent below line of main orogenic trends CA in subcalcareous-alkaline part of the calcareous-alkaline field II. The exception of this regularity is made only for the most basic rocks – basalts of Central Transcarpathian region and also Western Carpathians and Pannon Massif that points took place in the calcareous (I) and alkaline-basaltic (IV) fields accordingly. On the same diagram with the purpose of finding of geodynamic type of primary sources of volcanites show the points of chemical composition of oceanic and continental toleite-basalts (“standart”) and their alkaline species. Information about their composition is adopted from the monograph of Borodin L. (1981). Continental “standart” toleite have the best closeness to the points of basalts of Transcarpathians. It allows to assume, using principle of «nearest neighbors», that only continentals basalts were a primary origin of the successive series of the volcanites of Central Transcarpathian region.

Directly in the field of typical orogenic calcareous-alkaline magmatites, near main orogenic trend CA, locate the points of the Elbrus and effusives of Caucasian area and their intrusive species. Previously intrusive rocks occur in the Elbrus area as granodiorites of Dzhungusu, granite-porphyrries of Kyrtyk and granites of Eldjurta. On the basis of comparison of composition of neovolcanites of the Elbrus and Eldjurta granites, and also locations of their points on a similar diagram, Borodin L. (1998) came to conclusion, that exactly peculiarities these rocks are substantial argumentation (Borsuk 1975) concerning of comagmatism of volcanites and Eldjurta granites. Therefore, they probably belong to the mutual volcano-plutonic structure. That facts confirm development of tin exploration activities on erosion-free intrusives in spite of absence of strong genetic relation between the Mo-W mineralization of Tyrniauz and the effusives of the Large Caucasus. Thus, Sn-trend located on the proper diagram is conducted a little bit higher than “standard” calcareous-alkaline trend CA and





**Figure 1.** Trends of magmatism of modern geodynamics on a classification diagram (Na+K)/Ca-Ac.

**Fields of alkalinity** (I – IV): I – calcareous, II – calcareous -alkaline, III – subalkaline, IV – alkaline.

**Main standard trends:** AB – alkaline-basaltic, CA – calcareous -alkaline.

**Objects:** 1 – 5 – basalts, andesite-basalts, andesites, dacites, rhyolites Central Transcarpathian region; 6 – basalts of Western Carpathians and Pannon Massif; 7 – 9 – andesite-basalts, andesites, dacites of Matra, Čierna hora and Tokaj; 10 – dacites of the Zemplín-Berehovo Elevation; 11 – rhyolites of Matra, Bükk; 12 – rhyolites of Neogen of the Elbrus; 13 – dacites of Quaternary of the Elbrus; 14, 15 – the rods and the veins of rhyolites of Tyrniauz; 16, 17 – granite-porphyrates of Kyrtyk and Eldjurtja; 18 – vitrophyres of the basal layer of Verkhnechegemsky Massif; 19 – 21 – rhyolites of lower, middle and upper parts of profile of Verkhnechegemsky Massif; 22 – granodiorite-porphyrates of Dzhungusu; 23 – the dykes of rhyolites of Sarynsu; 24, 25 – rhyolites of Neogen of the Verkhnechegemsky and Nizhnechegemsky Massifs; 26 – dacites of the rukhs-dzuar set (the Kazbek area); 27, 28 – andesites and dacites of the Kazbek; 29–31 – andesite-basalts, andesites and dacites of Kelli; 32 – andesites of Dzau; 33, 34 – basalts of the western and east parts of Georgian Massif; 35, 36 – basalts of the lori-akhurian thick (Armenia). Volcanites of Kechut Range or Wet Mountains: 37 – andesite-basalts of the upper part of profile; 38, 39 – andesites, dacites; 40 – hyalodacites. Volcanites of Gegham Ridge: 41 – andesite-basalts of Manycharsk; 42, 43 – dolerites of Kamo (the Saakasar area); 44 – andesite-basalts of second stage of eruption; 45, 46 – andesite-basalts, andesites of 3-th stage of eruption. Volcanites of the Vayots Dzor: 47, 48 – andesites, andesite-basalts of first stage of eruption; 49 – olivine basalts of 2-th stage of eruption (the Gulliduz area); 50, 51 – andesite-basalts and andesites of 2-th stage of eruption (the Gndevaz area, the Jermuk area); 52 – andesites of 3-th stage of eruption. Rhyolites of Armenian Upland: 57 – 60 – Arteni, Satanakar (collected sample), Satanakar (top part of profile), Aghvorik. 53 – ocean toleite, 54 – continental toleite (Borodin L. (1981)); 55 – basalt alkaline continental, 56 – ocean basalt (Borodin L. 1981).

practically coincides with trends of the points of volcanites and granitoids of the Elbrus (Borodin, 2004). Direct confirmation of promising of the Elbrus' intrusives on Sn-mineralisation are high concentration of tin in the Neogen-Quaternary effusives of the Elbrus Volcanic Centre. In the vein rhyolites of Tyrniauz concentration of tin are in 3 times the exceeding of clarke.

The points of rocks of association «basalt – andesite-basalt – andesite» of the Small Caucasia and basalts of Georgian Massif are mainly located in subalkaline field III. There are here the points of alkaline “standard” ocean and continental “standard” basalts too. The location of the points of basic volcanites of lori-akhurian thick of Armenia and Georgia with the points of “standard” volcanites into mutual field testify their belonging to continental or ocean formations.

Only into the alkaline (alkaline-basaltic) field IV occur the points of alkaline basalts of Western Carpathians and Pannon Massif that scattered below rift-alkaline trend AB – dolerites of Kamo, Saakasari and Gulliduz. Alkaline basalts of Western Carpathians and Pannon Massif exceptionally belong to the products of post-orogenic volcanism, so dolerites of Armenia are strongly pronounced as last-orogenic volcanism' products.

According to Kostyuk P. (1961), the alkaline basalts of Carpathians-Dinaria province petrochemically relate with magmatism of most area of Central Europe (in particular, the periphery of Bohemia (Czech) Massif) but not Carpathians only. On results of cluster-analysis of petrogeochemical data there analogues of basalts of Western Carpathians and Pannon Massif are basalts of Georgian Massif that probably belong to post-orogenic stage of volcanism.

## Conclusions

1. There is marked directed growth of alkalinity rocks in row of provinces of Alpine belt of East Europe: Carpathians-Dinaria > the Large Caucasia and Forecaucasia > Armenian Upland.
2. It is assumed that on territory of the Large Caucasus is possible to discovering of tin-mineralization, besides well-known Mo-W ores.
3. It is probably that basalts of Georgian Massif, as well as their analogues in Carpathians-Dinaria province, could determine to the products of eruptions of post-orogenic stage of volcanism, but not to last orogenic stage.

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## MULTIVARIATE RELATIONSHIPS AND SPATIAL DISTRIBUTION OF GEOCHEMICAL CHARACTERISTICS OF LOWER PALEOGENE BAUXITES IN CROATIA

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### Abstract

For a long time, bauxites were treated only as an aluminum ore, focusing all research towards their detection, exploitation and refining. Despite a great number of mineralogical and chemical analyses from bauxite deposits and occurrences in Croatia being available in various studies and professional reports, the bauxite genesis was largely underestimated. Only lately, the models of orogenic evolution of the Adriatic Carbonate Platform (AdCP) region have underlined the importance of a number of hiatuses of variable duration marked by bauxitic deposits. Since bauxites are recently recognized as tectonic and climatic event markers at regional unconformities, new investigations call for additional correlative studies within and across different stratigraphic horizons, thus enabling the utilization of this immense potential indispensable in building the regional models of platform evolution.

Croatian bauxites are hosted in carbonate rocks marking the regional unconformities between several stratigraphic levels of which the Lower Paleogene bauxites are specifically targeted, owing to their variable time span of emplacement (Lower Cretaceous to Lower Eocene) within the AdCP as the extent of subaerial exposure during the stratigraphic gaps is of particular importance in understanding the origin of bauxites. The main purpose of this investigation was to assess the geochemical contrast (aided by qualitative mineralogical analysis) among the several groups of Lower Paleogene bauxites previously defined in relation to their paleogeographical/paleotectonic settings and thus gain an understanding of the conditions and intervening processes prevailing on the emergent carbonate platform. A total of 50 bauxite samples of Lower Paleogene age were collected from various sites in Istria, on North Adriatic islands, in North Dalmatia and in Central Dalmatia and chemical and mineralogical analysis was performed on bulk samples.

Multiple discrimination analysis (MDA) is a statistical technique that by maximizing between-group variance in comparison to the variance within each group is particularly useful when applied to distinguish between several pre-defined groups based on the great number of observations. Two discriminant function models (DFM) were created and four groups of bauxites have been neatly separated into their characteristic compartments according to specific combinations of major and trace elements. These models expound characteristic conditions and processes prevailing in the karst environment during subaerial exposure of the carbonate platform. In both models, the first discriminant function explains the most part of the system variability. The major-element DFM demonstrates a lower degree of separation between groups (86 %) with respect to the trace-element DFM (100 %) owing to the fact that major elements participate in a variety of processes during the sedimentary cycle, thus creating a mixed geochemical signal. Trace-element DFM proves itself as a more helpful predictive tool and more suitable for both discriminating and identifying purposes as the accumulation or depletion of trace elements usually narrows the scope of research to some particular segment of the cycle.

## GEOCHEMICAL CHARACTERISTICS OF THE ERENLERDAGI (KONYA, CENTRAL TURKEY) VOLCANITES AND THEIR ENCLAVES

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### Abstract

Extensive Late Miocene to Pliocene Erenlerdagi volcanism produced lava domes, pyroclastic flows and ignimbrite deposits in west and southwest of the Konya in relation with the subduction of the African plate underneath the Anatolian plate during Miocene. The lava domes in Yatagan village and Sağlık town (Konya) may contain various enclaves, which range in size from a few cm to a few meters, and in shape cornered to spherical. The enclaves are more mafic and finer-grained (MFE) than their hosts, with sharp to transitional contact. The host rocks are made up of plagioclase (15-45%), brown amphibole (3-15%), brown biotite (5-10 %), quartz (0-5%), sanidine (0-5%), clinopyroxene (0-5 %), epidote (0-8%), opaque iron ore (3-20%) and accessory acicular apatite and zircon in a holocrystalline porphyric texture. MFE contain plagioclase (10-50%) with sieved texture, green amphibole (10-15%), quartz (0-10%), biotite (0-5%), epidote (0-5%), opaque iron ore (5-50%) and accessory acicular apatite in a porphyric texture. There are at least two types of MFE generations; younger and older. The older one is mostly < 15 cm in size while the younger one is usually larger and forms sometimes as dikes. Between host rocks and their enclaves, particularly in the younger ones, there is a well-developed chilly zone, ranging mostly from 1.25-2.5 mm in thickness.

Al samples are clearly high-K calc-alkaline and mostly metaluminous in composition. The host rocks are rhyodacite to andesite in composition while MFEs are andesite and to basalt in composition. But, the chilly zone has trachyandesitic composition. The REE pattern of MFE shows less fractionated REE patterns [(La/Lu)<sub>N</sub>: 6.8-17.4.] in comparing with that of host rocks [(La/Lu)<sub>N</sub> 8.2-18.0]. Based on textural and geochemical data, it has been suggested that the Erenlerdagi volcanics could have been formed by chemical mixing of felsic and mafic magmas possibly coupled with fractional crystallisation of hornblende ( $\pm$  pyroxene, olivine) and titanite, whereas its MFE is igneous in origin, and could have been formed by hybridisation of basic magma mingled with partially crystallised felsic magma.



## HIGH CL AND F MINERAL ASSOCIATIONS OF THE BIELY VRCH PORPHYRY GOLD DEPOSIT, SLOVAKIA

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### Abstract

The recently discovered Biely Vrch porphyry gold deposit (34 t Au at 0.8 g/t Au) with an exceptionally low Cu/Au ratio (0.018 wt.% Cu/ppm Au) evolved in an extremely shallow level of 500-1000 m below the paleosurface. Koděra et al. (2014) demonstrated that due to a low pressure environment, this deposit was formed from nearly anhydrous Fe-K-Na-Cl salt melts containing ~10 ppm Au, coexisting with hydrous vapor of very low density. Interaction of these fluids/melts with host diorite porphyry in the temperature range 725-400 °C created early high-temperature Na-Ca and K-silicate alterations including minerals with extremely high Cl and/or F contents.

K-silicate alteration and associated veinlets in the upper part of the system (0-300 m) is represented by mineral association K-feldspar, biotite, magnetite and apatite. Fine-grained biotite aggregates replacing former mafic minerals is either Cl- or F-rich with maxima of 7.5 wt.% Cl, and 5.8 wt.% F respectively. The halogen-rich compositions of biotite represent Cl-dominant analogue of annite with up to 1.08 apfu Cl (a new members of the mica group with end-member formula  $KFe^{2+}_3AlSi_3O_{10}Cl_2$ ), Cl-rich annite, phlogopite, and fluorophlogopite. Other biotite compositions represent hydroxyl-dominant annite to siderophyllite, locally phlogopite with low to moderately increased Cl and F. Associated chlorapatite and fluorapatite locally show up to 4.4 wt.% Cl, and up to 3.7 wt.% F respectively.

A similar K-silicate mineral association in the lower part of the porphyry system (borehole DVE-52 /700 – 780 m) shows lower values of halogen elements: biotite contains up to 3.2 wt.% Cl, or up to 1.8 wt. % F.

Na-Ca silicate alteration and associated veinlets in deep parts of the system (500-760 m) is represented by mineral association plagioclase,

actinolite/hornblende, epidote, magnetite, ilmenite, apatite and minor K-feldspar, biotite and titanite. Actinolite/hornblende is enriched either in Cl or F with max. of 1.1 wt.% Cl and up to 1.0 wt.% F. Associated apatite shows max. 3.7 wt.% Cl, and up to 2.9 wt.% F. Also secondary biotite is enriched in Cl or F, titanite shows up to 2.1 wt.% F.

Roughly in the depth interval of 550-700 m, a specific mineral association of the Na-Ca silicate alteration with Fe-K-Cl amphibole, Fe-rich clinopyroxene and titanite is present. Dark green amphiboles contain up to 37 wt.% FeO+Fe<sub>2</sub>O<sub>3</sub>, 3.5 wt.% K<sub>2</sub>O and 5.0 wt.% Cl; they represent hastingsite series solid solution between hastingsite, potassic-hastingsite, a new Cl-analogue of hastingsite and the most widespread chloropotassichastingsite with maximum Cl occupancy (1.06-.43 apfu). An unique grain of Ca<sub>2</sub>(PO<sub>4</sub>)Cl-phase (“chlorspodiosite”) shows 16.3-16.6 wt.% Cl.

In the depth range of 300-550 m, at the margin of the mineralized system, there is a zone of pseudobreccias enriched in disseminated sulfides. Aggregates of plagioclase, quartz, F-rich biotite, F-rich actinolite/hornblende, fluorapatite, F-rich titanite with rutile and minor fluorite, ilmenite, K-feldspar and corrensite form finer grained pale domains, while plagioclase, corrensite, pyrrhotite, pyrite, apatite, fluorite, calcite and minor quartz and F-rich actinolite/hornblende form coarser grained dark domains. The F content varies between 1.8-2.8 wt.% in biotite, 0.5-1.5 wt.% in amphibole-group minerals, over 3.5 wt.% in fluorapatite, around 2.8 wt.% in titanite, and up to 0.55 wt.% in corrensite. However, chlorine content in these minerals is generally low here.

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## FROM NUCLEAR FUEL MANAGEMENT TO CEMENT AND ARCHAEOMETRY: INTERFEROMETRY TECHNIQUES AND THE STUDY OF SURFACES

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### Abstract

Modern industrial societies face a mix of environmental and technical challenges such as fighting/avoiding water pollution, generating safe (nuclear) waste deposits, controlling cement quality, and managing carbon sequestration successfully and safely. Therefore, societies rely critically on comprehensive mineral and material dissolution and corrosion rates. In many cases it is not sufficient to just measure the reaction rates but it is also mandatory to predict the behavior of complex systems into the future. Such challenging task requires contributions from various scientific and engineering disciplines - and earth and material sciences are at the forefront. At the same moment, geologists, mineralogists and geochemists are used to measure the present state and reconstruct the past. Consequently, we now need to develop a new approach with the necessary tools to predict future system behavior.

Understanding the processes involved in fluid-solid interactions ultimately demands the knowledge of reaction kinetics. Techniques allowing high-resolution observations of dissolving crystals have greatly improved our understanding of reaction kinetics at a variety of scales. Vertical scanning interferometry (VSI) often in combination with atomic force microscopy can reveal reaction mechanisms and permit tests of working hypotheses.

VSI is a fast, non-destructive, light optical method that allows the quantification of surface topographies and spatially resolved reaction rates at such surfaces. With a vertical resolution of about one nanometer this technique is very precise and is capable of covering large surface areas compared with atomic force microscopy methods. The recent development of interferometers generates some significant progress in measuring dissolution kinetics. In particular, VSI super-resolution techniques greatly improve lateral resolution whilst a unique VSI-RAMAN combination allows for the measurement of the chemical composition

of the dissolving surface. Here we present different examples of VSI application and demonstrate its wide range of capabilities. Most of our results show that the dissolving (crystal) surface is typically very complex in nature. This work has led to the so-called dissolution stepwave model (Lasaga and Luttge 2001) and more recently to the concept of rate spectra (Fischer et al. 2012; Luttge et al. 2013).

Thus, understanding the substantial complexity and heterogeneous distribution of surface reactivity cannot be provided by simple observation alone but requires significant advances in fundamental theory. Model simulations of molecular-scale processes provide the critical link between nano-scale surface observations of crystal dissolution and the phenomenological result, at scales of technical and environmental importance. We employ parameterized Kinetic Monte Carlo simulations in combination with *ab initio* and molecular dynamics calculations to decipher the mechanism and predict the evolution of dissolving crystal surfaces. Our simulations show indeed some potential for correctly predicting crystal dissolution. At the same time, these first results raise a surprising question: Do just a “handful” of simple basic processes govern the reaction kinetics and create at the same time the tremendous complexity that we observe? There are some interesting arguments that this may indeed be the case.

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## **A CONCEPTUAL MODEL FOR FORMATION OF BONANZA ELECTRUM ALONG STEEP VEINLETS IN EPITHERMAL LOW-SULFIDATION GOLD DEPOSITS. CASE STUDY FROM THE KHAN KRUM DEPOSIT, SE BULGARIA**

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### **Abstract**

The work presents a colloidal and physical transport texture of colloform-banded hair-line veinlet with electrum-quartz-adularia composition and a conceptual model for the formation of bonanza electrum from the low-sulfidation, sedimentary rock-hosted Khan Krum gold deposit, SE Bulgaria – a representative of the bonanza vein type gold deposits worldwide.

**Key words:** *bonanza electrum, epithermal gold, colloidal solution transport, boiling, Khan Krum deposit*

### **Introduction**

Epithermal, low-sulfidation (of adularia-sericite alteration) gold deposits are an economically important class of precious-metal deposits. Styles of mineralization include veins, stockworks, breccias and layer-like (tabular) bodies. Veins usually display a level of bonanza ores. Following Romberg (1992), bonanza is a descriptive, semi-quantitative and subjective term used to describe deposits from which large quantities of precious metals have been recovered from relatively small but high-grade orebodies. According to this author, most deposits with local gold grades which reach hundreds of grams per tone are referred to as bonanza type gold deposits. Such concentrations occur in deposits from the Pacific Rim, Australia, Carpathians, Zabaikalie (Russia). There, bonanza electrum forms agglomerations visible either under optical microscope or by macroscopically. Most authors support a colloidal origin of the bonanza precious-metal ores, but others think that colloids are not necessary for bonanza electrum formation. The origin of bonanza electrum is still poorly constrained because of paucity of direct observations, common re-crystallization of the ores and diverse origin of the quartz precursor (true or colloidal solutions) since epithermal quartz commonly is the main gang mineral

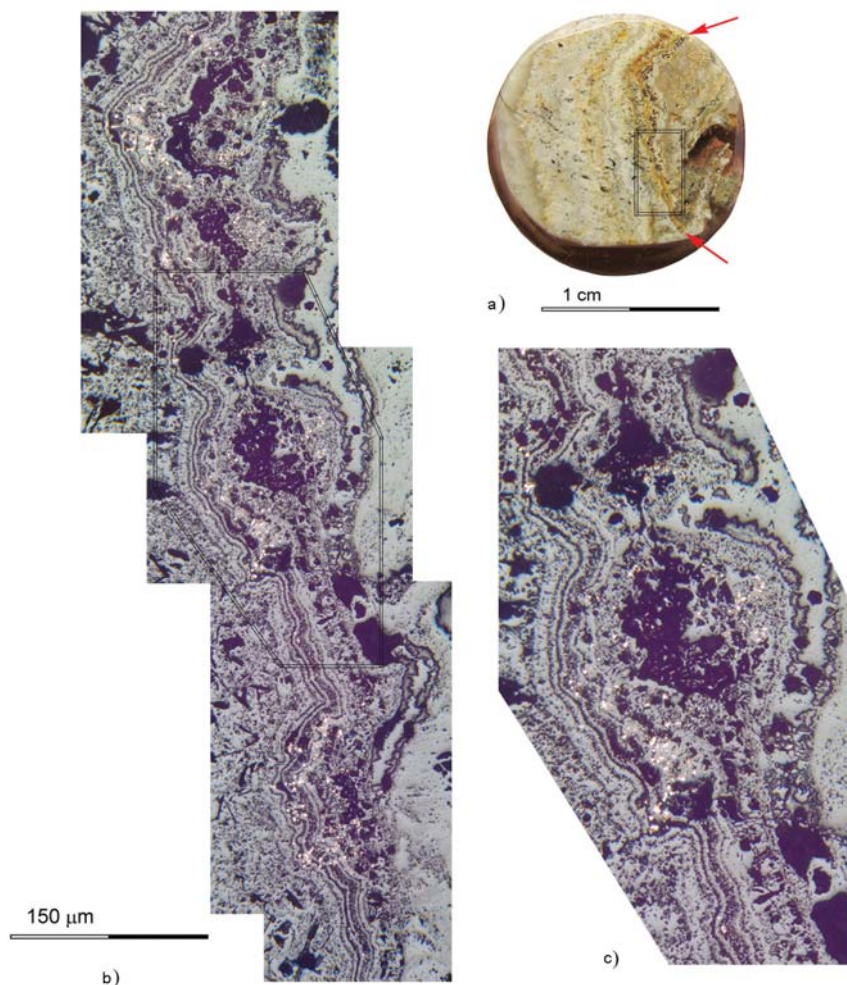
(review in Marinova et al. 2014). Experiments and simulations on the flow of colloidal solutions in thin channels like in the natural fractures in some extent imitate natural environment. Some of them have demonstrated that colloidal particles have been trapped in low velocity zones on the lee side of fracture walls, where some recirculation has happened (Boutt et al. 2006). Indeed, Saunders et al. (2011) have documented deposition of electrum AuAg and naumannite Ag<sub>2</sub>Se on the lee side of protrusions along vein walls explaining these textures as “colloidal and physical transport textures”.

In the present work we show similar colloidal and physical transport texture of bonanza electrum from the Khan Krum gold deposit, SE Bulgaria (also known as Ada Tepe deposit) and present a conceptual model for its formation. In samples from high-angle veins in the deposit, high gold grades are assayed reaching up to 639 ppm (Jelev 2007), indicating that the deposit is of the bonanza vein type gold deposits.

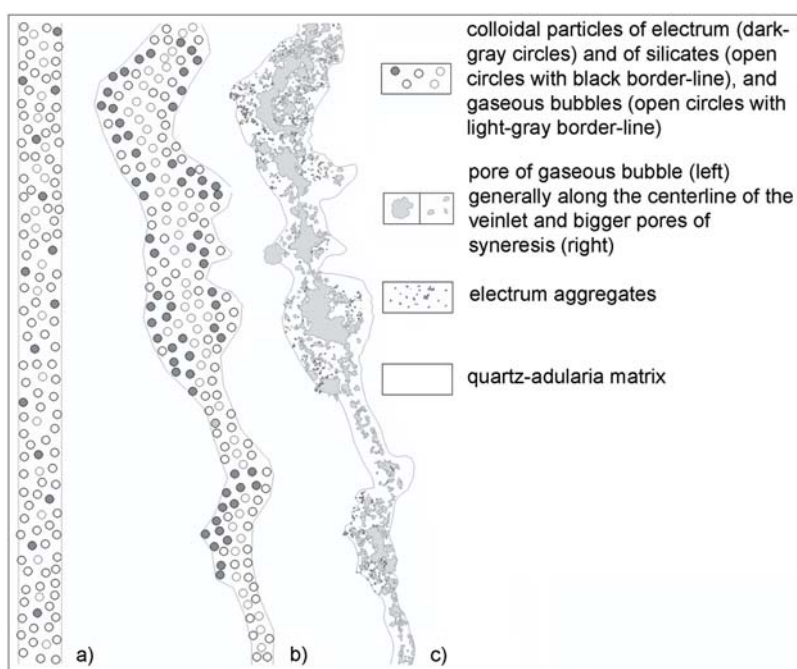
### **Material and Method**

To demonstrate the model, a polished section (Fig. 1a) is studied under optical microscope in reflected light. The section is prepared from a sub-vertical veinlet of colloform-banded texture about 2.5 cm wide. Veinlet composition, texture and trace element distribution have been investigated by Marinova et al. (2014). The studied polished section consists of 10 bands, 9 of which are almost barren and visible by naked eye. The electrum-rich band is hair thin (0.3 mm wide) with distinct brown color and a lot of oval voids inside. Under optical microscope, the hairline band consists of 4 individual micro-bands, separated by thin interrupted syneresis cracks. Only the rightmost micro-band that is a subject of the present study is abundant of electrum and pyrite aggregates as well as of adularia while the rest three micro-bands are almost entirely of quartz composition (Fig. 1b, c).





**Figure 1.** Bonanza electron in a colloform micro-banding: a) in polished section, designated with arrows. Pores seen as black spots and speckles (2×). The black rectangle enlarged in (b); b) photomicrograph of part of the micro-banding comprising four micro-bands; the rightmost one has a lot of pores (black spots), and abundant electrum aggregates (white speckles) concentrated exclusively in widened parts, in reflected light; c) detail from b).



**Figure 2.** Conceptual model of electrum enrichment in widened portions of steep veinlets: a) expected random distribution of electrum and silicate colloidal particles along a joint of constant width; b) expected distribution of colloidal particles of electrum and silicates and of gas bubbles along a joint with variable aperture in a Poiseuille flow with enrichment in electrum of widened portions and combining of gaseous bubbles along the centerline; c) real distribution of electrum aggregates, pores and silicate matrix (to scale) along the joint from figure 1b after coagulation of a boiling electrum-silicate colloidal solution with formation of quartz-adularia matrix, pores of gas bubbles and of syneresis, and electrum agglomerations.



## Results and Model

Under optical microscope it is observed that the studied micro-band consists of alternating wide and narrow portions and electrum forms considerable accumulations only in widened parts (with an aperture up to about 200  $\mu\text{m}$ ). As a rule, these portions contain dense micron-sized electrum aggregates, while the narrow ones (up to about 40  $\mu\text{m}$  wide) are almost barren. The ratio of the wide sections to the narrow ones reaches 4 to 5 (Fig. 1b). This apparent influence of the joint aperture reveals a flow under the laws of Bernoulli and Poiseuille. The Bernoulli's effect links the flow velocity ( $V_1$ ) and fluid pressure ( $P_1$ ) in wide portions to these ones ( $V_2$  and  $P_2$ , respectively) in next narrow portions in the following inequalities:  $V_1 < V_2$  and  $P_1 > P_2$ . According to the Poiseuille's law, the volume flow rate ( $F$ ) changes in direct proportion to the fourth degree of the channel radius ( $R$ ):  $F = \pi R^4 \Delta P / 8 \eta L$ , where  $\Delta P$  is the difference of the flow pressure in widened portion and next narrowed one;  $\eta$  is the dynamic fluid viscosity, and  $L$  is the length of the channel (Batchelor 1967). In a channel/joint of constant aperture the colloidal particles of electrum and silicates should be distributed randomly in the flow (Fig. 2a) but in a channel of variable aperture it is a priori expected an impact of the joint aperture due to the huge difference in the specific weight of electrum and that of silicates as it happens along river beds. In our case, the volume flow rate in the wide portions has to increase 256 to 625 times as compared to the narrow sectors considering the ratio of the wide portions to the narrow ones. This significantly would decrease the flow velocity in wide portions and according to the energy conservation law (Batchelor 1967) it should lead to delay of the heavy electrum colloidal particles in comparison with the light silicate ones. As a result, the wide portions will be enriched in electrum as compared to the colloidal silicate particles which continue their flow along the joint together with the dispersion medium (Fig. 2b). In addition, it is expected that in the lee sites of the wide portions, the electrum colloidal particles would re-circulate and in result collide and adhere due to increase of their abundance. Such a re-circulation has been observed in aqueous flow along micro-channels of similar geometry just after the entrance of widened portions (Campo-Deano et al. 2011). If the studied electrum micro-texture has been formed by true solution, then such an effect would not occur. During subsequent coagulation of the colloidal

solution electrum particles would further adhere; aggregate and form agglomerations in widened portions of joint (Fig. 2c). It is important to say that in figure 1b, c the largest pores are located along the virtual center line of the rightmost micro-band. Small pores are distributed all over the veinlet and have been identified as pores of syneresis since they are outlined with microscopic euhedral to subhedral crystals of quartz and adularia (Marinova et al. 2014). The location of the largest pores along the centerline indicates that they have been bubbles of gas separated during boiling of moving hydrothermal fluid (Fig. 2b, c) as in experiments with gas-liquid flow (Trifonov, 2010) (Fig. 1). In addition, they indicate a relatively high flow velocity when small gaseous bubbles have combined in larger ones (Wongwises and Pipathattakul, 2006).

By combining the present work with this one by Marinova et al. (2014) the following conclusions can be made.

## Conclusions

1. Presented here electrum micro-texture is evidence for transport of natural colloidal solution along micron-size wide veinlets under epithermal conditions in a boiling environment.
2. The electrum enrichment only of widened portions of the veinlet demonstrates apparent influence of the joint's aperture under the laws of Bernoulli and Poiseuille, and means a flow of three-phase colloidal solution that consists of dispersion medium, heavy electrum particles and light silicate ones. The location of largest pores along the centerline of the joint reveals a flow of gaseous bubbles during boiling, e.g. the flow was four-phase one, including as well as gaseous phase.
3. The widened portions being low velocity zones have acted as trapping zones for the heavy electrum colloidal particles causing their collision, adhesion and agglomeration inherited during further coagulation and gel formation.

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## COULD THE UPPER JURASSIC SEDIMENTARY ROCKS BE A LIQUID HYDROCARBON KITCHEN IN THE CARPATHIAN FOREDEEP, POLAND?

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### Abstract

Upper Jurassic sedimentary rocks from the Carpathian Foredeep were analyzed and correlated with crude-oils according to the potential source-rock character. In most of the Jurassic rocks, the  $CPI_{(25-31)}$  values are significantly higher than 1.5, what suggests a contribution of higher plants to the kerogen and their immature character. Oleanane, angiosperm biomarker has been identified only in crude-oils and hydrocarbon contaminations, whereas in the Jurassic rock samples was not found. Also distribution of other pentacyclic triterpenoids varies considerably between oils and Jurassic rocks. Organic geochemical studies have shown that the molecular composition of the Upper Jurassic sedimentary succession differs significantly from Carpathian Foredeep oils and should be excluded as potential source-rocks.

**Key words:** *crude-oils, Carpathian Foredeep, Upper Jurassic, biomarkers, correlation*

### 1. Introduction

Oil-source rock correlation in the Polish part of the Carpathian Foredeep and overthrust was a subject of several studies (e.g. ten Haven et al. 1993; Lafargue et al. 1994; Kotarba et al. 2007). The main conclusion of the above works was that menilite shales were the most possible source-rocks for liquid hydrocarbons (HCs) in the North Carpathian Province, but some doubts concerning their immature character in the major part of the Outer Carpathians were also postulated (e.g. Krüge et al. 1996; Köster et al. 1998). Recently, Matyasik (2011) suggested, that Upper Jurassic sedimentary rocks from the Carpathian Foredeep could be the potential source-rock for crude-oils from this area (excluding Nosówka field). Here, we show evidences against Matyasik (2011) conclusions, based on detail analysis of organic extracts from the Upper Jurassic sedimentary rocks and their correlations with oils.

### 2. Materials and methods

#### 2.1. Samples

Forty nine Upper Jurassic limestone and shale samples of marine origin were collected from 15 boreholes of the Carpathian Foredeep region. In addition, 6 crude-oil samples from: Brzozówka 21R, Grobla 50R, Grobla 70R, Jastrząbka 8R, Pławowice 53R, Pławowice 111R fields were analyzed.

#### 2.2. Extraction and thin-layer chromatography

Powdered samples were extracted in a Soxhlet apparatus with dichloromethane (DCM)/methanol (10/1 vol.) for 24 h. The solvent extracts were evaporated close to dryness with a rotary evaporator. Thin-layer chromatography (TLC) was carried out for rock extracts and crude-oils. Detailed description was presented in Marynowski et al. (2006).

#### 2.3. Gas chromatography – mass spectrometry

Aliphatic and aromatic fractions were analyzed using gas chromatography – mass spectrometry (GC-MS). GC-MS analyses were performed with an Agilent 6890 chromatograph equipped with an EPC Cool On-Column Inlet and fitted with one of the two fused silica capillary columns of different polarity, i.e. either HP-5 MS or DB-35 MS (60 m x 0.32 mm, 0.25 µm film thickness). Helium was used as carrier gas. For more details see Marynowski et al. (2006).

### 3. Results and discussion

#### 3.1. Rock extraction and group separation

Triangular diagram (Fig. 1) shows the percentage distribution of the contents of the organic fractions in the extracted bitumen's from the Jurassic rocks and crude oil from the Carpathian Foredeep. For comparison, two samples of crude oil, coming from the Polish part of the Carpathian Overthrust, have been added to the diagram.

From the diagram, it appears that crude oil, with the exception of Grobla 70R oil, contain

predominantly aliphatic fraction (over 50-60%), while the Mesozoic rocks are characterized by a wide range of group composition, however, rarely exceeding 50% of the aliphatic fraction. A similar distribution of organic fractions for crude oil from Poland, Ukraine and Romania were described Lafargue et al. (1994). Generally, crude oil containing high content of aliphatic fraction is mostly at a high level of thermal transformations.

### 3.2. Gas chromatography – mass spectroscopy (GC-MS)

#### 3.2.1. *N*-alkanes and isoprenoids

In the distribution of *n*-alkanes for samples of the Jurassic rocks, the predominance of odd- over even-carbon-number, between  $n\text{-C}_{23}$  and  $n\text{-C}_{33}$  is observed. Such differences in concentrations of *n*-alkanes in this range are connected with the contribution of the terrestrial organic matter to the kerogen. Parameters describing this feature are: CPI and  $\text{CPI}_{(25-31)}$ . In case these parameters, the values are clearly greater than 1, what indicates the presence of organic matter of terrestrial origin (e.g. Peters et al. 2005). When the values of these parameters are 1 or close to unity, the organic matter does not include land component, and/or is at a high level of thermal transformations. In the case of the Upper Jurassic rocks, parameter values for the CPI and  $\text{CPI}_{(25-31)}$  are diverse. In many tested samples of the Jurassic rocks, the  $\text{CPI}_{(25-31)}$  value is significantly higher than 1 (and even higher than the 2 – e.g. Nieczajna-1; 795m), which conclusively proves a contribution of higher plants to the kerogen. At the same time, such values for this parameter are characteristic for the not thermally transformed organic matter.

In many samples, short-chain *n*-alkanes are also present, forming the main constituent of the aliphatic fraction. Very often, even if samples of Jurassic rocks show a distinct advantage of short-chain *n*-alkanes, the predominance of odd carbon number is noticeable between  $n\text{-C}_{23}$  and  $n\text{-C}_{33}$ . The above data suggest mixed, terrestrial-marine organic matter type, with a predominance of marine origin.

What is interesting, comparison of *n*-alkanes distribution of crude oil Brzozówka and Pławowice as well as extract of Łękawica borehole rock sample, showed that the relative concentrations of *n*-alkanes and the ratios of individual compounds (including pristane and phytane distribution) are very similar to the aforementioned samples.

#### 3.2.2. Pentacyclic triterpenoids

Biomarkers of pentacyclic triterpenoids group (hopanes and oleananes) are found only in the part of the analysed samples. These biomarkers were used in Carpathian crude oil correlations (ten Haven et al. 1993; Lafargue et al. 1994; Kotarba et al. 2007) and the geochemical characteristics of the source rocks (Kruge et al. 1996; Köster et al., 1998). Figure 2 shows the plot of moretanes to hopanes (30 M/H) ratio of and the oleanane to  $\text{C}_{30}$   $\alpha\beta$ - hopane  $\text{Ol}/(\text{Ol Hop})$ . Due to the fact that oleananes occur widely in organic matter from Upper Cretaceous and younger sediments, because its sources are angiosperms (e.g. Moldowan et al. 1994; Marynowski et al. 2006), the presence of these compounds in the organic matter of the investigated area suggests that OM originating from the Upper Cretaceous rocks or younger. These compounds are present in all crude

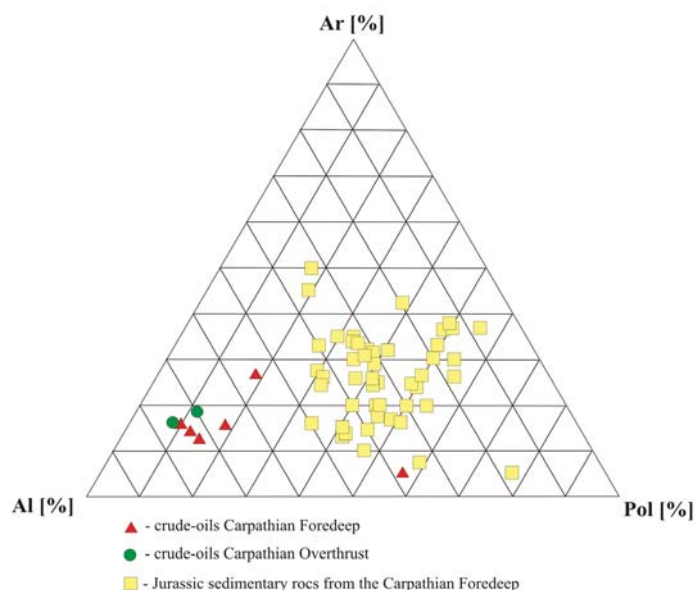
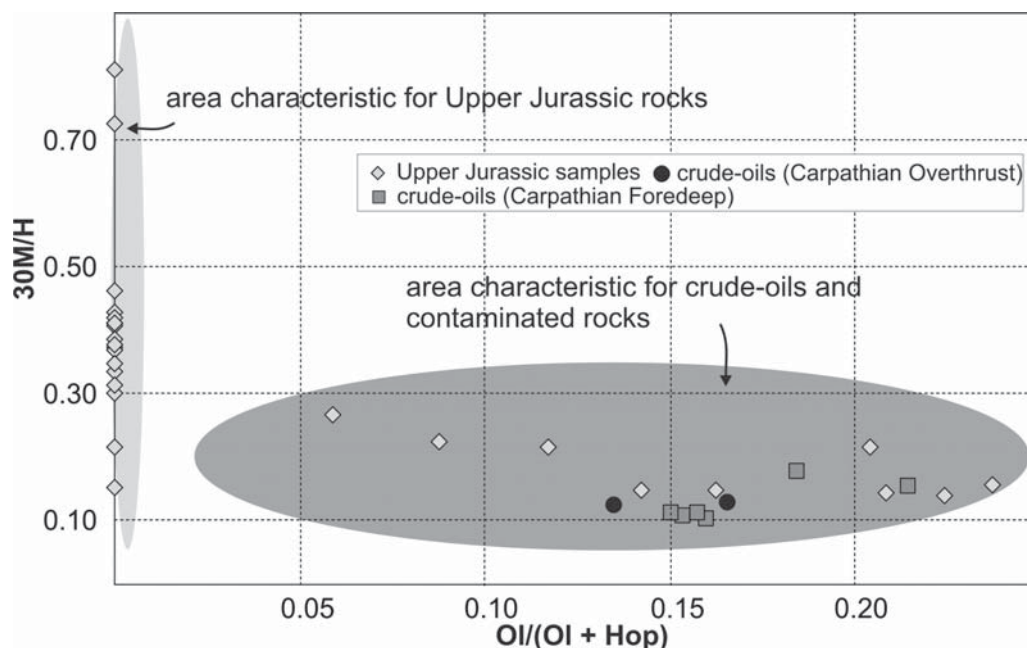
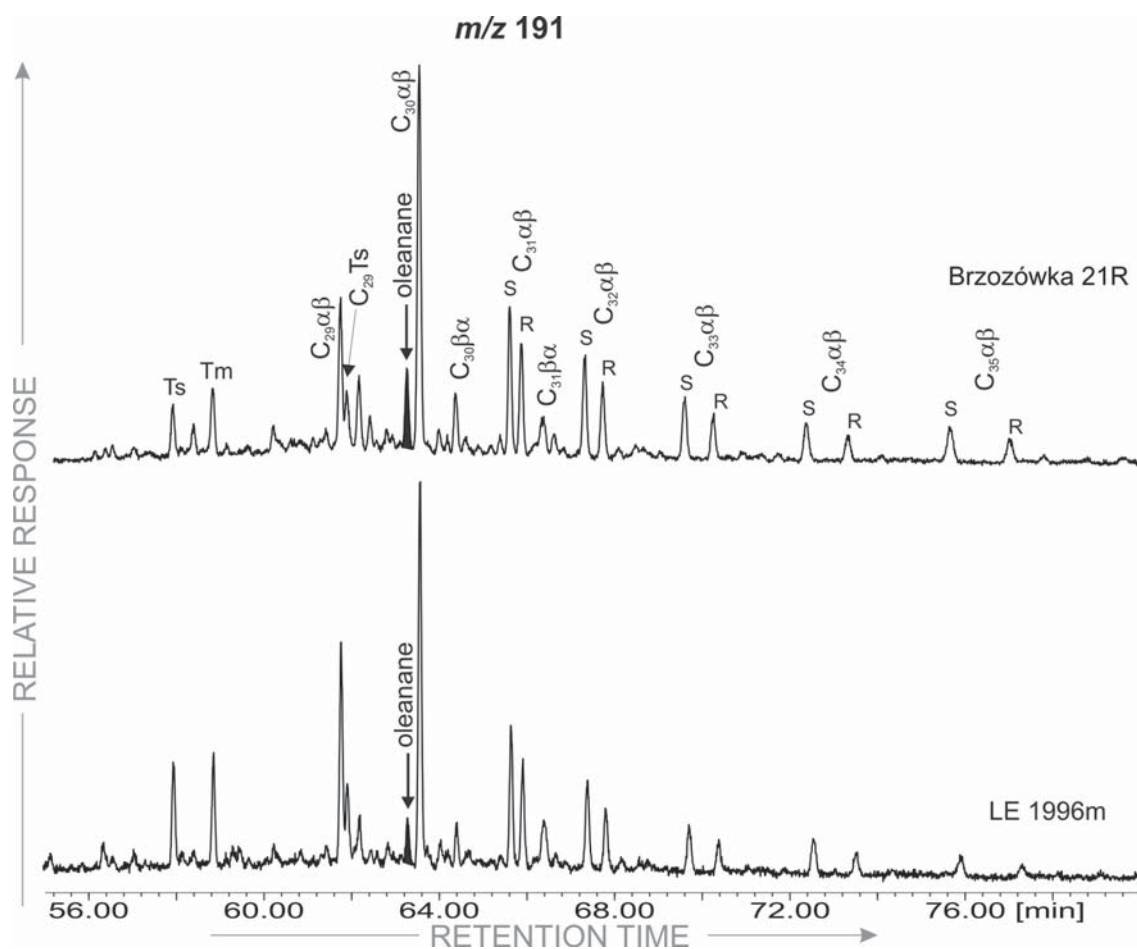


Figure 1. Triangular diagram, which illustrates the fractional composition of the tested samples.





**Figure 3.** The comparison of hopanes distribution of crude-oils: Brzozówka and Pławowice as well as rock extract from the sample contaminated by migrated HCs (borehole Łękawica, 1996m). Oleanane is marked by the arrow.



**Figure 2.** The plot showing moretanes to hopanes (30 M/H) vs. the oleanane to  $C_{30} \alpha\beta$ -hopane OI/(OI Hop) ratios.

oil and some samples of the Jurassic rocks. Based on the presence of oleananes, there is possibility to identify those rocks through which HCs were migrated and which rocks are "contaminated" by migrating HCs. Interestingly, rock extracts with detected oleanane compound, characterized by elevated extract amounts and the samples with oleanane shows low values of moretanes to hopanes ratio (Fig. 2). Moreover, uncontaminated by migrating HCs Jurassic samples characterized by low values of the ratio of  $C_{29}Ts$  to  $C_{29}$  and diverse values of the  $31S/(S+R)$  ratio. In many immature Jurassic rock samples the values for this parameter are lower than 0.5. The distribution of pentacyclic triterpenoids characteristic for crude-oil and oil-contaminated rocks is shown in Figure 3. Distribution of these group of compounds have been compared for crude-oils Brzozówka and sample impregnated by allochthonous HCs (borehole Łękawica: 1996 m). Oleanane, the compound characteristic only for crude-oil and absent as a primary compound in the Jurassic rock samples (excluding that with allochthonous HCs), is marked by the arrow. Very similar distribution of pentacyclic triterpenoids was shown by Lafargue et al. (1994), to mention that this is typical distribution of these compounds for almost all of the Carpathian crude-oils, both from Foredeep and Overthrust. Importantly, the clear indication of the contamination is that samples lying above and below the impregnated samples, characterized by relatively immature organic matter, where a significant prevalence of epimer R over S in the distribution of homohopanes is noted. Immature character of the Jurassic rocks from the Polish Carpathian Foredeep was also recently postulated by Kosakowski and Wróbel (2012) based on hydrocarbon modeling.

#### 4. Conclusions

Geochemical correlative studies have shown that the Upper Jurassic sedimentary successions are not source-rocks for the generation of hydrocarbons in the Polish part of the Carpathian Foredeep. The local generation of liquid hydrocarbon from the Jurassic area in the southern part of the research area (boreholes Pilzno-40 i Nawsie-1) cannot be excluded, but without industrial importance.

Most of the Upper Jurassic rocks contain thermally immature organic matter, which was not reach the maturation level for generation of liquid hydrocarbons (oil window stage). Part of the Upper

Jurassic rocks (mainly limestones) is "polluted" by secondary, migrating hydrocarbons generated from rocks being kitchen for crude oils. Liquid hydrocarbons from the Carpathian Overthrust and Foredeep characterized by very similar molecular composition and probably are closely genetically connected.

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## MINERALOGY AND PETROGRAPHY OF THE NW TINOS ISLAND OPICALCITES, CYCLADES, GREECE

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### Abstract

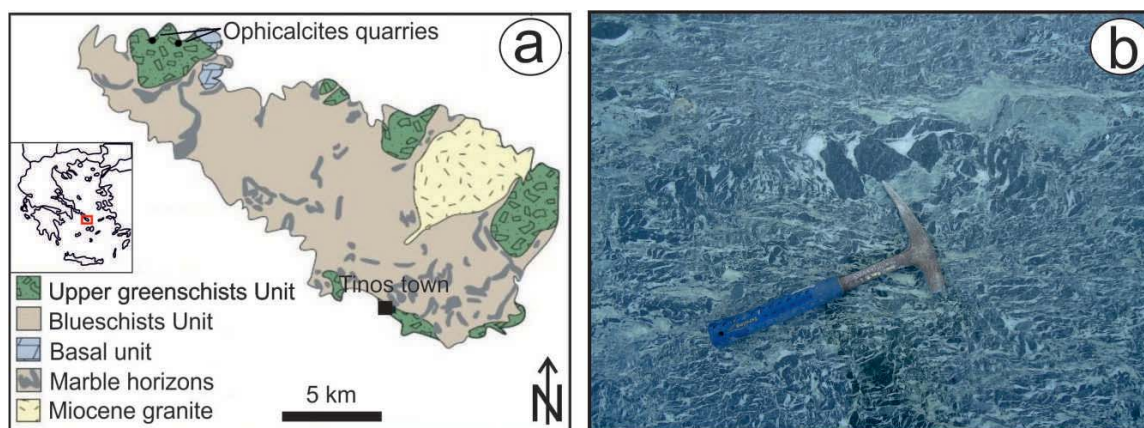
Opicalcites from Tinos Island, Cyclades, Greece, better known as ‘green marble of Tinos’, comprise polygenetic serpentinitic breccias with calcitic matrix and numerous carbonate veins crosscutting the formation. They have undergone intense exploitation for building and decorative purposes since ancient times. Serpentinitic clasts of the opicalcites are composed mainly of antigorite and they show characteristic mesh textures, while locally pseudomorphic and non-pseudomorphic textures are developed. The carbonate phase consists mostly of calcite, whereas dolomite replaces calcite locally, especially along zones of intense tectonic activity. Calcite, mostly as cement material, presents a strong granoblastic texture that bonds tightly the serpentinitic clasts. Chlorite is present in many samples and seems to be a quite common accessory mineral of the formation whereas talc, spinel, hematite and magnetite can also be found. Meter-sized bodies of chromitites with irregular shapes were also observed in the studied opicalcites. They consist of aluminian chromite, partially replaced by magnetite, Cr-chlorite, calcite and base metal sulphides. Mineralogical, textural and field relationships data support the idea of a combined tectonic-hydrothermal origin of these opicalcites, while

sedimentary mechanisms have played a minor role to their formation.

**Keywords:** *Cyclades, Tinos Island, opicalcites, serpentinite*

### Introduction

Opicalcites are tectono-sedimentary breccias consisting of serpentinitic fragments set in calcitic matrix and its formation is strongly connected to the exposure of mantle rocks at the sea floor due to tectonic activity (Bernoulli et al. 2003 and references therein). They can be found in many places on Earth but they are very well studied as members of the Mesozoic Alpine ophiolitic sequences in the Western Tethyan region. One of the most important occurrences of opicalcites in Greece is the studied case of Tinos Island, where three tectono-metamorphic units have been identified (Fig. 1a). The lowermost unit is exposed in a tectonic window and comprises Cenozoic metasediments. It is tectonically overlain by the Cycladic Blueschist Unit (CBU), which consists of various rock types metamorphosed during Late Cretaceous-Eocene (Bröcker and Enders, 1999), to blueschist and eclogite facies. A retrograde metamorphic event, during Late Oligocene-Early Miocene, accompanied the exhumation of the



**Figure 1.** (a) Simplified geological map of Tinos Island, modified after Breeding et al., 2003; (b) opicalcites occurrence devastating cataclastic features

blueschists under greenschist to amphibolite facies and lead to extensive overprinting of the HP/LT rocks. The CBU is in turn tectonically overlain by relics of the Upper Unit (UU) which consists of varying lithological sequences from Permian to Tertiary sediments, Mesozoic ophiolitic relics and low-to-medium grade metamorphic rocks (Katzir et al. 1996) that were never affected by HP/LT metamorphism. Both CBU and UU are crosscut by syn-extensional granitoids of Miocene age (14-18 Ma, Altherr et al. 1982). The opicalcites are

thin metasomatic blackwall zone between opicalcites and greenschists. The studied samples come from five opicalcite quarries that nowadays are not in operation.

### Materials and Methods

A total of 50 rock samples were collected from the opicalcites for petrographical and mineralogical studies. From these rock samples, 30 thin sections were made and underwent detailed mineralogical

**Table 1.** Representative SEM-EDS analytical data for spinels (1-2); serpentine (3-4) and chlorites (5-6) from the opicalcites formation.

	1-	2	3	4	5	6
SiO <sub>2</sub>	0.00	0.00	44.74	42.26	34.00	35.63
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.04	0.00
Al <sub>2</sub> O <sub>3</sub>	16.96	17.67	0.00	0.00	6.33	7.30
Cr <sub>2</sub> O <sub>3</sub>	53.53	52.47	0.00	0.00	7.47	6.20
Fe <sub>2</sub> O <sub>3</sub>	2.25	2.85	2.33	2.10	0.00	0.00
FeO	14.02	12.39	0.00	0.00	2.35	2.12
MnO	0.00	0.00	0.00	0.00	0.00	0.13
MgO	13.60	14.67	39.07	38.12	33.78	34.59
CaO	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.00	0.00	0.00	0.00	0.32	0.00
total	100.37	100.05	86.14	82.48	84.29	85.97
cations	cations based on 4 O		cations based on 9 O		cations based on 28 O	
Si	-	-	2.690	2.658	6.767	6.882
Ti	-	-	-	-	0.006	0.000
Al	0.625	0.646	-	-	iv: 1.233 vi: 0.251	iv: 1.118 vi: 0.544
Cr	1.322	1.287	-	-	1.175	0.947
Fe <sup>3+</sup>	0.053	0.067	-	-	-	-
Fe <sup>2+</sup>	0.366	0.321	0.117	0.110	0.391	0.342
Mn	-	-	-	-	-	0.021
Mg	0.634	0.679	3.502	3.574	10.022	9.960
Ca	-	-	-	-	-	-
Ni	-	-	-	-	0.051	-

located at the NW part of the Island, 4km north from the Marlas village. They are found in close spatial association with greenschists, metagabbros, metapyroxenites, talc schists and metasediments of the upper tectonic unit. They usually form elongated bodies, ranging significantly in length and have a mean thickness of about 40m. The long axis of the opicalcitic bodies is following the NNW-SSE folding direction of the adjacent greenschists. Talc schists usually form a relatively

investigation using optical microscopy and 18 thin-and-polished sections were examined using a JEOL JSM-5600 scanning electron microscope. Moreover, powders from 10 samples were reprocessed by X-ray diffraction, using a Brooker (Siemens) 5005 X-ray diffractometer, in conjunction with the DIFFRACplus software. Results were evaluated using the EVA 10.0 software. All the studies took place at the laboratories of the University of Athens.



## Results and Discussion

The ophicalcites of Tinos Island comprise a complex tectono-sedimentary breccia formation. It mainly comprises of serpentinite clasts set in carbonate veins and matrix, while individual chromitite irregular bodies are also found in some cases. The main part of the formation shows strong to pervasive cataclastic deformation whereas in the uppermost stratigraphic part the ophicalcite is represented by a matrix-supported breccia consisting mostly of reworked serpentinitic clasts floating in fine-grained carbonate matrix.

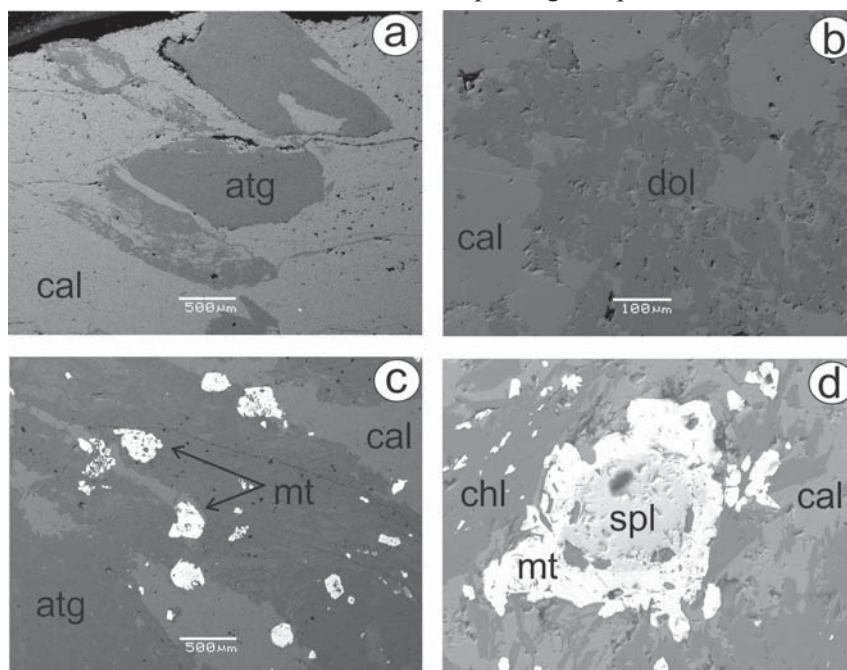
### *Serpentinite Clasts*

The serpentinite clasts are characterized by intense tectonic fracturing and cataclastic phenomena (Fig. 1b). They consist of randomly oriented blades of antigorite (Tab. 1) forming characteristic mesh

mimic the cleavage of the magmatic pyroxene. Later on, these lizardite crystals were replaced by antigorite, forming occasionally typical hourglass texture. Moreover, in some serpentinite clasts small veinlets of late talc were observed. The abundance of opaque minerals, mainly spinels and base metal sulfides is common to all serpentinites of the formation. Talc, hematite and chlorite, are locally formed as assemblage in between the serpentinite and the carbonate probably formed during a hydrothermal metasomatism stage, which mostly followed the tectonic fracturing of the rock.

### *Carbonate phase*

The second most important component of the ophicalcites is the carbonate phase. It is mostly represented by calcite whereas dolomite presence was revealed only in a few samples. Calcite is mainly found as fracture filling material or replacing serpentine minerals (Fig. 2a). The



**Figure 2.** SEM - BS electron images of ophicalcites samples: (a) Calcite (cal) replaces antigorite (atg); (b) dolomite (dol) replaces calcite; (c) magnetite (mt) grains in antigorite and calcite; (d) partial replacement of spinel (spl) by magnetite.

and pseudomorphic textures. The latter are being both symplectitic and interpenetrating, regarding how the fibrous antigorite crystals connect to each other. X-ray diffraction patterns were used for the discrimination of serpentine polymorphs and showed that lizardite and chrysotile are quite rare. Serpentine crystals range from 0.01 to 2mm in length, growing in random orientation. In some places, bastites were observed. These bastites sized up to 1cm, consist of very small platy crystals of lizardite) which grow in directions that tend to

white coarse-grained calcite crystals have well-expressed rhombohedral cleavage. Minor dolomite has formed only along areas of tectonic activity (e.g. shear zones) replacing calcite (Fig. 2b). The most common feature in the matrix regards the replacement of antigorite by calcite. Antigorite breaks down and calcite grows in a dense granoblastic texture that bonds tightly the serpentinitic clasts. In addition, fine-grained crystals of talc, tremolite, hematite and magnetite (Fig. 2c) can also be observed in the matrix. In

the numerous veins that crosscut the formation in randomly oriented directions, calcite forms sparry rhombohedral crystals that grow bigger towards the inner part of the vein. Twinned crystals of calcite were also observed, while no dolomite was found in these veins.

#### *Chromitites*

Rounded or pod-shaped chromititic bodies were found in two of the study sites. SEM examination of such samples revealed that aluminium chromite predominates in a mean percentage of ca. 80%. Intense cataclastic texture is the most important characteristic of these chromitites under the microscope. The spinels have been partly replaced by magnetite, mainly along fractures and at the periphery of the crystals (Fig. 2d). The rest of the rock consists of planar Cr-rich clinocllore crystals (Tab. 1) and small veins of carbonate material, mostly calcite with minor amount of dolomite. In many cases, base metal sulfides (violarite, millerite) were observed in close spatial association with the spinels.

#### **Petrogenetic Implications and Conclusions**

The ophicalcites of Tinos Island consist mainly of fractured serpentinite clasts that are crosscut by numerous, randomly-oriented calcitic veins. The main part of the formation shows strong to pervasive cataclastic deformation, whereas in the uppermost parts a poor-sorted and matrix-supported ophicalcite breccia shows intense characteristics of reworking and redeposition processes, indicating a sedimentary origin. Taking into consideration all these features, a mixed hydrothermal – tectonic – sedimentary origin can be suggested for the whole formation. In particular, the upper stratigraphic part may represent deposition of serpentinitic blocks and smaller fragments onto a cataclastically deformed serpentinitized ultramafic body exposed to seafloor, along conjugate shear planes and fault zones, due to intense strike-slip or extensional tectonic forces. Recycling of hot carbonate seawater within the fractured and brecciated ultramafic body in conjunction with its serpentinitization caused hydrothermal leaching and precipitation of calcite in the fractures. Moreover, the presence of hematite in the formation indicates that these fluids were oxidizing. The abundance of talc that in many places surrounds the ophicalcitic bodies might be a further evidence that the ophicalcites are related to tectonic fault rocks in

an intraoceanic environment (cf. Boschi et al., 2006). Geochemical and isotopic studies of the Tinos Island ophicalcites and comparison to other analogous studied formations in Greece (Melfos et al., 2009) are the next steps to be done in order to fully understand the mechanisms that took part in the formation of such a polygenetic rock and may help us define important paleogeographic conclusions regarding the Tethys Ocean.

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## ASSESSMENT OF OIL/GAS GENERATION POTENTIAL OF THE BULGARIAN PART OF THRACE BASIN BY MEANS OF ORGANIC GEOCHEMISTRY

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### Abstract

For appraisal of oil/gas generation potential of some basins is very important to define the source rocks in these sedimentary sections and to evaluate their hydrocarbon generation capacity. In the last decade, an intensive application of a complex of analytical geochemical techniques for potential evaluation of the sediment for oil/gas production is applied and is still current nowadays. To define particular rocks as “source rocks” it is necessary not only to prove sufficient content of organic matter (TOC), but to determine their potential for hydrocarbon generation as well as to define their maturity degree. Such evaluation is easily done by Rock Eval technique. By its application, the generation potential of some source rocks in the Turkish part of the Thrace basin with proven potential for oil/gas generation has been already performed. Organic matter content (TOC) in the main generating formation in the Turkish part of the Thrace basin is in the range of 1.5-2.6%. In this study, the source rocks with proven properties for oil/gas generation from the Turkish part will be compared with sediments, considered as promising source rocks in the Bulgarian part of the Thrace basin. They are characterized by a similar geological age and lithology as in the Turkish part.

“Free” and “bound” bitumoids of all sequences are characterized by methods of organic geochemistry, i.e. extractions, fractionations, gas-chromatography/mass spectrometry (GC-MS). A broad range of chemical species are considered, i.e. *n*-alkanes, regular isoprenoids, diterpenoids, hopanes, steranes, fatty acids, polar diterpenoids, etc. Results are quantitatively interpreted.

For the sediment formation at a depth of ~ 550 m, a very good correlation of Rock Eval data with the results obtained by geochemical proxies is depicted. This interval corresponds to one of the main source rock intervals in the Turkish part of the Thrace basin and is considered as especially perspective for oil/gas generation.

Rock Eval data and component analysis give us ground to assume Type III or mixed Type II/Type III for the organic matter of the sediment formation. The following results support this assumption: (i) *n*-alkane distribution is characterized by high contents of long-chain members and this reflects in high magnitudes of CPI values; (ii) the position of the samples in Pr/*n*C<sub>17</sub> vs. Ph/*n*C<sub>18</sub> diagram; (iii) the presence of 4-methyl-sterane; (iv) low magnitudes for sterane/hopane ratios. Sterane distribution pattern argues for organic matter formation in a bay or estuary;

The assumption for Type III organic matter is strongly supported by the results for triterpenoids compositions. High contents of oleanane/ursane triterpenoids, i.e. saturated, aromatized, polar analogues, partly destructed, argue for a terrestrial vegetation of angiosperm type rather than conifers. Organic matter is immature with highly expressed microbial activity inasmuch extracts are rich in ββ hopanoids.

In conclusion, some samples of the formation, especially at ~550 m depth, are promising as gas/oil source rocks. It could be assumed that at suitable conditions of sedimentation they will be able to generate biogenic gas.

## SOURCE ROCKS OF DETRITAL GARNETS AND SPINELS FROM CLASTIC SEDIMENTS OF THE GOSAU GROUP (WESTERN CARPATHIANS, SLOVAKIA)

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### Abstract

The composition of detrital garnets and spinels from conglomerate matrix and sandstones of the Gosau Group in the area of Dobšinská Ľadová Jaskyňa village and Jaklovce (Kurtova skala hill) quarry provides evidence that they were derived from three types of source rocks: (1) gneisses, amphibolites, metagabbros, metamafic rocks and eclogites/retrogressed eclogites of the pre-Alpine basement of the Western Carpathians; (2) the same rock types recycled in the Upper Carboniferous conglomerates of the Gemeric Superunit and (3) Triassic and Jurassic ophiolites of the Meliata Superunit.

**Keywords:** *spinel, garnet, provenance analysis, Late Cretaceous–Paleocene, Western Carpathians*

### Introduction

Clastic sedimentary rocks may serve as proxies for reconstruction of geological structure of their source areas, which is particularly important when these sources were nearly destroyed by subsequent geological processes and/or hidden under younger overstepping deposits or nappe units. Composition of conglomerate pebbles, petrofacies of sandstones and heavy mineral spectra and chemistry may all provide irreplaceable information in this aspect. We present data about detrital garnets and spinels from the Upper Cretaceous to Paleogene, Gosau-type sediments of the Central Western Carpathians, which allow for definition of three different sources. In addition to pre-Alpine supply terrains, an important part of detrital minerals was likely derived from Triassic–Jurassic ophiolite and mélange complexes of the Meliatic Unit.

### Geological setting

Sedimentary rocks of the Late Cretaceous to Paleocene age in areas of Dobšinská Ľadová

jaskyňa (DLJ) village and Jaklovce – quarry are regarded as equivalents of the Gosau Group sediments of the Eastern Alps (Stern and Wagreich 2013). Their position is similar to the internal Alpine Gosau basins (Kainach and Krappfeld), but their composition is more similar to the Gosau basins of the Northern Calcareous Alps. In the localities described here, sediments of the Gosau Group rest in an overstepping position on the Triassic carbonates of the Silicic Unit or on the Jurassic melanges of the Meliatic Unit.

The Gosau sedimentary rocks near DLJ village occur in a small erosional relic squeezed between two slices of the underlying Triassic carbonates of the Silicic Stratená nappe (Mello et al. 2000). They are composed of two sequences: (1) the lower sequence of freshwater limestones with coal seams grading into marine, reddish-brownish marls with Campanian foraminifers; (2) the upper sequence is represented by two types of polymict conglomerates differ in petrographic character of the sedimentary material. First type contains mostly pebbles of Cretaceous freshwater limestones, Triassic and Jurassic carbonates and radiolarites, rarely also quartzites, amygdaloidal basalts, serpentinites, greenschist and rhyolite metavolcaniclastics, whereas second type is composed mostly of metaultramafite (serpentinite) pebbles together with the clasts of ophitic basalts, dolerites, gabbros, radiolarites, marbles and rarely also rhyolites and blueschists (Hovorka et al. 1990, Ivan et al. 1998). Both types of conglomerates alternate with sandstones – lithic greywackes.

Clastic deposits found in the active quarry on the Kurtova skala Hill near Jaklovce village (Eastern Slovakia) occur as fillings of palaeokarst cavities in Middle Triassic crystalline limestones (Pelsonian). They consist of conglomerates, sandstones and siltstones. Composition of conglomerates is similar to those described as the second type from the Dobšinská Ľadová Jaskyňa locality (ultramafics, serpentinites, basalts, metamorphosed limestones). Garnets and spinels



were found in the conglomerate matrix and in the sandstones. Also the magnetite, zircon, rutile and apatite have been identified among the most frequent heavy minerals.

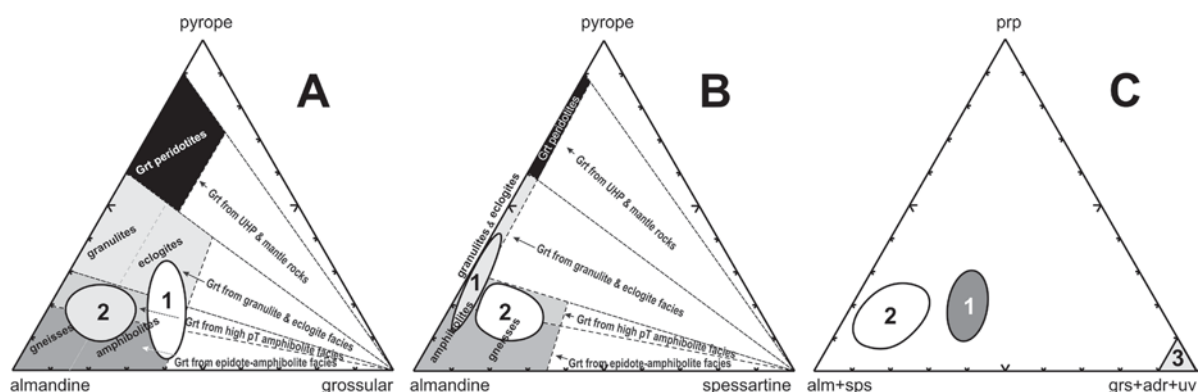
## Results and Discussion

### Detrital garnets

Composition of the detrital garnets (Grt) from the Gosau sediments suggests their derivation from source areas containing: (1) high-grade metamorphic rocks – granulites and retrogressed eclogites; (2) rocks metamorphosed under the amphibolite-facies conditions – gneisses and amphibolites and (3) the ophiolitic ultramafic rocks.

content of spessartine (10–27 mol %) than Grt from granulites. Content of grossular is less than 10 mol %. Garnets coming from amphibolites metamorphosed in epidote-amphibolite to amphibolite facies conditions differ from Grt from gneisses by a higher grossular content (> 10 mol %)

Continual transition of Grt composition in the first and second groups (figure 1 A,B, field 1 and field 2) reflects a dominance of one source area composed of rocks metamorphosed in the amphibolite to granulite facies. Such rock complex in the pre-Alpine Western Carpathian basement is represented by the leptynite-amphibolite complex (LAC, Hovorka et al. 1997), which contains retrogressed eclogites too (Janák et al. 2007)



**Figure 1.** Composition of the detrital garnets from the studied Gosau Group sequences. A, B and C - field 1: detrital garnets coming from amphibolites, mafic granulites and retrogressed eclogites, field 2: detrital garnets coming from gneisses, C - field 3: detrital garnets coming from the low-grade metamorphosed ultramafic rocks (serpentinites). Diagram and fields source rocks of detrital garnets according Méres (2008, 2009).

(1) Garnets coming from mafic granulites and/or high-grade amphibolites (figure 1A,B - field 1) have relatively higher content of pyrope (prp) component (20–25 mol %) in comparison to the Grt from gneisses (field 2). Furthermore, the high content of almandine (alm) component (50–60 mol %), relatively low proportion of grossular (grs) component (~ 30 mol %) and very low content of spessartine (sps) component (~ 2 mol %) are typical.

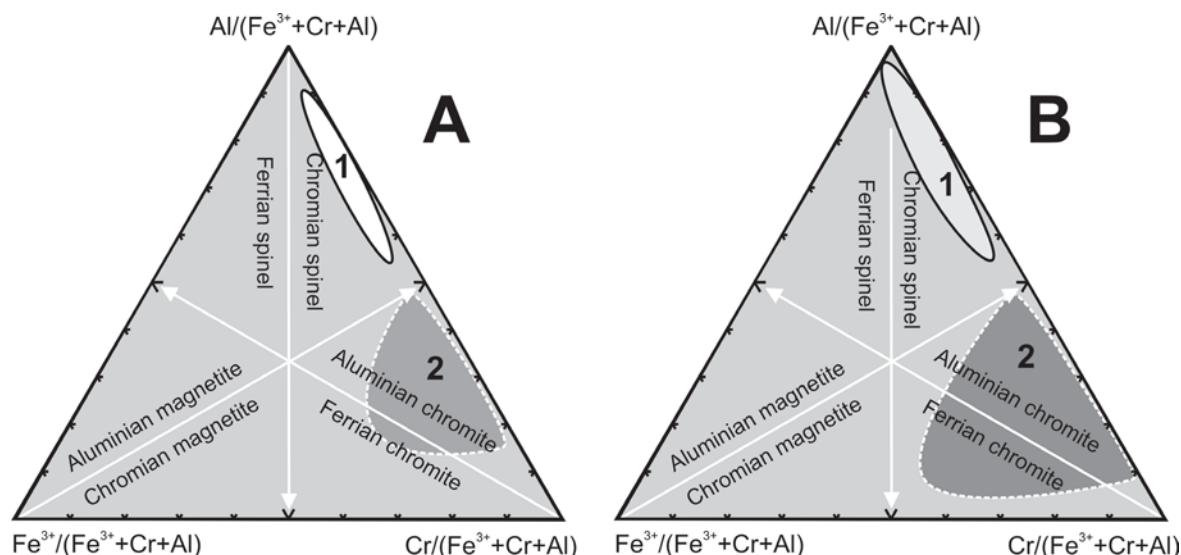
Garnets derived from retrogressed eclogites (figure 1 A,B - field 1) display pyrope content higher than 25 mol %, almandine content of 40–50 mol %, grossular content of 25–30 mol % and spessartine less than 1 mol %. They differ from the group 1 especially by a higher proportion of the pyrope component (>25 mol %).

(2) Garnets originated from gneisses (figure 1 A,B - field 2) have high almandine content (~ 55 mol %), low pyrope (< 10 mol %) and higher

(3) Detrital garnets from the low-grade metamorphosed ultramafic rocks (serpentinites) display green colour and typically high content of the andradite (adr) component (66–97 mol %), variable content of uvarovite (uv) component (0.8–31 mol %) and low contents of grossular (grs) component (< 3 mol %, figure 1C field 3). Similar garnets from the serpentinized ultramafic rocks of the Meliatic Superunit, which form several small bodies embedded in the ophiolitic mélange representing relics of the Triassic-Jurassic Meliata Ocean, were described by Fediuková et al. (1976), Hovorka et al. (1985) and Méres et al. (2008).

### Detrital spinels

As follows from microprobe analyses of detrital spinel grains, their composition varies from aluminian chromite to chromian spinels (figure 2A). Source rocks of spinels plotted in the chromian spinel field (figure 2A, field 1) were metaultramafics rocks, metamorphosed under the



**Figure 2.** Composition of the detrital spinels (A): field 1 – Gosau Group detrital spinels derived probably from metaultramafics rocks, metamorphosed under the granulite to eclogite facies conditions, field 2 – Gosau Group detrital spinels derived probably from the serpentinized ultramafic bodies of the ophiolite complexes. (B) Composition of the rock-forming spinels from pre-Alpine basement of the Western Carpathians (field 1, Méres et al. 2008) and spinels from the serpentinized ultramafic bodies in the Triassic sequences of the Meliatic Superunit (field 2; localities: Rudník, Jasov, Jaklovce, Dobšiná, Danková; data from Rojkovič et al. 1978, Mikuš and Spišiak 2007).

granulite to eclogite facies conditions. Identical spinels were described from the metamafic rocks of the LAC in the Veporic Unit (Méres et al. 2006, figure 2B, field 1). The spinels plotted in the aluminian chromite field (figure 2A, field 2) are typical for ultramafic rocks. Identical spinels have been found in the ultramafic rocks of the Meliata Unit (Rojkovič et al. 1978, Hovorka et al. 1985, Mikuš and Spišiak 2007, figure 2B, field 2). These rocks are considered as the second possible sources of analyzed spinels. Moreover, the Upper Devonian/Lower Carboniferous ophiolite mélange of the Zlatník Group in the Gemeric Superunit (Ivan and Méres 2012) with some detrital spinels in the mélange matrix cannot be fully excluded as another additional source.

## Conclusions

Detrital garnets and spinels from the clastic sequences of the Gosau Group near Dobšinská Ľadová Jaskyňa village and Jaklovce quarry were probably derived from three different sources: (1) the first source could have been gneisses, amphibolites, metagabbros, metamafics and eclogites correlated with the leptynite-amphibolite complex in the pre-Alpine basement of the Western Carpathians, (2) the second source could have been also Late Carboniferous conglomerates of the Gemeric Superunit containing the same rock types in their clasts and (3) the third possible source rocks

were probably the Triassic and Jurassic ophiolites of the Meliatic Superunit. These data indicate dominantly local sources from various basement and ophiolite-bearing units, which are still present in the geological structure of surrounding areas, e.g. the Gemeric medium- to high-grade pre-Alpine basement complexes (Klátov Unit) or the Meliatic mélange units occurring in a nappe position above the Gemeric basement.

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## FORMATION OF THE URANIUM AND REE BEARING PHOSPHATITE OCCURRENCE OF PÉCSELY (BALATON HIGHLAND, HUNGARY)

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### Abstract

The studied phosphatite occurrence is located in the Balaton Highland, in the SW part of the Transdanubian Ridge (W-Hungary). Earlier investigations have revealed radioactive anomaly, which have drawn the attention to the uranium bearing sedimentary phosphatite layer. The studied phosphatite layer together with some fluorite veins is located in Triassic limestone and dolomite. The last research was done in the area nearly half a century ago, although the formation of the phosphatite layer and the origin of the U content have not been answered, so this work aims to contribute with our knowledge on the characteristics and origin of this mineralization.

The studied uranium-bearing layer is located in a Triassic limestone (Vászoly Limestone Formation) which is unconformably overlapping an Anisian dolomite bearing (Tagyon Limestone Formation). The latter contains epigenetic fluorite veins and was formed as basinal carbonate with volcanic tuff intrabeds. The phosphatite is thought to have formed syngenetically with the shallow marine limestone during sedimentary processes. The horizontal extension of the layer is large, but the thickness is small (below 30 cm). The main component of the layer is carbonate-fluorapatite, associated by some calcite, rare hematite, pyrite and zircon.

Based on our studies, the main mineral phase, the carbonate-fluorapatite is located around the primary rock-forming calcite whereas the remaining space is filled by a later generation of calcite. The fluorite grains found in veins and cavities below the phosphatite layers are euhedral and have dark purple colour and rarely, calcite occurs together with them, too. The cathode-luminescence pictures of the fluorite shows a fine zonation which may be caused by the radioactivity of the phosphatite layers.

Based on the quantitative analyses (EPMA) of the carbonate-fluorapatite grains, the uranium content of the studied layer is most likely related to this phosphate mineral, as it contains 0.023-0.3

mass% U, while no other U-bearing phases were observed. However, the carbonate-fluorapatite grains contain also rare earth elements: 0.031-0.889 mass% total REE content (La, Ce, Nb, Dy, Sm, Nd, Tb, Pr, Ta, Y, Gd, Eu) was proven. Based on the elemental mapping, both the U and REE occur homogeneously distributed in the crystals. The data analysis revealed that the uranium and sulphur content and the uranium and calcium content are positively correlated, while the uranium and phosphorus content correlates negatively. Quantitative analyses of fluorite showed that it contains ~0.01 mass% U and <0.174 mass% total REE content. The elemental mapping prepared on the fluorite revealed that its REE content is most likely related to submicron sized REE mineral inclusions. Future geochemical analyses may help in understanding the origin of the P, U and REE content as well may explain the possible relationships among the phosphatite layers, the fluorite veins and cavities and tuff levels which are settled into the host rock (limestone) and the nearby Permian red sandstone.

Based on the now available data, it can be concluded that the source of the U was most likely an older rock, e.g. the nearby Permian alluvial sandstone or the volcanic tuff layers, whereas the high relative phosphorous content may derive from the high amount of fishbone and organic materials of the host rock. However the found euhedral carbonate-fluorapatite crystals along the cavities of the studied layer, the concentrating role of a hydrothermal fluid has to be taken into consideration, too. Since brecciated phosphatite occurs among the fluorite veins, it is suggested that the fluorite formed most probably later than the phosphatite layer with the leaching of the fluorine content of the carbonate-fluorapatite.

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## GEOCHEMISTRY AND GEOCHRONOLOGY OF GNEISSES IN BODE SAADU AREA, SOUTHWESTERN NIGERIA

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### Abstract

Two suites of migmatitic and granodioritic gneisses outcropping in the Bode Saadu area, Southwestern Nigeria have showed Paleoproterozoic ages of  $2228 \pm 32$  Ma and  $2179 \pm 28$  Ma. They were obtained by LA-ICP-MS in-situ U-Pb dating of

enabled constraints to be placed on the timing of the development of some of these structures with the  $S_1$  fabric and their tight-to-isoclinal folds being of Eburnean age while the ductile shears and the close open folds are probably of Pan-African age.

**Key words:** Geochemistry, Geochronology, Gneisses, Paleoproterozoic, LA-ICP-MS

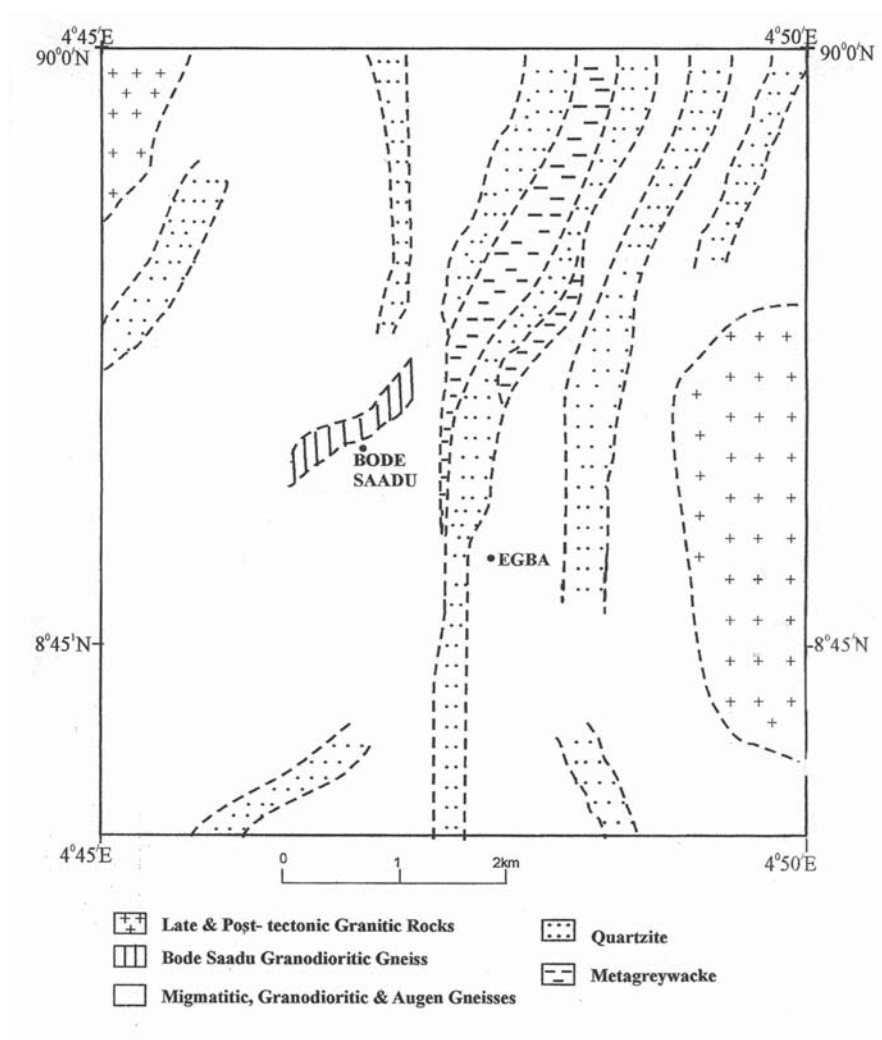


Figure 1. Geological map of Bode Saadu area.

zircons and indicated the time of crystallization of these rocks. The gneisses bear the imprints of several deformation events in the form of foliations, folds and shear zones. The geochronological data

### Introduction

The Nigerian basement complex forms the southern part of the internal zone of the Pan-

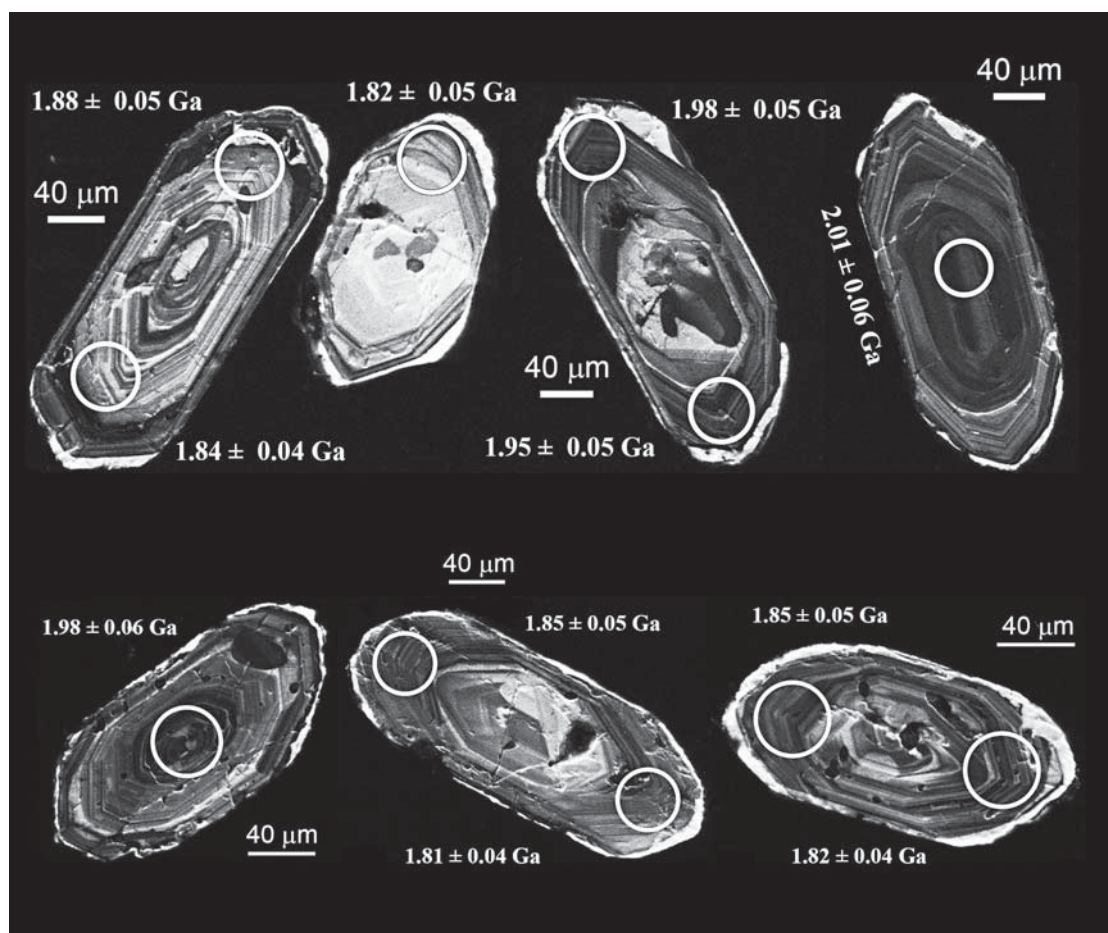
African Trans-Saharan orogenic belt (Ferre et al. 2002). Available till now, geochronological data show that it is made of rocks ranging in age from Archean to Neoproterozoic. In the northwest, Early Archean ages have been documented from orthogneisses by Dada et al. 1993. These are followed by Neoproterozoic ages obtained from intrusive granitoids and leucocratic veins in some migmatites. However, in the southwest younger ages ranging from Late Archean to dominantly Paleoproterozoic have been recorded from orthogneisses. Intruding these rocks are granitic rocks which have yielded Neoproterozoic ages.

Bode Saadu area (Fig. 1) forms part of the southwestern sector of the Nigerian basement complex which contains rocks that have yielded Archean, Proterozoic and Early Paleozoic ages (Rahaman et al. 1983, Fitches et al. 1985, Dada et al 1993, Dada 1998). In this region, several suites of orthogneisses occur, however the geochemical affinity and the age of these rocks have not been determined. Their relationships with one another have been difficult to ascertain because of their complex deformation. This investigation reports

first geochemical data as well results of U-Pb dating of zircons from these rocks by in-situ LA-ICP-MS method and attempts to correlate them with similar rocks in other parts of the region.

### Materials and Methods

Four samples of the Egba migmatitic gneiss and two of the Bode Saadu granodioritic orthogneiss were analyzed for major, trace and rare earth elements by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Mass Spectrometry (ICP-MS), respectively. The U-Pb dating of zircons were performed by LA-ICP-MS technique using a PerkinElmer ELAN DRC-e ICP-MS connected to the NWR/ESI UP-193FX ArF excimer laser ablation system. A cathodoluminescence (CL) imaging of each selected for dating zircon grain, previously mounted in epoxy and finely polished was performed on the Zeiss EVO 25LS SEM prior to the mass spectrometry measurements. The representative zircon selection was made from an initial sample set of more than 100 grains from each rock. The LA-ICP-MS machine was



**Figure 2.** Representative set of CL images of zircons from Egba migmatitic gneiss (top panel) and Bode Saadu granodioritic gneiss (bottom panel). Ablation points are marked with circles. Measured ages are according 206/208 isotope ratios.

calibrated and optimized to the proper U-Pb ratios at high sensitivity level by repeated measurements of natural zircon standard and second one was used as reference material for data verification purposes. Each five sample unknowns were bracketed by two standard measurements performed under the same analytical conditions. After off-line data reduction and correction procedure of the measured U-Pb ratios, final age estimation was performed by Isoplot toolkit (Ludwig 2003).

## Results and Discussion

On the total alkali versus  $\text{SiO}_2$  plot after Cox et al. 1979, the rocks plot mainly in the quartz diorite (granodiorite) field. On the  $\text{K}_2\text{O}$  versus  $\text{SiO}_2$  plot after Peccerillo and Taylor 1976, they plot in the fields straddling the calc-alkaline and high-K calc alkaline series. On the  $\text{FeOt}/(\text{FeOt}+\text{MgO})$  versus  $\text{SiO}_2$  plot after Frost et al. 2001, the rocks fall in the magnesian field. Chondrite normalized REE patterns of the orthogneisses are taken from Sun and McDonoghue 1989. The patterns show strong REE fractionation and LREE enrichment with a negative Eu anomaly suggesting garnet, pyroxene and plagioclase fractionation in their sources. On the tectonic setting discrimination diagrams of Pearce et al. 1984, the orthogneisses plot in the field of Volcanic Arc Granites and Volcanic Arc + Syncollisional Granites.

Zircons from the studied gneisses are largely euhedral. The grains exhibit well-developed oscillatory (concentric) growth zoning (Fig. 2) indicative of originally igneous zircons. The obtained average Th/U ratios (0.55-0.58) are also typical of zircons formed by igneous processes. The Wetherill Concordia diagrams are shown in figure

3. The data from Egba migmatitic gneiss (Fig. 3 left) define Discordia line with Concordia upper intercept age of  $2228 \pm 32$  Ma which is interpreted as the time of crystallization of the igneous protolith and also as time of the emplacement of igneous rock. The lower intercept age of  $426 \pm 85$  Ma indicates a period of variable Pb losses but in this particular case could be associated with some late Pan-African orogenic disturbance.

The data from Bode Saadu granodioritic gneiss are presented in figure 3 (right). They yielded an upper intercept age of  $2179 \pm 28$  Ma on the Concordia plot which could be taken as the time of crystallization of the igneous protolith and therefore the time of its emplacement. The lower intercept value of  $287 \pm 23$  Ma is considered as a record of variable Pb losses and has no geological significance.

The results obtained from these granodioritic rocks indicate Paleoproterozoic calc-alkaline magmatism in Bode Saadu area beginning with the Egba Migmatitic Gneiss and then the Bode Saadu Granodioritic Gneiss. Tectonic affinity shows that these rocks were emplaced in a volcanic arc/syncollisional field and considering their ages, it denotes their emplacement during the Eburnean orogeny. These rocks have undergone polyphase deformation and metamorphism starting with foliation development, migmatization and tight, isoclinal folding during the Eburnean event. The later ductile shears and tangential displacements were probably formed during the later, NeoProterozoic, Pan-African orogeny (ca. 600 Ma). Late, brittle, normal faulting was probably associated with exhumation and uplift. These rocks contain xenoliths of the metasedimentary

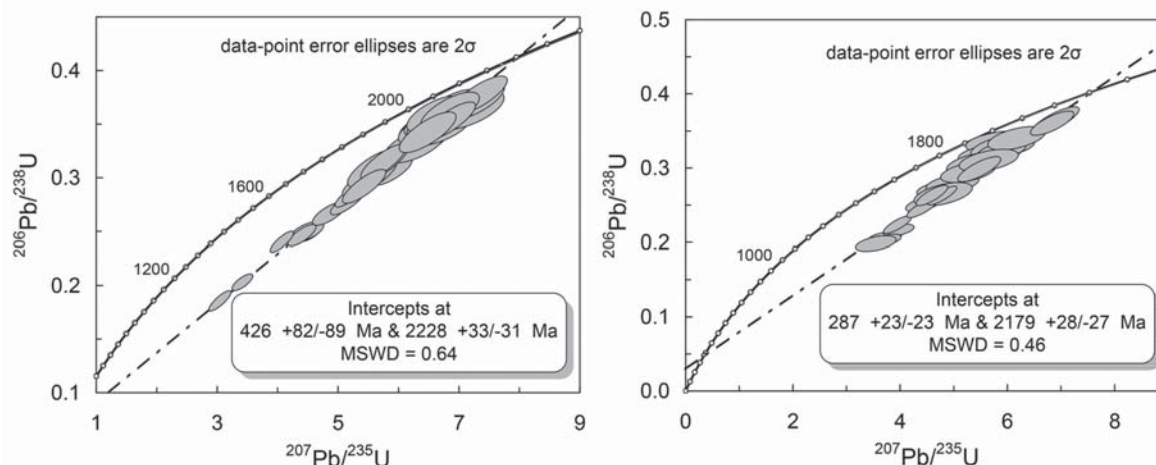


Figure 3. Wetherill Concordia plots of Egba migmatitic gneiss (left) and Bode Saadu granodioritic gneiss (right).

rocks i.e. the metagreywackes which indicates that the metasedimentary rocks are at least Paleoproterozoic in age. Similar Paleoproterozoic orthogneisses have been documented from other parts of southwestern sector of the Nigerian basement complex e.g., Jebba Granitic Gneiss (Okonkwo and Ganev 2012).

## Conclusions

The geochemical and geochronological results from the orthogneisses of Bode Saadu area indicate an important period of crust formation, associated with the orogenic activity during the Paleoproterozoic as well as that the Eburnean orogeny affected this part of the Nigerian basement complex. The older members of the orthogneiss suite (i.e. the Egba Migmatitic Gneiss) carry structural fabrics and early, isoclinal folds ( $D_1$ ) which were developed before the emplacement of the Bode Saadu Granodioritic Gneiss. These metamorphic rocks were intruded by a suite of largely undeformed granitoids ranging in composition from granodiorites through granites to pegmatites of probable Neoproterozoic age emplaced during the Pan-African orogeny. Similar Paleoproterozoic orthogneisses have been documented in some other parts of southwestern Nigeria and in Central Hoggar area of the Tuareg Shield.

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## PRELIMINARY BIOMARKER RESULTS OF THE LOWER JURASSIC BLACK SHALE FROM HUNGARY, AND PALEOENVIRONMENTAL IMPLICATIONS

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### Abstract

Approximately 12 m thick, organic-rich marine sediments – commonly referred to as black shale – represents a part of the Lower Toarcian in Réka Valley section, Mecsek Mountains, Hungary. Although achievements in geological investigations and petroleum resource assessments during recent years have been remarkable, the environmental conditions, mechanics, and process that resulted in the deposition of high-organic sediments during the Early Toarcian (183–176.5 Ma, Early Jurassic) Oceanic Anoxic Event (OAE) are still a matter of discussions. The Réka Valley black shale, named as Rékavölgy Siltstone Formation (RSF), composed of laminated and thin-bedded lithotypes with intercalations of mixed carbonate-siliciclastic turbidites. Sedimentological and paleontological features indicate anoxic/disoxic conditions near the sea bottom during deposition and early diagenesis. Based on previous biostratigraphic investigations, this black shale horizon can be exactly correlated with the Early Toarcian OAE. According to published data, in the black shale samples collected from the Réka Valley section of the RSF, total organic carbon (TOC) contents vary between 1.2 and 12.0 % for laminated lithotype and between 6.0 and 3.0% for thin-bedded one. From a previous research campaign

in the study site, Rock Eval data indicate a type II, immature kerogen throughout the section and optical analysis reflects that the organic matter is composed almost exclusively of liptinitic kerogen linked to algal origin. According to the present biomarker analyses made on samples from the lower 5 m thick part of the section, the black shales are characterized by a marked predominance of short chain *n*-alkanes. Furthermore, a series of hopanes are present in the samples. The above mentioned parameters indicate that the organic matter source is attributed to an algal/bacterial contribution, at least for the lower 5 m thick part of the section. The biomarker distribution and some important parameters show that the studied black shales appear to be characterized by marine-derived (mixed algal/bacterial) organic matter, and contrary to the previous Rock Eval data, a higher level of thermal maturity.

## MOLECULAR AND PALYNOLOGICAL STUDY OF THE INTERNAL SEDIMENT FROM THE SILESIAN-CRACOW Zn-Pb DEPOSITS, POLAND – PRELIMINARY RESULTS

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### Abstract

Nine samples of the internal sediments (IS) from the Silesian-Cracow Zn-Pb deposits were studied using total organic carbon (TOC) and total sulphur (TS) measurements, gas chromatography-mass spectrometry (GC-MS) and palynological analysis. IS are organic matter (OM) rich rocks with TOC values ranged from 5.75 to 12.97%, and highly variable content of TS (from 0 to 20.45%), depending on degree of sulfides mineralization. The study of OM extracts of IS samples using GC-MS revealed its low degree of thermal maturity. The majority of the samples contain hop-13(18)-ens, hop-17(21)-ens and 17 $\beta$ ,21 $\beta$ (H)-hopanes – compounds typical for an immature OM. In addition, low values of the C<sub>31</sub> $\alpha\beta$ S/(S+R) ratio (ranged from 0.09 to 0.28) confirm the immature nature of studied sediments. However, in some cases oxidation processes resulted in significant differences in hydrocarbon distribution. Differences in the range of OM oxidation may be connected with the complex karst system developed within the ore-hosting dolomites. The *n*-alkane distribution differs significantly between samples. Some samples are characterized by definite preponderance of short- over long-chain *n*-alkanes, what usually is interpreted as derived from marine precursors, while other samples shows bimodal distribution with maxima at *n*C<sub>16</sub> and *n*C<sub>27</sub>. These differences in *n*-alkane distributions may indicate a multi-sourced origin of OM in IS with both marine and terrestrial input. The palynological data indicates the Mid-Triassic to Jurassic age and shows that IS contain both marine and terrestrial palynomorphs which is in agreement with geochemical results.

**Keywords:** *Internal sediments, molecular analysis, palynology, Zn-Pb deposits*

### 1. Introduction

The Silesian-Cracow Zn-Pb deposits are occurring mainly within the so-called ore-bearing dolomites of the Mid-Triassic age (Muschelkalk) and are commonly classified as a Mississippi Valley-type (MVT) deposits (e.g. Leach et al. 2001). Internal sediment (IS), an organic matter (OM) rich sedimentary rock that fills caverns in the bottom parts of ore bodies and open spaces between the collapse breccia fragments has been reported frequent times, but the problem of its age and the origin of contained OM is the subject of numerous discussions and to present day has not been clearly resolved (Kolcon and Wagner 1983; Sass-Gustkiewicz 1996; Sass-Gustkiewicz and Kwiecińska 1999; Karwowski et al. 2001). These preliminary results provides the first palynological and molecular data for the IS from “Pomorzany” and “Trzebionka” mines, and their purpose is to clarify age and geochemical transformations of OM from the karstic caverns of the ore-bearing Mid-Triassic dolomites.

### 2. Samples and experimental procedures

Nine samples from exposed fresh-rock in the walls of the underground “Pomorzany” (8 samples) and “Trzebionka” (1 sample) mines were collected for the geochemical and palynological studies.

#### 2.1. Total organic carbon and total sulphur

Total carbon contents (TC), total inorganic carbon contents (TIC) and total sulphur contents (TS) were determined by using an Eltra CS-500 IR-analyser with a TIC module. For more details see Marynowski and Wyszomirski (2008).

#### 2.2. Extraction and thin-layer chromatography

Cleaned and powdered samples were Soxhlet-extracted with dichloromethane in pre-extracted thimbles. The extractable organic matter (EOM)

was further separated by thin layer chromatography (TLC). Detailed description is presented in Marynowski and Wyszomirski (2008).

### 2.3. Gas chromatography – mass spectrometry

Aliphatic fraction was analysed using gas chromatography – mass spectrometry (GC-MS). GC-MS analyses were performed with an Agilent 6890 chromatograph equipped with an EPC Cool On-Column Inlet and fitted with one of the two fused silica capillary columns of different polarity, i.e. either HP-5 MS or DB-35 MS (60 m x 0.32 mm, 0.25 µm film thickness). Helium was used as carrier gas. For more details see Marynowski and Wyszomirski (2008).

then mounted onto glass slides using 2-part epoxy resin. The slides were then analysed and imaged using a Leica DMRX microscope.

## 3. Results and discussion

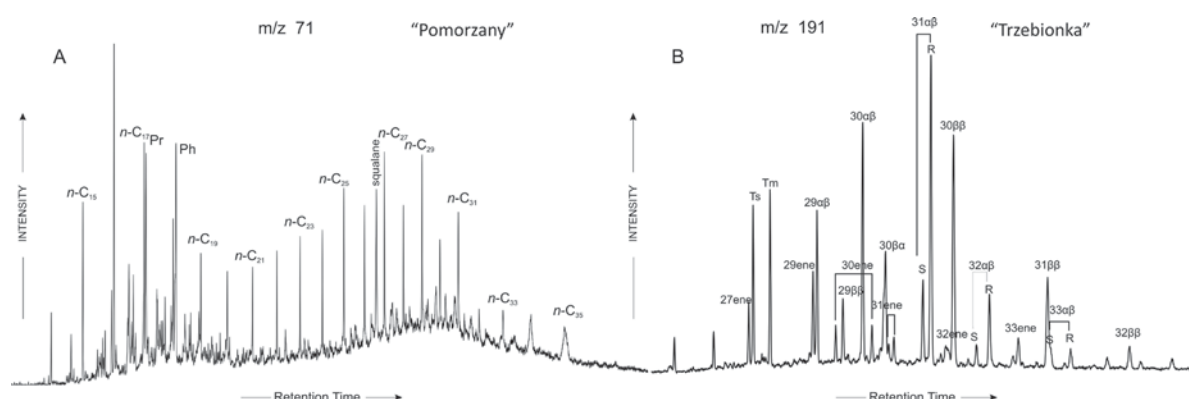
### 3.1. General geochemical characteristics

TIC, TOC and TS measurements indicate that studied sediments are OM rich rocks with TOC values between 5.75% and 12.97%. Total sulphur content is highly variable (from 0% to 20.45%) and depends on degree of sulfides mineralization (Tab. 1).

**Table 1.** Bulk geochemical data and basic molecular parameters based on n-alkane distributions.

Sample	TC%	TS%	TIC%	TOC%	CPI	CPI25-31	Cmax	Pr/Ph	SCh/LCh	Pr/n-C17	Ph/n-C18
ISPM1	6.68	20.45	0.93	5.75	0.97	1.57	18	0.77	2.78	1.19	1.17
ISPM2	13.16	5.73	1.23	11.93	0.77	0.89	18	0.90	33.12	0.83	0.64
ISPM3	7.68	17.83	0.84	6.84	0.64	0.98	18	0.77	52.04	0.49	0.70
ISPM4	12.88	12.71	1.34	11.54	0.71	1.25	18	0.99	7.45	0.63	0.38
ISPM5	8.41	9.49	0.54	7.87	1.02	1.31	16	0.96	0.99	1.13	1.62
ISPM7	10.19	13.73	0.68	9.51	0.95	1.75	17	1.09	7.51	0.84	1.24
ISPM8	13.58	14.06	1.02	12.56	1.04	1.01	14	0.73	6.41	0.25	0.82
ISPM9	12.89	2.44	1.21	11.68	1.25	1.34	18	1.36	3.36	0.91	0.89
SWTR4	12.97	0	0	12.97	0.91	0.96	17	0.94	21.25	0.80	1.01

TC = total carbon; TS = total sulfur; TIC = total inorganic carbon; TOC = total organic carbon;  $CPI_{(Total)} = \text{Carbon Preference Index: } 0.5 [\sum (C_{25}-C_{33})_{odd} + \sum (C_{23}-C_{31})_{odd}] / \sum (C_{24}-C_{32})_{even}$ ;  $CPI_{(25-31)} = \text{Carbon Preference Index: } (C_{25}+C_{27}+C_{29}) / (C_{26}+C_{28}+C_{30})$ ;  $C_{max}$  = carbon number maximum; SCh/LCh = short chain to long chain n-alkanes ratio:  $(nC_{17}+nC_{18}+nC_{19}) / (nC_{27}+nC_{28}+nC_{29})$ ; Pr = Pristane; Ph = Phytane;  $nC_{17}$  = n-heptadecane;  $nC_{18}$  = n-oktadecane.



**Figure 1.** Distribution of (A) n-alkanes and isoprenoids and (B) hopanoids in studied sediments.

### 2.4. Palynological preparation

The samples were processed for their palynological content using HCl and HF techniques according to the specific lithology of each sample. The resulting residues were then sieved at 15 µm and

### 3.2. Molecular analysis

The dominant compounds for all samples were n-alkanes and isoprenoids. Although the n-alkane distribution differs significantly between samples, all of them contain homologues with carbon chain

**Table 2.** Molecular parameters based on hopanoid distributions.

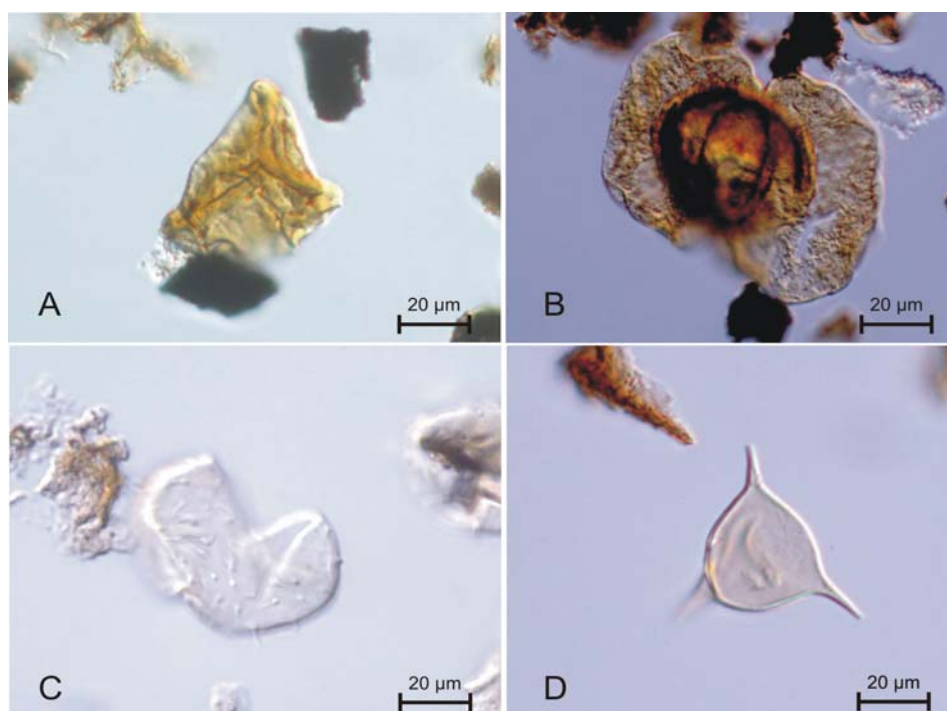
Sample	Ts/(Ts+Tm)	C29/C30	C30M/C30H	C31 $\alpha$ BS/(S+R)	C33 $\alpha$ BS/(S+R)/C31 $\alpha$ BS/(S+R)
ISPM1	0.61	0.52	0.76	0.26	0.16
ISPM2	0.35	0.79	0.54	0.28	0.20
ISPM3	0.43	0.79	0.60	0.28	0.31
ISPM4	0.36	0.50	0.86	0.09	0.06
ISPM5	0.51	0.59	0.72	0.19	0.49
ISPM7	0.34	0.52	0.56	0.27	0.22
ISPM8	0.41	0.30	0.94	0.09	0.25
ISPM9	0.54	0.53	0.82	0.23	0.23
SWTR4	0.47	0.60	0.61	0.22	0.12

Ts/(Ts + Tm) = C<sub>27</sub>-18 $\alpha$ -trisorhopane/(C<sub>27</sub>-18 $\alpha$ -trisorhopane + C<sub>27</sub>-17 $\alpha$ -trisorhopane); C<sub>29</sub>/C<sub>30</sub>H = C<sub>29</sub>-norhopane/C<sub>30</sub>-17 $\alpha$ -hopane; C<sub>30</sub>M/C<sub>30</sub>H = C<sub>30</sub>-17 $\beta$ -moretane/C<sub>30</sub>-17 $\alpha$ -hopane; C<sub>31</sub> $\alpha$ BS/(S+R) = C<sub>31</sub>-homohopane 22S/(22S + 22R); C<sub>33</sub> $\alpha$ BS/(S+R)/C<sub>31</sub> $\alpha$ BS/(S+R) = C<sub>33</sub>-homohopane 22S/(22S + 22R)/C<sub>31</sub>-homohopane 22S/(22S + 22R).

length from C<sub>14</sub> to C<sub>35</sub> (Fig. 1a). Almost in all cases, the short chain (*n*-C<sub>17</sub>-*n*-C<sub>19</sub>) over long chain (*n*-C<sub>27</sub>-*n*-C<sub>29</sub>) *n*-alkane predomination was observed with C<sub>max</sub> = 18 (Tab. 1), but in some extracts the bimodal distribution occurred (Fig. 1a). The short chain homologues, with carbon number lower

the studied IS samples is probably derived from both: marine and terrestrial sources.

The hopanoid distributions revealed the immature nature of the studied samples (Fig. 1B). The C<sub>31</sub> $\alpha$ BS/(S+R) ratio of the C<sub>31</sub> homohopane which is commonly used to evaluate thermal maturity of



**Figure 2.** Palynomorph assemblages in studied sediments.

A - Example of simple trilete spore. ?Concavissimisporites spp. B - Bisaccate pollen. C - ?Acanthomorph acritarch. D - Acritarch of the genus Veryhachium

than C<sub>22</sub>, are commonly considered as marine algal and/or bacterial derivatives (Spangenberg and Herlec 2006), while the long chain *n*-alkanes originate from terrestrial higher plants (Eglinton and Hamilton 1967). This indicates that OM from

sedimentary OM (Peters et al., 2005) characterized by relatively low values for all samples (from 0.09 to 0.28, Tab. 2). Moreover, in the majority of the samples such compounds as: hop-13(18)-ens, hop-17(21)-ens and 17 $\beta$ ,21 $\beta$ (H)-hopanes have been



identified what indicates immature OM character (Karwowski et al. 2001). However, significant differences between samples in the  $C_{30}M/C_{30}H$  ratios (Tab. 2) and the absence of hopanes with  $\beta\beta$  configuration in some IS samples could be connected with oxidation processes which have been described elsewhere based on experimental data (Elie et al. 2000) and observations of the natural oxidation of sedimentary rocks (Marynowski and Wyszomirski 2008).

### 3.3. Palynological analysis

The internal sediment samples contain palynomorphs (Fig. 2). None of the palynomorph specimens recovered though, were age diagnostic, which is surprising taking into account the abundance and preservation. The morpho-types (bisaccate pollen, simple trilete spores, Tasmanitids etc) are all relatively long-ranging through geological time and can occupy assemblages of many different ages. There are a few key points however, about the whole assemblage which may provide circumstantial evidence for a potential age: (i) The bisaccates within the assemblages were relatively abundant. There were degraded specimens which potentially exhibited striate/taeniate features. If this is the case, this would indicate an age no younger than Triassic; (ii) The acritarchs recovered are relatively simple forms which is typical of post-Palaeozoic assemblages; (iii) There is a marine influence in the assemblages with the occurrence of the prasinophycean algae and acritarchs, however these organisms were well adapted and often indicators for restricted salinity environments. Nonetheless, dinoflagellate cysts which are marine indicators are not present in the studied samples. Either, this indicates a very restricted marine environment or that the age of the sediment precludes the appearance of dinoflagellate cysts in the fossil record; in Europe no dinoflagellate cysts are known before the Late Triassic.

If these circumstantial points are to be collated then a potential age of Mid-Triassic - Jurassic could be inferred.

## 4. Conclusions

The organic matter present in internal sediment samples is characterized by very low degree of maturation and is a mixture of hydrocarbons of both: marine and terrestrial origin. However, oxidation processes affected some of the IS

samples and in consequence caused by significant differences in IS molecular composition. These oxidation processes could result due to complex karst system developed within the ore-hosting dolomites. The palynological observations confirm that studied OM has a multi-sourced origin and indicate the Mid-Triassic to Jurassic age.

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## GEOCHEMISTRY OF OLIGOCENE POST-COLLISIONAL VOLCANIC ROCKS IN NORTH DINARIDES IN BOSNIA AND HERZEGOVINA

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### Abstract

Tertiary volcanic rocks of the central (Maglaj, Teslić and Kolići) and northeast Bosnia (broad area of Srebrenica) belong to a volcanic formation of Oligocene shoshonitic and high-potassium calc-alkaline rocks. These rocks are separated within the Tertiary formations of igneous rocks which emerged between 55 and 29 Ma and are associated with the geodynamics of collision of the African and Eurasian plates in the Dinaric orogen segment.

Examined rocks from both areas show similar mineralogy, petrographic and geochemical characteristics. The rocks have holocrystalline to hypocrystalline porphyritic textures with phenocrysts of plagioclase, sanidine, biotite, quartz, hypersthene, hornblende and augite with variable compositions and percentages. Volcanic rocks of central Bosnia are high-K calc-alkaline dacites and subordinate andesites, while rocks of the Northeast Bosnia form the differentiation series of basaltic andesite-andesite-dacite. Relatively increased content of incompatible elements in volcanic rocks of central Bosnia indicate that they are more evolved.

The variations of most elements with respect to SiO<sub>2</sub> are consistent with the observed mineral fractionation, while the ratios of some diagnostic elements cannot be explained by crystal fractionation from a primary magma generated in the metasomatized mantle wedge. These ratios correspond to ascending magmas that continue to fractionate, and that in the meantime have undergone changes in the composition with different levels of contamination and assimilation of continental crustal rocks (AFC processes). The reaction rims on phenocrysts of quartz (resorption textures) and reversed zoning in plagioclase and amphibole phenocrysts is indicative of magma mixing of varying degrees of fractionation and their incomplete homogenization.

The studied rocks represented in spider diagrams show enrichment of LIL elements relative to HFS elements and have prominent Ta-Nb, P and Ti negative anomalies, and positive U and Pb anomalies. Chondrite-normalized REE patterns show strong enrichment in light REEs relative to heavy REEs with (La/Yb)<sub>n</sub> ratio between 15.3 and 33.4. These geochemical characteristics are typical for subduction related high-K volcanic rocks and volcanic rocks generated in post collisional zones.

Geochemical and geotectonic analyses show that the rocks have common characteristics of volcanic rocks from volcanic arcs on the margins of continents (Andean type of subduction). The differences in composition of Oligocene volcanic rocks in central and northeast Bosnia arise from different compositions of sub-continental mantle, amount of partial melt and intensity of assimilation of the crustal rocks or thickness of the crust.

The disagreement between the geotectonic regime determined in the field (transpressional-transensional regime) and geotectonic position of the Oligocene magma eruptions in Bosnia and Herzegovina based on the conclusions derived from the geochemical data (subduction or orogenic regime) can be explained by metasomatic character of sub-continental mantle which was inherited by an earlier (Variscan?) subduction.

Finally, Oligocene volcanic rocks in Bosnia and Herzegovina occupy an important place within the Tertiary volcanic formations of the Dinarides and Sava-Vardar Zone. According to petrological, geochemical characteristics and geotectonic conditions of the genesis, the studied rocks can be correlated with genetically related rocks of Periadriatic lineament, east and southeast Dinarides and Northern Hellenides.

## **GEOCHEMISTRY, SR-ND ISOTOPIC COMPOSITION AND $^{40}\text{Ar}/^{39}\text{Ar}$ AGE OF MAFIC ROCKS FROM THE TOZLU METAOPHIOLITE IN THE BIGA PENINSULA, EASTERN MEDITERRANEAN: INSIGHT INTO A DEPLETED MANTLE SOURCE REGION**

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### **Abstract**

Ophiolites contain valuable information on the origin and evolution of oceanic lithosphere. Mafic rocks from the Tozlu ophiolite within the Biga Peninsula represent remnants of an oceanic lithosphere. These mafic rocks are mainly represented by amphibolites and hornblend gabbros. Geochemical and Sr-Nd isotopic data are reported for mafic rocks exposed on the Kazdağ Massif, in northwest Turkey, and have been determined to reveal their origin, tectonic setting and mantle source. The mafic rocks are basaltic in composition with tholeiitic character and are enriched in both large ion lithophile elements (LILE: e.g. Rb, Ba, and Pb) and light rare earth elements (LREEs), with a wide range of Eu anomalies, but are depleted by high field strength elements (HFSEs: e.g. Nb and Ta). Geochemical characteristics of mafic rocks show MORB geochemistry that underwent deformation and metamorphism. Most mafic rocks are characterized by relatively narrow

range of isotopic compositions with low initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.70309-0.70366), high initial  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51292-0.51300) and high  $\epsilon\text{Nd}_t$  (+7.4 to +7.6), indicating derivation from a MORB-like depleted mantle source without noticeable crustal contamination. The depleted-type mafic rocks are also characterized by high Zr/Nb (21.7-40), Y/Nb (6.3-46.5) and low Zr/Y (1- 3.5) ratios suggesting that a depleted mantle source (N-MORB source) has been involved in their petrogenesis. Mafic rocks from the Tozlu ophiolite resulted from a very low-degree fractional magma as evidenced by high MgO and compatible elements such as Cr, Co and Ni contents. The negative Nb (Ta) and positive Th anomalies from mafic rocks clearly exhibit a suprasubduction zone tectonic setting. Amphibole crystals were analyzed by  $^{40}\text{Ar}/^{39}\text{Ar}$  method and amphibole ages yielded  $32.52 \pm 3.54$  Ma. This age is interpreted as a cooling age of the mafic rocks in the Kazdağ Massif.

## MINERALOGICAL, FLUID INCLUSION AND STABLE ISOTOPE CHARACTERISTICS OF THE SASA Pb-Zn SKARN DEPOSIT, REPUBLIC OF MACEDONIA

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### Abstract

The Sasa Pb-Zn skarn deposit (10 Mt of ore at 7.5% Pb+Zn) is situated in the Serbo-Macedonian massif (SMM), approximately 100 km east from Skopje, Republic of Macedonia. The SMM is the N-S extending zone, situated between the Vardar ophiolite zone in the west and the Rhodope massif in the east. It comprises an Upper (low-grade) and a Lower (medium to high-grade) unit. The protoliths of both units are reported as volcano-sedimentary series of Precambrian to Paleozoic age, metamorphosed up to green schist and amphibolite facies. During the Cretaceous and Tertiary time, the SMM was penetrated by andesitic to trachytic volcanic rocks. Associated ore deposits could be subdivided into two distinct groups: 1) Porphyry Cu-Mo-Au and subordinated epithermal gold deposits, and 2) Pb-Zn(-Ag) hydrothermal deposits.

In the Sasa Pb-Zn deposit the mineralization is represented by skarn and hydrothermal mineral parageneses that are hosted in medium to coarse grained cipollino marble of late Paleozoic age.

The skarn parageneses comprise anhydrous Ca-Fe-Mn silicate minerals, such as pyroxenes and pyroxenoids (a prograde skarn assemblage), and hydrous silicates, such as epidote and chlorites, accompanied with magnetite, carbonates and quartz (a retrograde skarn assemblage).

The hydrothermal parageneses are characterized by the presence of galena, sphalerite, pyrite and chalcopyrite. Carbonates and quartz are the most abundant hydrothermal gangue minerals. The mineralogical composition of the skarn and hydrothermal parageneses is estimated combining transmitted and reflected light microscopy with XRD analyses.

The mineral paragenetic sequence as well as fluid inclusion and stable isotope data distinguished

three major mineralization stages preceded by the stage of isochemical metamorphism of country rocks. The isotope composition of the host cipollino marble overlaps with values published for marine carbonates worldwide ( $\delta^{13}\text{C} \approx 1.4 \text{ ‰}$ ;  $\delta^{18}\text{O} \approx 26.3 \text{ ‰}$ ) suggesting that original geochemical features were not disturbed by metamorphism and supports an isochemical character of the process.

The prograde stage (Stage 1) is characterized by metasomatic replacement of the host marble with anhydrous Ca-Fe-Mn silicates. Fluid inclusions hosted by pyroxene are moderate saline (14.5–16.4 wt % NaCl equiv.) with homogenization temperatures ( $T_H$ ) between 400° and 420°C. Formation temperatures above 400°C and the presence of anhydrous minerals suggest formation in a ductile lithostatic system insulated from significant infiltration of connate and meteoric waters.

According to the isotope composition of hydrothermal gangue carbonates ( $\delta^{13}\text{C} = -5.0 \text{ ‰}$ – $-6.4 \text{ ‰}$ ;  $\delta^{18}\text{O} = 8.4 \text{ ‰}$ – $14.8 \text{ ‰}$ ) and fluid inclusion data ( $T_H = 270^\circ\text{--}300^\circ\text{C}$ ; salinity=6.3–7.9 wt % NaCl equiv.), hydrothermal alterations of anhydrous skarn minerals followed by precipitation of ore and gangue minerals resulted from the mixing of magmatic and meteoric fluids during the retrograde stage (Stage 2). Cooling of the country rocks below 400°C may move the system from the ductile to brittle fashion and allowed infiltration of meteoric water which would contribute to the increase in oxygen fugacity. Consequently prograde minerals are altered by mixture of hydrous silicates and magnetite. At the same time, the pressure drop from a lithostatic to hydrostatic value would favored sulfur degassing from the cooling magmatic body. The increased sulfur fugacity resulted with the sulfide deposition. The post-ore stage (Stage 3) deposited gangue minerals, mostly carbonates, from cooler ( $T_H = 125\text{--}233^\circ\text{C}$ ) and slightly diluted fluids (5.5–6.2 wt.% NaCl<sub>equiv.</sub>).



## SULFUR-PYRITE OUTCROPS IN CARBONATE ROCKS

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### Abstract.

The carbonate deposits from Borizan area are part of Kruje-Dajt shallow water carbonate platform, in Makaresh-Borizan anticline. They are represented by crystalline algaal limestones of sugary view, slightly dolomitised, clayey-marly limestones, clastic limestones, bioclastic limestones and dolomites. The surface and deep karst is intensively developed. These deposits are of biochemical origin and were formed in shallow water environments where limestones of very high purity (CaO more than 54.2%) predominate. A high negative correlation ( $r = 0.9867$ ) between two main constituents: CaO and MgO was emphasized. Characteristic of these rocks are a lot of veins or pockets filled with a sulphur content. The chemical mechanism of sulfur-bearing outcrops formation is related with the mutual action between ground waters, with  $\text{SO}_4$  ions content and carbonic gas ( $\text{CO}_2$ ).

**Key Words:** Limestone, dolomite, Kruja zone, pyrite, sulfur occurrences.

### Introduction

The Borizan carbonate deposits are located in Makareshi anticline and are part of Kruje-Dajt carbonate platform. Borizan anticline is overthrust on molasse deposits of peri-Adriatic Depression (PAD) to the west, and passes normally to Oligocene flysch, to the east. The carbonate deposits from Borizan represent today an important source for cement production operated by Titan Co.. As unexpected case was drilling 5/13, crossed in depth from 83.50m down to 99.50m, for its high sulfur content, up to 12%  $\text{SO}_3$ . The core sample consists of clayey brecciated limestone of slightly blue color and containing pyrite crystals. Commonly, the high sulfur content has negative influence during the technological process of

cement production. That is why the detailed study of sulfur content of rocks was carried.

### Geological Setting

The Upper Cretaceous carbonate rocks cover 58-60 % of the surface of deposits, while the other part is covered by the red clay sediments with pebbles of of  $\text{N}_2\text{-Q}_1$  and alluvial deposits with a thickness less than 10-15m. Carbonate rocks are represented by limestones, clayey-marly limestones and dolomites. The transition kinds of rocks such as dolomite limestone there are found as well. There were mapped crystalline limestones of sugary view, clay-marly limestones slightly dolomitised, clastic limestones, bioclastic limestones forming some times "storm deposits" beds.

They do not form separate beds and packets, but in blocks and lenses between limestones. In the most cases, dolomites have sharp contacts with limestone. In these deposit, the surface karst is intensively developed in form of holes, funnels or small depressions. The deep karst is developed up to 10-15-20 m. The karst is mostly developed according to the cross strike crack system.

In the triangle diagram of chemical analysis distribution is clearly seen that of about 95% belongs to the field of pure limestones. The high negative correlation ( $r = 0.9867$ ) between two main constituents CaO and MgO was emphasized. Carbonate rocks are of pure carbonate composition, where predominate calcite and dolomite with very few clay material mixture.

### Sulfur-bearing rocks

The sulfur-bearing rocks are crossed in drillings 5/13 (in depth from 83.50m down to 99.50m) and 5/14 (in depth from 21.0m down to 27.0m). There are a lot of sulfur-bearing outcrops of different sizes. They are located in tectonical-karst cracks in vein form and became thinner from the depth up towards the surface. Sulfur-

bearing clays in blue color are characterized by high hygroscopic features and spheric grains of sand, iron hydroxides and small pyrite crystals.. In some cases they are of black color possibly due to the content in organic and bituminous matter. It is observed a transition from clay-pyrite veins to brecciated blue limestones and to white compact limestone. Sulfur-bearing veins become wider to the depth and closing towards the upper part.

### Genesis of Sulfur-bearing rocks

Different from near surface cracks filled by soils and brown clays, which are pegged toward the depth, the bodies of brecciated limestone with blue clays are pegged up, towards the surface.

The mechanism of their formation is explained by mutual action between ground waters which were infiltrated toward the depth and carbonic gas ( $\text{CO}_2$ ) of oil and bitumen, which came up from the

conditions of physical-chemical weathering. High contents of silica, iron, aluminum and lower content of calcium oxide testify about. The total absence of  $\text{Na}_2\text{O}$  content in chemical analyses excludes the possibility of primary formation of clays. Sulfur-bearing aerobic and anaerobic bacteria must have influenced in process of sulfur concentration in these clays formed in karst cracks. Based on chemical analyses, the dolomite rocks could have been the sulfur source.

### Conclusions

Sulfur-bearing rocks and pyrite represent interesting geological phenomena which is characteristic for the Makaresh-Borizan anticline. They outcrop mainly in the lower part of the carbonate stratigraphic section, in quarries next to the over thrust fault of Upper Cretaceous limestone on molasses of PAD.



**Figure 1.** Geographical Position 1- Burizane Cement Plant; 2- Buriyane limestone deposit; 3- Droja flysch deposit

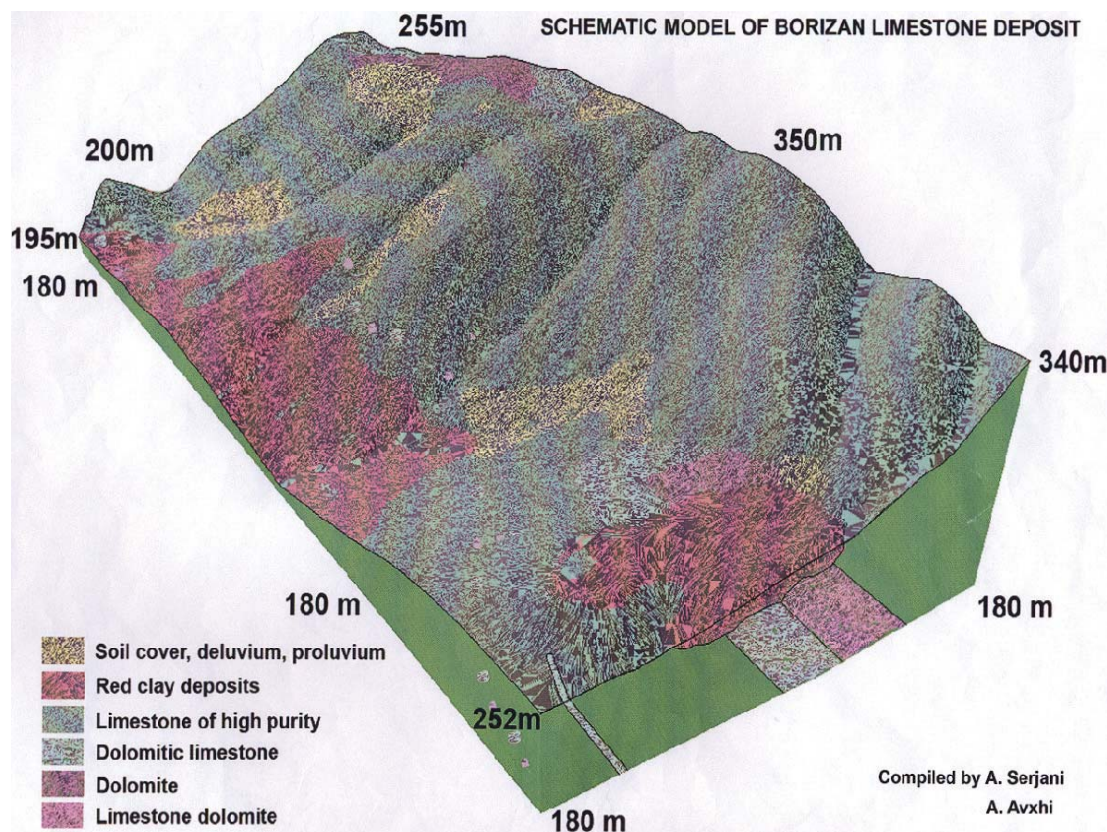
depth. The bitumen pockets which are observed in quarries support this hypothesis. The ground waters carried with them ion  $\text{SO}_4$ , which get in their way into the carbonate rocks. Native sulfur it is formed by full oxidation of  $\text{H}_2\text{S}$ , separated from thermal waters getting up through over thrust fault in contact of carbonate rocks of Kruja Zone and molasse deposits.

The process of formation happened in exogene

The carbonate deposits of Borizan area are represented by dolomitic limestones and less dolomites and limestone dolomite. They are of very high purity ( $\text{CaO} > 54.2\%$ ) and show a high negative correlation ( $r = 0.9867$ ) between two main constituents,  $\text{CaO}$  and  $\text{MgO}$ .

Sulfur-bearing rocks are characterized by high content of S, S, Al, Fe, and lower content of Ca.

They are of hydrothermal genesis, due to reaction



**Figure 2.** Schematic model of Borizan limestone deposit

between ground waters and  $\text{CO}_2$ , which comes up from the depth, through deep tectonic faults.

Sulfur is formed as result of oxidization of  $\text{H}_2\text{S}$  of thermal waters, getting up through thrust fault.



## LOWER SILURIAN IREVIKEN EVENT RECORDED IN RAPID FLUCTUATIONS OF REDOX CONDITIONS – EXAMPLE FROM THE WILKÓW BOREHOLE OF THE HOLY CROSS MOUNTAINS

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### Abstract

Ireviken event (IE) is one of the Silurian extinction events at the Llandovery/Wenlock (L/W) boundary. The redox history of the event has been constrained through a multiproxy study of sedimentology, total organic carbon (TOC), total sulphur, inorganic proxies, and pyrite framboid distributions from the Wilków IG1 borehole from Poland. Up to data, palaeoenvironmental reconstruction of oceanic conditions during the mentioned event were provided using mainly stable carbon and oxygen isotope studies, however, the obtained results and interpretations were not always converge and cohesive with other sedimentological and geochemical studies. Thus far, Ireviken event was characterized mainly from shallow shelf environments. In this work, palaeoredox conditions have been investigated using geochemical, petrographical and sedimentological methods. For the first time, the redox conditions in the deep-shelf succession of the Ireviken event were reconstructed using the combination of pyrite framboid diameters study and trace metals analysis. Forty-seven samples were collected from the Wilków IG1 borehole, comprising various claystones and black shales. Due to the relatively high thermal maturation of the sediments, our research has focused on redox proxies that are not susceptible to alteration by heat, such as pyrite framboids study and trace metals. Analysis of biomarkers and other organic compounds was not carried out. Based on these results, total organic carbon (TOC) content pattern corresponds to the inorganic proxies values, reflecting changes in redox conditions across the Llandovery-Wenlock boundary in the

Wilków borehole section. The U/Th, V/Cr, U<sub>authg</sub>, and U/Mo values show that during the described Silurian event, bottom-water conditions changed from oxic (Telychian) to being mostly suboxic/anoxic (the first phase of IE) and oxic again (the last phase of IE). The general similarities between patterns of all used redox proxies and U/Mo ratio are detected. Pyrite framboid diameter results are in agreement with bulk and inorganic proxies. Aeronian sedimentation starts with dysoxic to anoxic/euxinic conditions. Almost the entire Telychian is characterized by lack of pyrite framboids. L/W boundary distinguished by rapid changes of redox conditions from dysoxic to anoxic/euxinic, even in the millimeter scale of sediments. The youngest investigated sedimentary rocks of Sheinwoodian stage contain exclusively small pyrite framboid diameters typical for anoxic/euxinic conditions. The three major stages of L/W boundary sedimentation were reconstructed: a) before the event – oxic to sporadically dysoxic sedimentary conditions with lowstand, intensive water circulation and low productivity reflected ocean regression maybe connected with icehouse pulses. b) during the event - very intensive chemocline fluctuations caused by transgressive sea level changes with moderate productivity, c) after the event - relatively stable conditions with euxinic zone in the water column and dysoxic to sporadically anoxic bottom water and moderate productivity. Rapid fluctuations of the chemocline during Llandovery/Wenlock boundary seem to be a major cause of extinction affected pelagic and hemipelagic fauna.



## ALBANIAN (MIRDITA) OPHIOLITES GEODYNAMIC EVOLUTION AND THEIR PRE-, SYN- AND POST OPHIOLITIC FORMATIONS

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### Abstract

Albanian (Mirdita) ophiolites are the most important part of the Dinaric-Albanian-Hellenic ophiolite belt; they occur in a 250 km. long and up to 70 km. wide with an outcrop area about 4000 km<sup>2</sup> (or about 7000 km<sup>2</sup> without sedimentary cover). Albanian ophiolite belt crops out in a generally NNW with a sharp bend toward NE in the northern continuation. It has a regional structural conformity with bordering margins; the fault (strike-slip, reverse faults, moderate to high angle faults) contacts between them preserves a narrow belt of thin slivers of synophiolitic metamorphics (amphibolites, paragneisses, micaschists, greenschists) and associated Lower Jurassic rift-related preophiolitic volcano-sedimentary formation. The age determinations of synophiolitic metamorphics range from 174 Ma in the southern part to 162 Ma in the northeastern part of the ophiolite belt.

Albanian ophiolites are divisible in two different types: Western (MOR) and Eastern (SSZ). Western (MOR) incomplete ophiolite consists the western-southwestern part of the ophiolite belt; their composite sequence consists of ultramafic sequence (harzburgite-lherzolite, plagioclase lherzolite, plagioclase dunite), overlain by limited and thin plutonic sequence (troctolite, olivine gabbro, ferrogabbro) with ol-pl-px crystallization order; volcanic sequence (massive and pillow basaltic, basalt-andesitic MORB-type lavas) lies on plutonic rocks without any intervening sheeted dike complex or isolated dikes, or directly (rarely through synophiolitic oceanic amphibolites) on serpentinized ultramafic rocks, and is overlaid by Bajocian-Bathonian radiolarites and Tithonian ophiolitic mélange. Eastern (SSZ)-type complete ophiolite consists the eastern-northeastern part of the ophiolite belt: their composite sequence consists of harzburgite, interbedded harzburgite-dunite, transitional dunite, overlying by gabbro-norite-type (layered and massive gabbro-norite, gabbro, amphibole gabbro, quartz diorite and plagiogranite) plutonic sequence with ol-px-pl crystallization

order, on which lie sheeted dike complex within which four dike generations are distinguished (diabasic, andesitic, rhyodacitic and boninitic), on them lie basalt-dacitic (basalt, basalt-andesite, boninite, andesite, dacite, quartz dacite, rhyodacite) volcanic sequence of IAT-boninitic affinity, covered by Late Bathonian-Oxfordian radiolaritic cherts and by Tithonian postophiolitic mélange. Despite clear petrologic differences between two ophiolite types, undisturbed lateral transition exist between them. Recent geochemical studies show for a shift from typical MORB- to typical SSZ-type in the top of western-type ophiolite volcanic sequence. The plutonic sequences of both ophiolite types are intruded by ultramafic intrusions, which represent the latest magmatic activity for each ophiolite type.

The origin of the Albanian ophiolites was interpreted differently: as differentiated product of basaltic magma developed as submarine pluton-volcan; sea-floor spreading in a marginal basin west of Korab-Pelagonian microplate; formation of western ophiolites by sea-floor spreading, followed by increased asthenospheric upwelling and displacement of the spreading ridge to the east to form eastern-type ophiolite; sea-floor spreading to form western-type ophiolite, followed by an intraoceanic subduction (ensimatic island arc) to form eastern-type ophiolite; both western and eastern-type ophiolite are related to an infant subduction zone environment; formation of the two ophiolite types as a result of cyclic operation of a slow-spreading ridge system. Future interpretations of the geodynamic evolution of Albanian ophiolite should take in consideration particular features of the Albanian ophiolite belt and related formations: sharp change of the NNW general trend to NE in Mirdita-Kukes region; presence of two

distinct ophiolite types with normal transitions; wide range compositional variation along and across the strike of the ophiolite belt; presence of the synophiolitic metamorphics and associated volcano-sedimentary formation along both sides of the ophiolite belt including Devolli massif and wide range age variation.

## GARNET ORTHOPYROXENITE AND PHLOGOPITIC ROCKS IN A MANTLE SEQUENCE OF THE ALBANIAN OPHIOLITE

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### Abstract

Several ilmenite bearing garnet orthopyroxenite and phlogopitic rocks (phlogopitites) are found in the mantle sequence of the Albanian “eastern” ophiolite, representing a unique occurrence in the Albanian and Alpine-Mediterranean ophiolites.

Garnet orthopyroxenite form small lenses of the coarse-grained cumulate with trahitoidal, poikilitic and postcumulate texture; they consist of orthopyroxene (En57.23-58.56, Fs40.99-42.25, Wo0.45-0.67), garnet (AL42.57, PY32.11, GR17.26, SP6.28, AD1.69) and ilmenite, and are rich in Fe, Ti, Mn and K.

They are considered to have crystallized by alkali basaltic Fe, Ti-rich silicate melt below upper mantle conditions. Garnet orthopyroxenite represents a mantle segregation linked with earliest stages of the partial melting of the mantle peridotite, and have undergone potassic mantle metasomatism and other pneumatholitic-hydrothermal events.

The vein-lense Phlogopitic rocks are developed mainly among mantle harzburgite, serpentinite and garnet orthopyroxenite; they are lepidoblastic, porphyroblastic and poikilitic where several mineral assemblages are distinguished: phlogopite-amphibole; phlogopite-ilmenite, phlogopite; rarely they contain relics of orthopyroxene or garnet grains. Some varieties resemble glimerite-MARID facies.

Phlogopitic rocks are partly of a magmatic origin. Mainly they are formed by local mantle metasomatism caused by interaction of the K, Fe, Ti-rich silicate melt and K-rich fluids with depleted mantle rocks and garnet orthopyroxenite, while the hydrothermal metasomatism caused their partial chloritization.

The presence of the garnet orthopyroxenite and phlogopitic rocks provide new information about restricted mantle magmatic and metasomatic processes and represent an important occurrence for the petrology of the upper mantle processes and ophiolite genesis.

## APATITE FROM PETROHAN PLUTON (WESTERN BALKAN, BULGARIA) AS INDICATOR FOR MAGMA MIXING

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### Abstract

The Late Paleozoic Petrohan pluton is located in the core of the Berkovitsa anticline, in Western Balkans. The pluton is of meta-aluminous I type with calc-alkaline and high-potassium calc-alkaline affinity and is built up of gabbroic to granitic rocks with prevalence of the acid and intermediate varieties, formed via combined assimilation and fractional crystallization processes. The specific feature of the Petrohan pluton is the presence of mafic magmatic enclaves (MME), whose composition varies between gabbro and diorite as result of the magma mixing and mingling. The rocks of the pluton are characterized by diverse accessory mineralogy including titanite, apatite, allanite-(Ce), thorite, zircon, garnet, and Fe-Ti oxides – magnetite, ilmenite, hematite, and rutile. In the present work, several indicative features evidencing the magma mixing processes in the Petrohan pluton were identified in the accessory apatite. Apatite crystals from both mineral separates and thin sections were analysed with Electron probe microanalyses (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS).

Apatite is identified as an early crystallized phase over nearly the whole duration of magma cooling. Needle-type apatite crystals found in the MME and in the host granodiorite in the contacts with MME is direct indication for the magma mixing. The content of Sr in the apatite correlates with the silica content in the rocks due to the influence of basic magma incoming into the magma chamber. The established values of  $Sr_{Ap}/Sr_{HostRock} > 1$  in the host granitoids and some hybrid rocks with dioritic composition confirm essential participation of mafic magma in the pluton formation. The magma mixing process affects the chondrite normalized ratio  $Ce_{cn}/Yb_{cn}$  in the apatites which is the highest in the granitoids.

## TECTONO-MAGMATIC DISCRIMINATION AND RADIOLARIAN AGES OF BASIC EXTRUSIVES IN THE SE ANATOLIAN SUTURE BELT (ELAZIG-MALATYA, EASTERN TURKEY)

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### Abstract

The Yuksekova Complex between Elazığ and Malatya in eastern Turkey, comprises representatives of an oceanic lithosphere. Also, they are the remnants of the Southern Branch of the Neotethys. The dominating rock unit is grayish to red colored massive and pillowed basic volcanic rocks associated with radiolarian cherts and micritic limestones around Maden, west-northwest of the Hazar Lake, and in the vicinity of Malatya, Pütürge and Yaygın towns. In accordance with the petrographical and paleontological findings, incompatible element diagrams point out two different compositional rock groups, transitional between IAT and N-MORB, and E-MORB. Tectonic discrimination diagrams suggest the presence of an intra-arc and back-arc pair. Melting modeling based on REE shows that parental magmas of the basalts were formed by partial melting of a spinel lherzolitic mantle source. This shows also that the source deepened from intra-arc to back-arc and the melting degree decreased, by the change of the source. Radiolarian cherts within the basalts of the Yuksekova Complex yielded two groups of ages. Morphological, mineralogical-petrographical and petrochemical data suggest that the first group is Cenomanian-Turonian and the second group is Santonian-Campanian in age. Radiolarian taxa (*Pseudoaulophacus*

*putahensis* Pessagno, *Dactyliosphaera* sp., *Pseudodictyomitra pseudomacrocephala* (Squinabol), *P. tiara* (Holmes), *Thanarla veneta* (Squinabol), *Dictyomitra formasa* Squinabol, *Crolanium* sp., *Stichomitra* spp.) revealing the Middle Cenomanian- Early Turonian age have been determined from the chert samples, associated with the basic volcanics? having a transitional geochemical signature between IAT and MORB. Radiolarian cherts associated with E-MORB basic volcanics include diverse radiolarian taxa (*Alievium gallowayi* (White), *A. superbum* Squinabol, *Archaeospongoprunum bipartitum* Pessagno, *Crucella espartoensis* Pessagno, *Spongodiscus multus*, *Patellula verteroensis* (Pessagno), *Pseudoaulophacus floresensis* Pessagno, *P. lenticulatus* (White), *P. pargueraensis* Pessagno, *Dictyomitra formasa* Squinabol, *D. koslovae* Foreman, *Stichomitra* spp, *Rhopalosyringium* spp.) indicating the Early Santonian - Early Campanian age. All geological and petrological features prove that the studied Yuksekova volcanics were successively formed in intra-arc and back arc settings related to intra-oceanic subduction within the Southern Branch of Neotethys.

**Key Words:** eastern Turkey, Yukseova Complex, radiolarians, basic volcanics, intra-arc, back arc



## MINERALOGICAL STUDY OF INTERMEDIATE INORGANIC SEDIMENTS FROM THE LIGNITE DEPOSITS OF KLEIDI, AMYNTEO AND NOTIO PEDIO IN WESTERN MACEDONIA, GREECE

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### Abstract

The aim of the present study is to examine significant mineralogical differences of inorganic intermediate seams from the Neogene "Kleidi", "Amynteo" and "Notio Pedio" lignite deposits, in Western Macedonia (N. Greece). Kleidi deposits are located at the eastern borderlands of the Florina basin, whereas Amynteo and Notio Pedio fields are located at the northwest and central parts of Ptolemais basin, respectively. Both the Florina and the Ptolemais sedimentological basins are part of the broader NNW-SSE directed tectonic trench of Monastiri-Florina-Ptolemais-Kozani-Servia. The basement of both basins consists of Mesozoic formations and upwards are the Neogene sediments including the examined lignite deposits. Quaternary-recent sediments occur on the top of the stratigraphical sequence. The mineralogical composition of bulk samples, which were macroscopically classified as marls, marly clays and clays, were examined by means of X-ray diffraction (XRD) analysis. Where necessary, pulverized and wet free samples were heated up to 550 °C for approximately 2 hours, then cooled at room temperature and re-examined by XRD in order to identify the clay minerals kaolinite and chlorite (whose typical peaks coincide at  $d=7.1\text{ \AA}$ ). Glass slides having a thin layer of the examined samples on the top were properly prepared under ethylene-glycol steam, in order to examine the possible presence of swelling minerals (smectites). The samples were also examined by means of Thermo-gravimetric (TG/DTG) and differential thermal analysis (DTA) confirming the XRD results and providing important information about the percentage contribution of carbonate and clay minerals in the examined sediments. FT-IR spectra obtained from Fourier Transform Infra-Red (FT-IR) spectroscopy report also the calcareous and clayey

composition of the examined materials and indicate important variations towards depth. The samples from Amynteo area show significant mineralogical differences on a depth basis suggesting alternations of inorganic seams with high clay content (illite-muscovite, kaolinite, and montmorillonite) and inorganic seams rich in carbonate minerals. The latter shows prevalence of calcite in shallow depths and dominance of dolomite towards higher depths. In the case of Notio Pedio, the samples show variation of mineralogical composition towards depth. Aragonite is the major mineralogical phase in higher depths, calcite dominates in the intermediate depths and the clay minerals illite-muscovite, kaolinite, and chlorite coexist along with carbonates towards lower depths. Quartz and feldspars show minor contribution, whereas no smectite was found. Low carbonate content and prevalence of the clay mineral kaolinite were reported for the samples from Kleidi area (Florina basin) suggesting the major difference compared to the samples from Ptolemais basin. Gypsum, which is a common hydrous sulfate in lignite-bearing sequences, was observed only in some cases of Kleidi samples. Where gypsum is reported, the clay mineral illite prevails instead of kaolinite, whereas in all cases no montmorillonite was observed. The non-clay minerals quartz and feldspars were identified in minor contribution. The prevalence of clays instead of carbonates and reversely reports significant differences during the formation of the studied lignite deposits and suggests high energy depositional conditions at Kleidi case and slow precipitation at Ptolemais lignite deposits, where carbonate minerals were deposited in low-energy paleoenvironments.

## MINERAL SEDIMENT COMPOSITION OF MATI AND VJOSA RIVER (ALBANIA) DELTAIC DEPOSITS

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### Abstract

The Albanian coastline stretches from the Buna River in the north (Adriatic Sea) to Saranda in the south (Ionian Sea), comprising about 454 km of sandy beaches and rocky escarpments. While the Ionian coastline is characterized mainly by rocky escarpments, the Adriatic coastline (from Buna to Vlora) is characterized by several delta river systems (e.g. Buna, Drini, Mati, Ishmi, Shkumbini, Erzeni, Semani, Vjosa) and sandy beaches. The latter are frequently characterized by the presence of dark-coloured heavy mineral enrichment zones. In this study the Vjosa and Mati river sediment were studied.

The sediments in the Vjosa River consist of fine grained and well-sorted sediments. The drainage basin (6,700 km<sup>2</sup>) is composed by a large variation of geological formations. In the Vjosa delta sedimentary succession several layers of heavy minerals are identified.

The Mati River traverses volcanic and sulfide-bearing rocks, whereas the Mati branch intersects intrusive ophiolitic rocks and molasse deposits of the Bureli intrabasin. Mati deltaic sediments are characterized by fine to medium grain sizes and are well to medium sorted.

An initial petrographic characterization of samples revealed a broad variety of minerals, which was confirmed by X-Ray powder Diffraction (XRD) and microscopy. In both delta systems considerable amounts of chromite, magnetite, ilmenite, rutile, garnets and zircon were detected, as well as minor amounts of tourmaline, staurolite and gold. Considerable amounts of olivine, epidote, pyroxenes and amphiboles are also present. Besides chromite, which constitutes the majority of the heavy fraction of fine sandy deposits in Albania, in the deltaic sediments of Vjosa a large variety of garnets are detected, as well as different shaped zircons, as well traces of monazite and xenotime.

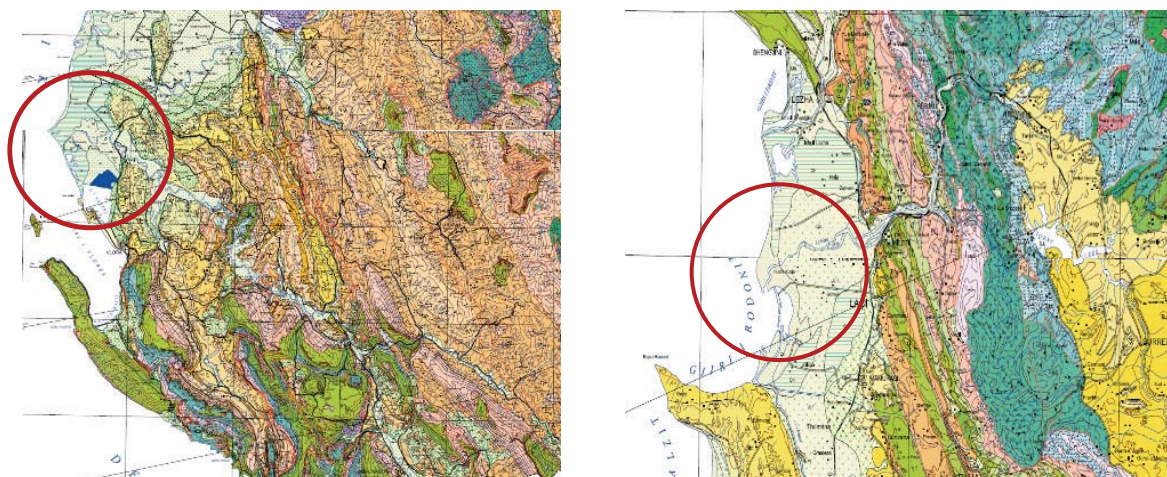
**Key words:** *Vjosa, Mati, XRD, delta sediments, heavy minerals*

### Introduction

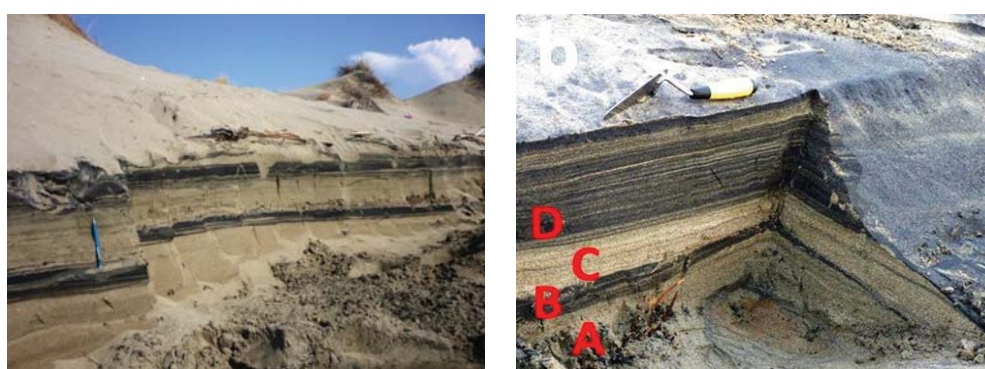
Vjosa River is the most important river of southern Albania with its source located in the Pindus mountains in Greece (where it is called Aoös River) with 272 km length and a drainage basin of 6,700 km<sup>2</sup>. The area occupied by the delta of Vjosa is 317 km<sup>2</sup>. It stretches from the Hoxhara channel to the Narta lagoon (Fig. 1a). It forms a littoral of about 22km. The deposits in this delta are characterized by fine grained and well-sorted sediments. In the Vjosa delta sedimentary succession several layers of heavy minerals are identified. The latter are characterized by a large variation in mineralogy like chromite, epidote, ilmenite, zircon, rutile, garnet and some gold grains due to the large variety of rock formation (limestones, ophiolites, molasses and flysch) that occur in the drainage of the Vjosa River.

Mati River (Fig. 1b) has a length of 115 km and is situated in the North of Albania with its delta situated within the Rodoni Gulf. Its source is located in the Bulqiza District (Albania). The surface basin is 2450 km<sup>2</sup> in size and includes two branches (i.e. Fani and Mati). The Fani River transects volcanic and sulfide-bearing rocks, whereas the Mati branch crosses intrusive ophiolitic rocks and molasse deposits of the Bureli intrabasin. Mati deltaic sediments are characterized by fine to medium grain sizes. They consist of well to medium sorted sediments. Also, in the Mati delta several chromite rich sediment layers associated by rutile, garnet, pyrite and some zircon grains are identified. The Albanian coastal plain includes several delta river systems that are characterized by the presence of dark-coloured heavy mineral enrichment zones. Heavy mineral strata up to 50 cm thick are observed in both deltaic deposits (Fig. 1b). Besides chromite, in the deltaic sediments of Vjosa traces of monazite and xenotime with different shapes are detected as well as considerable amounts of zircons compared with Mati deltaic deposits. Garnet was abundant in the Vjosa sediments, and is dominantly flysch - derived, while it was virtually





**Figure 1.** Geological Map a) of the Vjosa River Delta, b) of the Mati River Delta.



**Figure 2.** Heavy mineral deposits in deltaic sediments adjacent to dunes (a) and in the littoral (b): Light colored base with thin black layers (A), an enriched layer up to 5cm in thickness with nearly exclusively enriched black layers (B), Light colored zone comparable to unit A (C), more than 15cm thick unit of black enrichment parallel layers with individual interlayers (1-5 mm) of lighter material (D).

absent in the dominantly ophiolite - derived Mati sediments. Two types of garnets were observed with large anhedral shapes on the one hand, and generally smaller idiomorphic dodecahedra on the other hand.

### Methods and materials

The samples for this research were taken in September 2011 in the north and south parts of both deltas. An important step is the grain size range selection to perform the mineral identification. Mange and Maurer (1992) present a number of studies in which variable size ranges were applied. For our case, a size range of 63-425 $\mu$ m (sieving with Endecots ASTM E11 laboratory sieve – steel mesh) was chosen. So, the smallest grains were omitted as being too impractical to work with. Also, the coarsest ones are not of major interest, considering that heavy minerals normally are concentrated in the small size range. Furthermore, the coarsest particles may be too abrasive for the liquid

overflow separator. A necessary step in this study was to concentrate the heavy minerals by separating them from the light fraction (consisting mainly of quartz, feldspar and carbonates), the latter being especially important for the Vjosa delta in the south owing to the rich carbonate formations cropping out in its drainage basin. The preparation consisted of accurately weighted subsamples of 250g that were subjected to acid digestion to remove the undesirable carbonate particles. Dilute HCl (5%) is added in a beaker and boiled until no more reaction was observed. Subsequently, the sample was washed several times and placed into an ultrasonic bath for 15 min. to disintegrate remaining aggregates, and to clean the grains from clays or cement and to disperse flocculated particles. Both the finer and coarser fractions are weighted before and after acid treatment to quantify the carbonate content. The concentrate of Heavy Minerals (HM) was obtained using LOC (laboratory Overflow Centrifugation) that was developed by Ijlst (1973). The latter is based on the differences in density

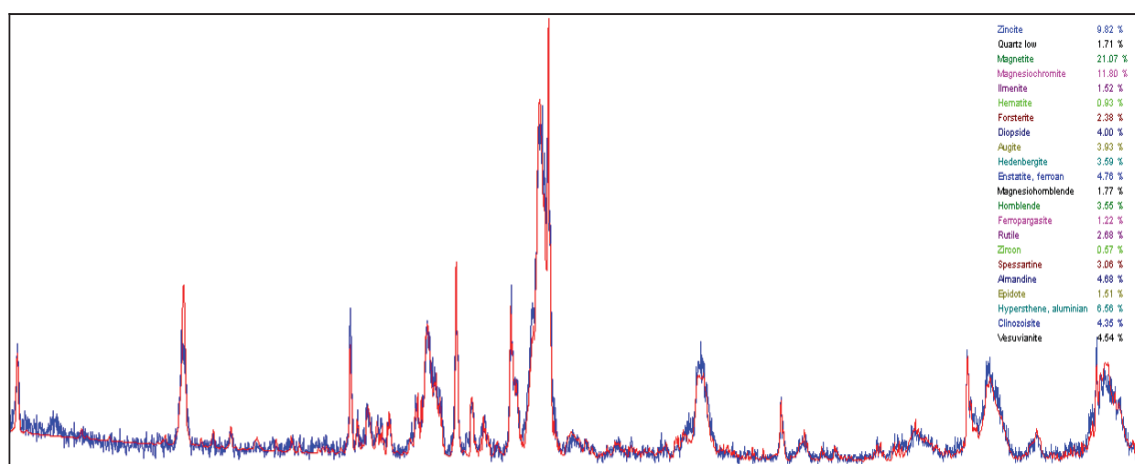
of particles. Mineral composition was inferred by X-Ray Diffraction (XRD) analysis (with pre-treatment (2.7 g crushed sample + 0.3 g ZnO + ethanol + dry). The XRD pattern was processed with Diffract plus Eva software using the Master database. Mineral quantification was performed by Topaz Academic software for Rietveld for quantitative analysis.

## Results

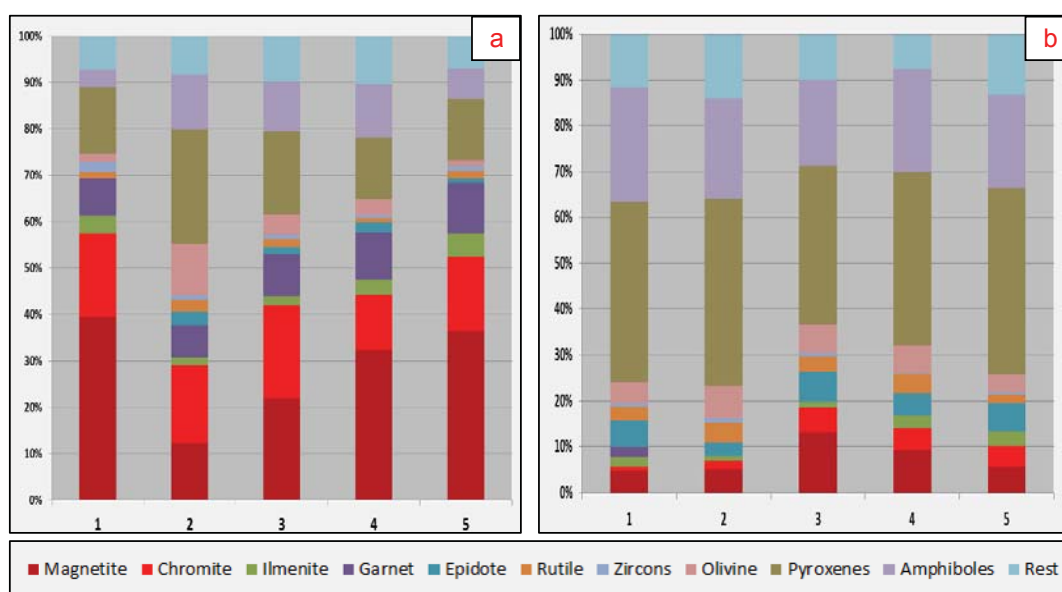
Separation of the HM was performed to assess the proportion of HM and comparison between the two deltas. HM ratios of successive layers from the same position can provide an indication of the operation of the process of concentration. Layers enriched in HM can pass values until 95 wt.%. The Vjosa delta deposits can possess HM contents from 1.24 - 95.4 wt.% and 3 - 45 wt.% of dissolved sed-

iments, 1.6 - 57.9 wt.% light particles and 0 - 0.4 wt.% particles > 425  $\mu\text{m}$ . The Mati delta deposits can possess HM contents from 35 - 88 wt.% and 2.6 - 8.1 wt.% of dissolved sediments, 7.4 - 48.8 wt.% light particles and 0 - 13.5 wt.% of particles > 425  $\mu\text{m}$ . Since the rivers passes through several rock types (ophiolites, molasses, limestones, flysch) the mineral composition of sediments present large variations. The variation on the mineral weight percentages are given in the graphic below. Of interest is that in Vjosa sediment some gold is detected, besides tourmaline, apatite, calcite and pyrite grains.

From the graph, it is clear that garnet and zircons compose a dominant fraction in the Vjosa delta deposits and that their content is low in the deposits of Mati River Delta, while pyroxene is more abundant in Mati than in Vjosa deposits.



**Graph.1** XRD pattern of sample ALEX033A from the Vjosa River Delta.



**Graph. 2** Results from XRD measurements, the samples of a) Vjosa River Delta, b) Mati River Delta.



## Conclusion

The correlation between lower HM enrichment and a higher amount of coarse grains supports the general observation that HM grains tend to have smaller grain sizes (Mange and Maurer, 1992). Another observation relates to the relative increase in dissolved materials until 45 wt. %, related to the exposure of limestones in the anticlines of the Ionian and Kruja zone. Heavy Minerals like Magnetite (igneous, metamorphic), Chromite (peridotites, ophiolites), Ilmenite (igneous, metamorphic), Olivine mainly forsterite (mafics, ultramafics, basalt, gabbro, peridotite), Pyroxene- Diopside, Augite, Enstatite, Hypersthene, Hedenberghite (peridotites, pyroxenite, harzburgite, Iherzolite, serpentinite), Amphiboles- Hornblende, Pargasite, Actinolite (product of metamorphism of siliceous dolomites), Rutile (schists, gneisses and amphibolites). There also exists the 'Rest group' with Hematite, Magnesite, Titanite, Clinoclase. They occur in high contents in both delta samples. Garnets were observed in minor amounts or absent in Mati delta sediments. This may be related to the limited exposure of amphibolite facies rocks since the western ophiolitic soles only constitute a limited thickness, while in the Vjosa delta samples, Almandine reaches until 5% and Spessartine up to 15%. Zircon is omnipresent with up to 2% in the Vjosa samples, while in Mati samples Zircon is present in minor amounts or absent. The presence of a significant amount of garnets and zircon in Vjosa sediments is related to the flysch deposits that are present in the catchment. XRD measurement was performed also on the light fraction, which consists of Quartz, Kaolinite, Glauconite, Mg-chlorite, Albite, Microcline, Augite, and Hornblende.

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## METHOD FOR MODELING OF HIGH-RESOLUTION QUASI-GEIDS

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### Abstract

This abstract presents a new technique for creating geoids of high resolution and precision. The first step is to find unique and stable models of the mass distribution in Earth's core, mantle and crust. This is followed by computation of the gravity potential of the optimized models which are used to find the geoid's surface. The created models consist of finite number of point-masses and the initial data are the absolute values of the gravity acceleration on Earth's surface. It's obvious that by a continuous increment of the number of point-masses the method will not only reach but overtake the current geoid heights accuracy on a relatively simple and economical way. The only obstacle for the method is the higher computational cost of the procedure.

**Key words:** *Quasi-geoid, absolute gravity data, optimization and regularization, point masses modelling.*

### Abstract

Creating optimized gravity point models by using absolute gravity acceleration data is an inverse problem where point gravity sources located in Earth's core, mantle, and crust have been searched. In general, the applied idea is to create density models of the Earth through gravimetrical equivalent redistribution of optimized point-masses or by direct calculation of their potential in order to represent the surfaces of the geoid, the Earth's core or other geospheres (Avdev et al. 2011).

### Application of the point-mass gravity model

The point-mass gravity model has some very valuable properties which make it very convenient for parameterization of geological models. It is universal (approximates arbitrary smooth enough functions of mass distribution), expressive (allows description of both the primary and the secondary

elements of complex mass distributions using finite number of parameters) and flexible (has the ability to switch between models which differ in complexity).

The gravity point-mass models have been put into practice for the purposes of geodesy in order to describe the surface of Earth's potential field. The advantages of this modeling class to the traditional expansion of the gravity potential in spherical functions are due to its properties, some of them mentioned above. However, in most cases some of the unknown parameters of the investigated model are a priori fixed. Mostly as fixed parameters are taken all or some of the spatial coordinates of the point-masses. In this case, the models can only be used to determine the external gravity field because the point-masses location hasn't got any geological sense so they can't be used for the purposes of geophysics to investigate the inner structure of Earth.

Otherwise the results achieved by the realization of Prof. Zidarov's original idea (1964) for seeking optimized models of point-masses with four unknown parameters (X, Y, Z and the mass) are very few and they doesn't exceed a handful of short reports published during the years. These isolated experiments of optimizing Earth's gravity field often finished with simple combinations of several point-masses (Zhelev et al. 1985; Avdev et al. 1999). The main reason for the lack of results has been the absence of clear and working technology for optimization of complex models consisting of hundreds unknown parameters that can provide simple and stable solutions. Other obstacles include the limited computing possibilities in the past and the insufficient amount and quality of the available gravity data.

### Theoretical fundamentals of the problem

The mathematical formulation of the inverse gravity problem can be described as follows: the absolute values of Earth's acceleration  $g(P_i)$  are given at  $n$  points  $P_i$ ,  $i = 1, n$  on Earth's surface and

also the relation between  $g_m(P_i)$  and the parameters  $m$  of the model is known. A unique and stable model  $m^*$ , whose field differs from the real geologic body (the Earth) with a minimum value, has to be found. The given values of Earth's acceleration form a data set  $y$  and define an  $n$ -dimensional vector  $Y$ . The function  $g(P_i)$  is the operator which solves the direct problem  $\Phi$ . The model  $m$  is a function of the parameters  $q_j, j = 1, s$ . In order to find a unique and stable model  $m^*$ , we have to determine the operator  $\Phi^{-1}$ , the inverse operator of  $\Phi$ . To solve this problem we apply automatic selection where the inverse operator will be the minimization procedure on the following objective function:

$$U = \sum_{i=1}^n [g(P_i) - g_m(P_i)]^2 \quad (1)$$

The minimization of the objective function  $U$  is

done by the least squares method (Gauss-Newton method of minimisation) using corrections' algorithm developed by the team, so that the optimization technique becomes similar to the Levenberg and Marquardt method.

### Modeling the point-masses geoid

A set of programs written in MATLAB environment is developed in order to satisfy the requirements of the calculations and the visualisations of the results. The main point model optimization program is developed under QBASIC.

The constant values of the reference ellipsoid are taken from the GRACE Gravity Model 02 (GGM02C) released October 29, 2004 and published to the public on <http://www.csr.utexas.edu/grace/gravity/>.

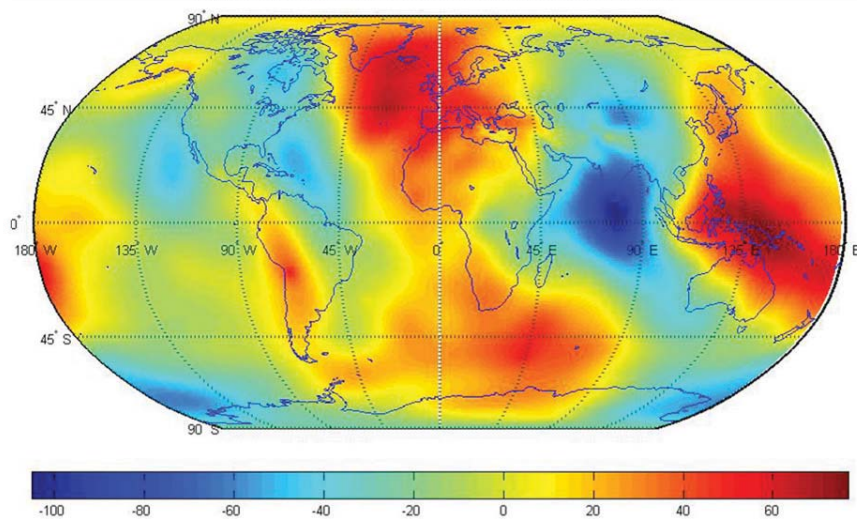


Figure 1. Input data geoid heights (1°x1° grid) extracted from the GRACE's GGM02C model

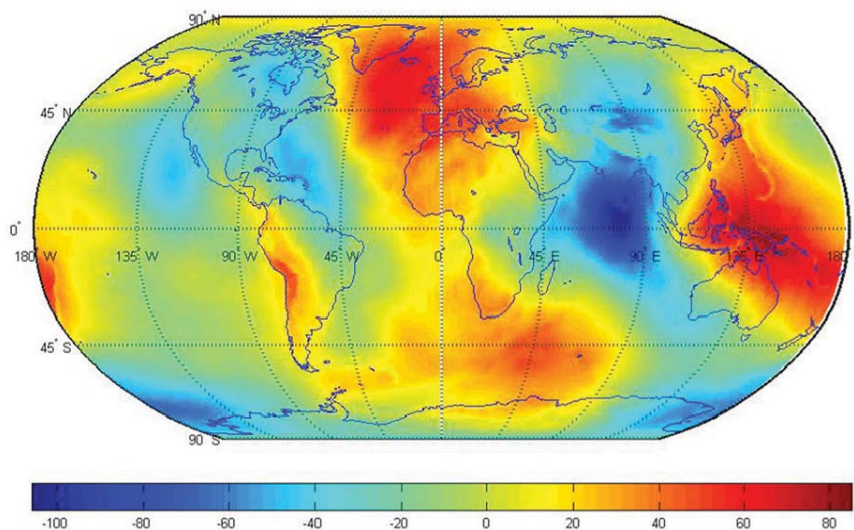
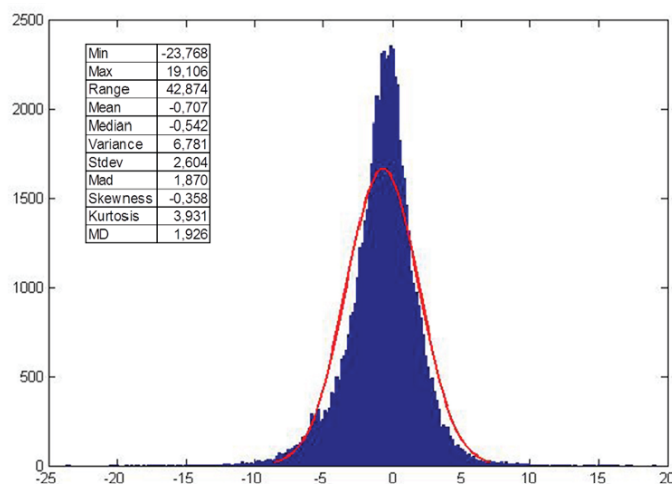


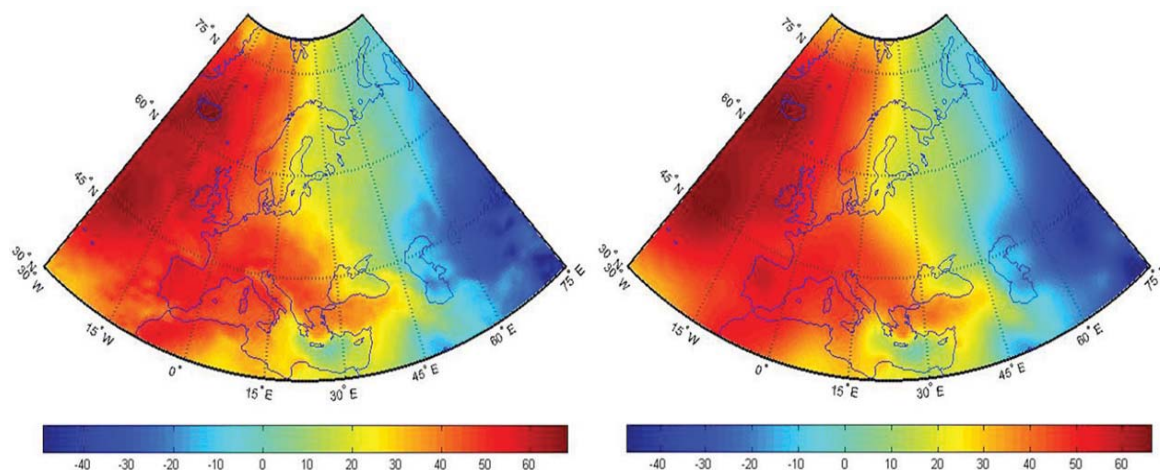
Figure 2. Undulations of the optimized with 177 point-masses geoid model in meters.

The extracted from the GGM02C model  $1^\circ \times 1^\circ$  grid data consist of 64 800 absolute gravity point values. For the purposes of the local geoid calculations, the data set (Fig. 1) was expanded with additional 15 750 data points which cover the surface of Europe and the adjacent areas (from

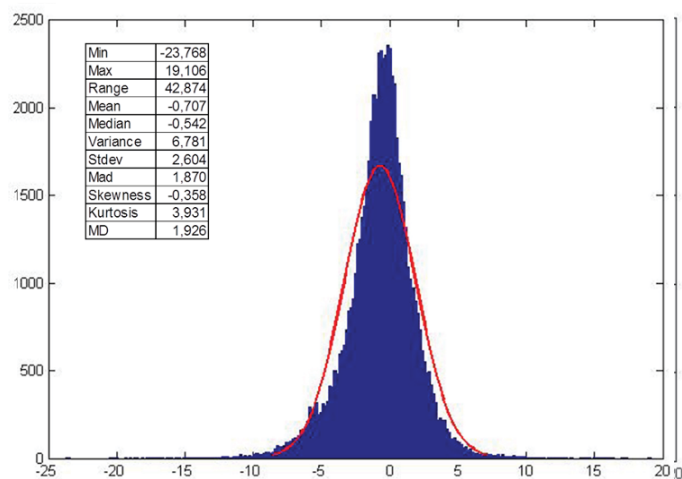
$30^\circ\text{W}$  to  $75^\circ\text{E}$  and  $30^\circ\text{N}$  to  $80^\circ\text{N}$ ). These additional gravity points are distributed on  $0.5^\circ \times 0.5^\circ$  grid and add new 15 750 values to the data set. For the territory of Bulgaria, the model was expanded with another 587 absolute gravity points.



**Figure 3.** Histogram of the distribution of the differences between the gravity acceleration of GRACE's input data and the 177 point-masses model for Earth.



**Figure 4.** Comparing the European undulations' map of the GGM02C model (left) with the optimized 177 point-masses local European geoid model (right) in meters.



**Figure 5.** Histogram of the distribution of the differences between the gravity acceleration of GRACE's input data and the 177 point-masses model for Europe.



## Testing the method

The proposed method for solving Earth's inverse gravity problem has been applied on the above mentioned data set. During the test an increasing consecution (from 4 to 177 sources) of stable and simple point-masses models was calculated. For every optimized source model a new geoid is computed (Fig. 2) and compared to the GGM02C.

## Conclusions

The suggested method for computing the geoid and local geoids gives reliable results dependent on the quantity and the quality of the input gravimetric data. Created once, the Earth's point-masses geoid can be used as a base for developing local and regional geoids by increasing the density of the gravimetric information in the area where those geoids have to be found.

The applied approach for solving the problem gives the opportunity to take into account the whole useful geological and geophysical information from the gravimetrical data set and in the same time to create highly precise density models of Earth and her gravity field.

The development of the Bulgarian local quasi-geoid is still pending but currently more than 200 000 absolute gravity points are being evaluated by the team and are prepared to be embedded in the main model.

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## GRAVITY AND SEISMIC MODELING IN THE CARPATHIAN-PANNONIAN REGION ALONG THE CELEBRATION 2000 TRANSECTS

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An overview of the results based on a combined interpretation of the potential field and seismic data in the 2D and 3D space in the Carpathian-Pannonian region along the CELEBRATION 2000 transects. The interpretation of the gravity anomalies is based on the unified and homogenized gravity database from different countries. An integrated 2D modeling of the surface heat flow, geoid, gravity, and topography data simultaneously was applied with the aim to determine the lithospheric thermal structure. At first, along nine transects crossing the Western and Eastern Carpathians, Pannonian basin and European Platform and then along four transects crossing the Central European area from the West European Platform, in the North, to the Aegean Sea, in the South and from the Adriatic Sea, in the West, to the East European Platform in the East, are presented. The results indicate pronounced differences in the lithospheric thickness across the chain, as well as along the strike of the Carpathian arc and show that the Moesian Platform is overthrust from the North by the Southern Carpathians, and from the South by the Balkanides and characterised by bending of this platform. Furthermore, the first 3D density model of the Western Carpathian-Pannonian region was constructed based on the results of the newest seismic experiments. The temperature and density distribution in the uppermost mantle was calculated using a combination of petrological, mineralogical and geophysical information. This calculation was performed in order to enhance the 3D gravity modeling, particularly in the Pannonian Basin. The Pannonian basin is characterized by an asthenospheric upwelling and thus by anomalous temperatures and densities in the uppermost mantle. The 3D model enabled also to perform gravity stripping that was applied as an additional analysis of the gravity field. It

allows to identify the sources of the anomalies, to separate their effects and localize the lithospheric inhomogeneities. The gravity stripped image of the region revealed significant differences of the nature of the microplates ALCAPA and TISZA-DACIA from the surrounding regions. Due to the different methodologies and data used for the modeling, the results from the 2D and 3D modeling are slightly different. This is particularly true concerning the resulting densities and depth to the major boundaries, such as Moho and lithosphere-asthenosphere, mainly in the Pannonian region. Nevertheless, the results are compatible and their main features are in agreement. In both models, a thick lithosphere (up to 130–150 km) is modeled underneath the Western Carpathians. Based on the 2D integrated modeling, the lithosphere reaches thickness of up to 240 km underneath the foreland of the Eastern Carpathians. Such lithospheric root is interpreted as a remnant of a subducted slab of the European plate. This is in contrast to the Western Carpathians, where no lithospheric root is observed modeled. The lithospheric thickness varies from ~160 km underneath the Eastern Alps, to 90–140 km below the Bohemian Massif, 115–160 km beneath the Polish platform and 180–200 km under the East European Craton. The lithosphere is very thin in the Pannonian basin, where it reaches thickness of 60–100 km. The results of integrated 2D and geophysical-petrological 3D modelling also confirm such lithospheric structure. The recent results of modeling of refracted and reflected waves with the use 2D of ray tracing technique for profiles CEL01, CEL04, CEL05, CEL06 and CEL11 are shown in poster presentation. Obtained P-wave velocity models of the crust and uppermost mantle are very complex and show differentiation of the seismic structure. The seismic models: (a) improved the knowledge on the crustal thickness

and the crustal structure, which reflects the Alpine consolidation within the microplate ALCAPA and its junction with the European platform; (b) solved the problem of the definition of horizontal and vertical crustal boundaries and inhomogeneities (crustal composition) in the different tectonic units; (c) estimated the deep-seated tectonic contact between the Western Carpathians and ALCAPA on the one side and the European platform on the other hand; (d) terminated the amount of the Tertiary accretionary prism of the Outer Western Carpathians and its position compared to the platform; (e) distinguished the physical differences of the crustal structure of the different tectonic units; and (f) helped to draft the geodynamic block model of the Carpathian-Pannonian region. The depth of the Moho discontinuity in the studied region is changing from about 25 to about 45 km. Beneath some profiles, reflectors in the lithospheric mantle were found 10-20 km below the Moho, following its shape and generally dipping to the north. Interpretation of seismic profiles was the background for the tectonic description of two colliding lithospheric plates. The northern one is represented by the older European tectonic units consists of the EEC and TESZ. The southern one - overthrusting - is built up by the younger tectonic units of the Western Carpathians and the back-arc Pannonian basin System (generating the microplates ALCAPA and Tisza-Dacia). It is suggested that present day complex structure is a result of the complicated continental collision between microplates ALCAPA and TISZA-DACIA and the south margin of the European Platform, which was accompanied by thermal back-arc extension beneath the Pannonian basin System.

**Summary results** of the seismic and geological interpretation brought much new knowledge about the structure and dynamics of the Carpathian-Pannonian lithosphere:

- Structural position of the Outer Western Carpathian Flysch zone represents the Tertiary overthrusting of the multi-nappes of the flysch sequence on the Carpathian foreland and bend EP. The overthrusting of the Western Carpathians on to the EP was documented.
- The total thickness of both tectonic units (OWCFZ and Palaeozoic Platform cover) has an extremely large thickness (23-25 km).

- The representative seismic crustal models for microplates TISZA-DACIA, ALCAPA, the Outer Carpathians and Carpathian Foredeep), together with the East European Craton showed the large differences in their structure and composition.
- The Moho depth map of the study area corrected some older and probably incorrect interpretation on the crustal thickness.
- The area between the Carpathians and the EEC including TESZ is one of the tectonically most complex areas in Central Europe. The results indicate 8-12% anisotropy, here.
- The crustal collision region (contact zone between EP and microplate ALCAPA) is indicated by a specific type of the crust. This crust was interpreted as the PIENINY CRUST. The definition of the PIENINY CRUST between the ALCAPA and PP microplates is a new original discovery.
- The PKB, except that it separates the Inner and Outer Western Carpathians, represents also a deep-seated boundary (contact) between the colliding EP lithospheric plate and the microplate ALCAPA.

**Key words:** *gravity, seismic, geothermics, petrology, topography, crust, lithosphere, Moho discontinuity, density and seismic modeling, geological models, Carpathian-Pannonian region*

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## SHARING SEISMOLOGICAL DATA WITH NEIGHBOR COUNTRIES USING SEISCOMP3

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### Abstract

In this work we present data from the Albanian Seismological Network (ASN) and the implementation of the ASN in SeisComp3 software, making possible to share seismological data in (near-) real time with seismological centers from worldwide, in particular with neighbor countries such as Montenegro, FYR of Macedonia, Kosovo which use the same software for data acquisition, processing, distribution and interactive analysis packages. This helps the seismologists for better interpretation of earthquakes, especially those occurring in the border areas.

**Key words:** *SeisComp3, SeedLink, ArcLink, nmxptool*

### Introduction

Earthquakes are geological phenomena that clearly demonstrate the dynamics of the planet we are living on. They express most directly the enormous energy that the Earth as a new planet hides inside. These phenomena are the causes of sharp changes on the surface of our planet accompanied with its continuous evolution. As disastrous phenomena, earthquakes have brought enormous damages to humanity in centuries. Only during the last 500 years more than 7 million people have been killed from earthquakes, and many other millions have lost their living resources worldwide.

Albania has one of the highest seismicity rate in Europe. From the current evidence it results that from 3<sup>d</sup>-4<sup>th</sup> centuries B.C until today, Albania was hit by 55 strong earthquakes with intensities  $I_0 \geq VIII$  degree (MSK-64), where 15 of them had intensities  $I_0 \geq IX$  degree (MSK-64). From these 55 earthquakes for a period of more than 2000 years, 36 of them happened in the 19<sup>th</sup> century which makes us to believe that the number of disastrous earthquakes we reported is underestimated and other disastrous earthquakes are hidden in the depth of history.

From the above mentioned data it results the importance to strengthen the capacity of existing

seismic monitoring systems of the country, in order to support earthquake risk reduction through provision of rapid and accurate data on the occurred and potential earthquakes. This objective could be achieved through enlargement and upgrading of the seismological network in order to enhance the knowledge of earthquake phenomenon and to increase the location accuracy of the earthquake parameters. Improvement of earthquake data processing and fast information dissemination would support disaster risk reduction through provision of rapid and accurate data on earthquakes, adapted to the needs of disaster risk managers in case of strong earthquakes. Integration of earthquake data and other kinds of relevant information within a unique database management system for their acquisition, data transfer, analyzing and displaying is very important not only to support the related research activity, but also to emergency preparation, disaster management and decision making processes.

### Seismicity monitoring in Albania

The Albanian Seismographic Network (AC) comprises today 9 seismic stations equipped with various digital instruments. A new fully integrated broadband digital seismograph system transmitting data continuously in real time via satellite communication (Nanometrics Libra VSAT) is under operation since 2003.

The satellite seismograph system includes a central VSAT Hub (Carina, Nanometrics) running the NaqsServer acquisition software and seven remote transceivers (Cygnus) configured to acquire respectively the three-component broadband sensors (five Trillium 40T, and two CMG-40T). Eight remote sites are installed on SRN, PHP, TPE, KBN, BCI, PUK, TIR and VLO. All these stations are equipped with 24 bits Trident digitizers and transmit at 100 sps rate. The Libra VSAT system has demonstrated reliability, efficiency, low cost of operation and is easy to be used.

A project to transmit via GPRS continuous real time seismic data at 100 sps from several short



period stations equipped with GBV-316 digital systems, is undertaken recently and is planned to be completed within this year. Actually, the LSK station is transmitting via this technology.

### Application of SeisComp software for seismological data exchange

Recently, the seismological software SeisComp (Figure 1) has been implemented in the monitoring center of IGEWE for data exchange purposes. This software has evolved within the last years from pure acquisition modules to a fully featured real-time earthquake monitoring software. SeisComp is likely the most widely distributed software package for seismological data acquisition and real-time data exchange over Internet.

The first version of SeisComp was developed for the GEOFON network and further extended within the MEREDIAN project under the lead of GEOFON/GFZ Potsdam and ORFEUS. The now very popular SeedLink protocol for seismic data transmission has been the core of SeisComp from the very beginning. Later additions included simple, purely automatic event detection, location and magnitude determination capabilities.

SeisComp3 provides the following features: data acquisition, data quality control, data recording, real-time data exchange, network status monitoring, real-time data processing, issuing event alerts, waveform archiving, waveform data distribution, automatic event detection and location, interactive event detection and location, event parameter archiving, easy access to relevant information about stations, waveforms and recent earthquakes.

SeisComp3 currently runs under most Unix or Unix-like operating systems, incl. Linux (all reasonably recent releases of Ubuntu, SuSE, etc.), Solaris, MacOSX (experimental!). Windows version is currently not supported. SeisComp3 has many other advantages because it is free and open source.

The waveform data acquisition is based on the well established SeedLink protocol and the new ArcLink protocol, both developed at the GFZ Potsdam. The applications in SeisComp3 can be divided in four different groups: data acquisition, processing, graphical user interfaces and utilities.

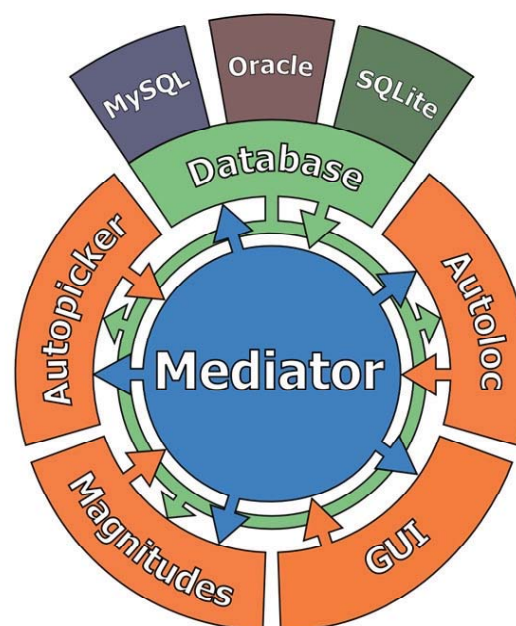


Figure 1. Simplified SeisComp3 system

### Visualisation of IGEWE seismological data and partner's data

SeedLink is a real-time data acquisition protocol and client-server software that implements this protocol. The SeedLink protocol is based on TCP. All connections are initiated by the client. During handshaking phase, the client can subscribe to specific stations and streams using simple commands in ASCII coding. When handshaking is completed, a stream of SeedLink "packets" consisting of a 8-byte SeedLink header (containing the sequence number) followed by a 512-byte Mini-SEED record, is sent to the client. The packets of each individual station are always transferred in timely (FIFO) order. The SeedLink implementation used in SeisComp is the oldest and most widely used, however, other implementations exist.

The data source of a SeedLink server can be anything which is supported by a SeedLink plug-in - a small program that sends data to the SeedLink server. Plug-ins are controlled by the SeedLink server, e.g., a plug-in is automatically restarted if it crashes or a timeout occurs. Data supplied by a plug-in can be a form of Mini-SEED packets or just raw integer samples with accompanying timing information. In the latter case, the SeedLink server uses an integrated "Stream Processor" to create the desired data streams and assemble Mini-SEED packets.

In IGEWE we use *nmix plugin*. Nmixptool and

libnmxp have been developed for interacting with NaqsServer and DataServer of Nanometrics Inc., which is the standard platform that we use. This is developed by Istituto Nazionale di Geofisica e Vulcanologia – Italy. SeedLink was designed for real-time data transfer. A SeedLink client can only access data that is in a relatively short real-time ringbuffer. Moreover, SeedLink have neither the functionality to query the station database nor deal with the instrument responses and thus does not support full SEED.

automatically locating seismic events in near-real time.

If scautoloc gives better results then *scmag* which have the purpose to compute magnitudes will give better results. *Scmag* takes amplitudes and origins as input and produces StationMagnitudes and NetworkMagnitudes as output will give better results for Albanian territory.

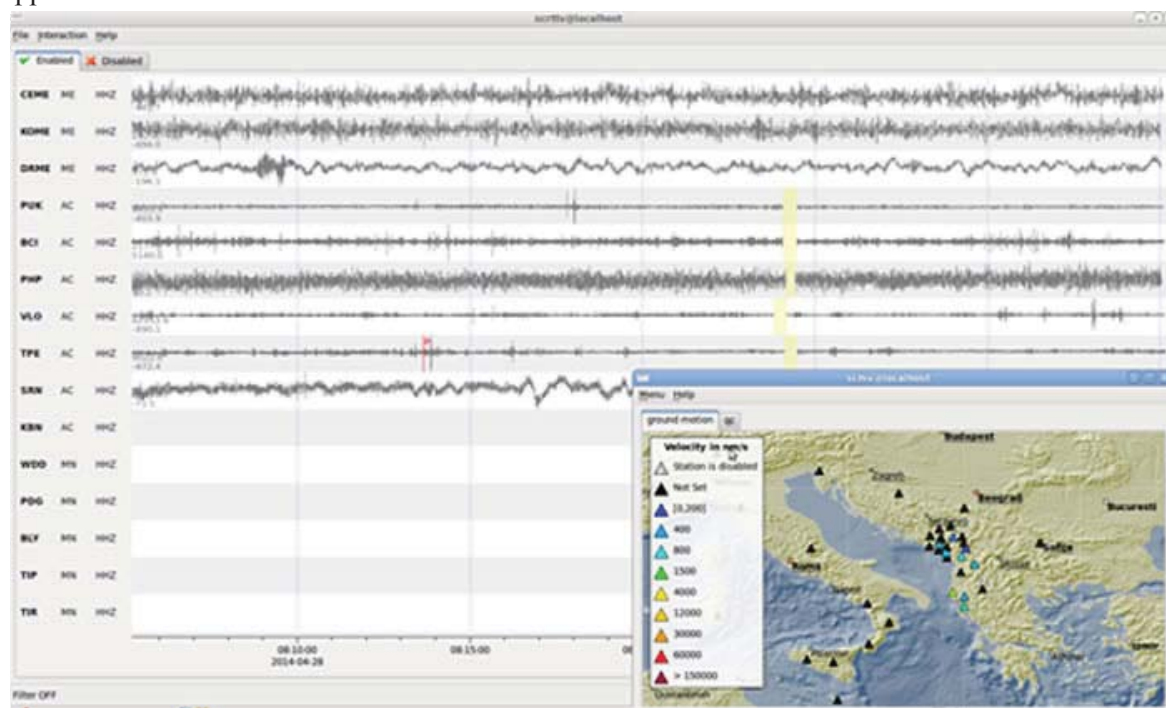


Figure 2. Near – Real – Time wave data visualisation

**ArcLink** complements SeedLink by providing the above functionality. The ArcLink protocol is similar to SeedLink: it is based on TCP and uses simple commands in ASCII coding. Unlike SeedLink, the data will not be sent immediately, but possibly minutes or even hours later, when the request is processed. We now are able to retrieve waveform data from neighborhood stations using these protocols and make available our Albanian Seismological Network (ASN), to interested partners (Fig. 2).

## Conclusions

Implementation of SeisComp is an added value of the seismology department, enabling the exchange of information and automatic location of an event. Further parameter settings before implementation in the real-time system must be done in *scautoloc* which is the SeisCompP3 program responsible for

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## FOCAL MECHANISM SOLUTIONS FOR LOCAL EARTHQUAKES ( $M > 3.0$ ), FROM ALBANIAN SEISMOLOGICAL NETWORK (ASN), BROADBAND RECORDINGS

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### Abstract

This work aims at a general description of the method and data used to compute the focal mechanism of local to regional earthquakes in Albania, applied from ASN (Albanian Seismological Network). Focal mechanism is the primary instrumental information to constrain the physics and geometry of different faulting types within a tectonic environment. Analysis for this purpose is based on the assumption of a double couple source dynamic mechanism and the different radiation pattern of seismic waves from the focal sphere towards the recording stations. Different inputs are used in this analyse like: *polarities* and *amplitude ratios*, for different  $P_{(g,n)}$ ,  $S_{(g,n)}$  and SV phases. It is well-known from different studies that the seismic activity in Albania and surroundings, during the instrumental period, has been characterized by micro, small and moderate earthquakes which have been recorded in analogue way for almost four decades. Accordingly, fault plane solutions have been determined based on first P-phase polarities only, considered as the most robust method worldwide dealing with this level of seismicity. Operation of the broadband seismological stations since 2004, as the backbone of ASN, brought forward the possibility for development in the focal mechanism analysis, as well. Nowadays improved techniques, using polarities data along with direct  $S_{(g,n)}/P_{(g,n)}$  and SV/P amplitude ratios, can be used increasing the accuracy of the results.

**Key words:** focal mechanism, polarities, amplitude ratios

### Introduction

The focal mechanism describes the orientation of the active fault and the slip on the fault relative to a geographical coordinate system. It is used to determine the actual geometry of the fault (s) as well as inferring the style of faulting and stress regime of a particular region. All seismological

methods of determining fault plane solutions are based on the *radiation pattern* sent out from the seismic source (Havskov and Ottemöller, 2011). Seismic waves introduce different amplitudes and polarities in different directions, in the real earth, with respect to the relative position *source-station*. This direct physical property is used to determine the focal mechanism using only the P ( $P_g/P_n$ ) wave polarity as the classical method used so far and furthermore using amplitudes and amplitude ratios along with polarity data of P and S phases, introducing a more advanced computation tool. The reliability of the estimate for a fault-plane solution is generally determined by station coverage for each given focal sphere (earthquake), the velocity structure of the region where the event occurs (a well determined structure) and the records quality (a good SNR), (Snoke A. 2003). Amplitudes, due to different radiation pattern, introduce a range of values changing from positive to negative between stations holding a lot of information on the source mechanism. In its simplest form the earthquake source can be described by a double couple of forces. For a homogeneous medium, and assuming a unit distance, the mathematical representation is rather complicated having the general expression form:

$$u_r = F(\Phi, \mathbf{d}, l, x_0, x) \quad (1)$$

In (1)  $F$  represents a function of the source parameters, position of the event  $x_0$  and the station  $x$ , (Havskov and Ottemöller, 2011). The  $F$  function, is a complicated nonlinear function in terms of  $\Phi, \mathbf{d}$  and  $l$  as well as distance and azimuth, however it is straight forward to calculate with known parameters. Practically, the displacement is calculated from (2), (Havskov and Ottemöller, 2011):

$$u_r = M_0 \cdot F(\Phi, \mathbf{d}, l, x_0, x) \cdot G \cdot A \cdot I \quad (2)$$

In (2)  $M_0$  is the seismic moment,  $G$  is the geometrical spreading including the effect of free surface,  $A$  represents the anelastic attenuation on the wave amplitude and  $I$  is the recording instrument effect. The effects of attenuation and the instrument are both frequency dependent, but assuming that the  $u_r$  represents the maximum amplitude of the first arrival for stations at similar distances, a simple time domain correction can be made routinely. Based on (2), there are four unknowns:  $M_0$ ,  $\Phi$ ,  $d$  and  $l$ , which can be determined based on four amplitude observations, respectively in the form of combinations: four  $P$  observations at four different stations;  $P$ ,  $SV$  and  $SH$  amplitudes at one station and one amplitude at another station. Considering the uncertainty in obtaining absolute amplitudes, using amplitude

ratios is more reliable since the effect of moment, geometrical spreading, wave directivity and instrument cancels out, and only the effect of free surface and different attenuation of the two amplitudes  $u_1$  and  $u_2$  (each pair, usually  $P$  and  $S$ ), must be corrected for:

$$u_2 / u_1 = F_r(\Phi, d, l, x_0, x) \cdot A_r \cdot R \quad (3)$$

In (3)  $F_r$  express the amplitude ratio function;  $A_r$  is the effect of the attenuation and  $R$  is the free surface effect. It is assumed that both used amplitudes are of the same type ( $P_g$  and  $S_g$  or  $P_n$  and  $S_n$ ).

**Table 1.** Focal mechanism solutions determined applying polarities and amplitude ratios in FOCMEC.

Date	Time	Lat	Lon	Dep	Mag	FP1			FP2			P		T	
						Strike	Dip	Rake	Strike	Dip	Rake	Strike	Dip	Strike	Dip
01/11/12	14:94	42.53	20.00	16	4.3	10	84	90	190	6	90	100	39	280	51
26/11/12	22:05	41.75	20.04	28	3.9	70	44	-59	211	53	-116	62	69	319	5
27/11/12	19:06	40.74	19.76	27	3.9	149	73	58	34	36	150	263	22	22	51
08/12/12	22:57	41.33	20.54	20	3.5	11	62	-66	147	36	-127	84	14	323	64
13/12/12	21:39	41.09	19.73	24	3.8	219	14	-44	352	80	-100	91	35	250	54
06/01/13	17:12	40.49	19.59	19	3.0	192	18	-90	12	72	-90	282	63	102	27
11/01/13	03:19	41.08	20.28	19	3.0	17	70	-85	183	21	-104	295	65	103	25
23/01/13	20:30	40.85	20.75	17	3.1	166	83	44	69	46	170	290	24	38	35
31/01/13	08:04	39.87	19.84	24	3.7	102	35	-81	271	56	-96	158	78	6	10
02/02/13	18:59	42.02	20.14	11	3.5	91	56	-78	250	36	-107	37	76	172	10
05/02/13	09:05	40.61	19.51	69	3.4	191	30	80	22	60	96	108	15	307	74
25/03/13	07:20	41.87	20.09	33	4.3	129	48	-31	241	68	-134	104	48	1	11
12/04/13	01:26	40.17	20.73	8	3.8	213	42	-31	327	70	-128	195	50	84	16
19/04/13	07:57	40.70	19.56	30	3.5	347	77	59	237	33	156	101	26	224	49
15/05/13	14:54	41.42	19.52	15	3.6	325	5	0	235	90	95	320	45	150	45
15/05/13	15:02	41.53	19.52	24	3.8										
15/05/13	17:11	41.44	19.49	25	3.5										
17/05/13	20:43	40.29	20.09	2	3.3	33	75	48	287	44	158	153	19	262	44
10/06/13	22:32	40.69	19.61	28	3.0	9	41	-75	170	51	-103	268	5	25	79
22/06/13	08:41	40.24	19.67	30	4.5	314	90	80	224	10	180	54	44	214	44
03/07/13	01:07	40.95	19.91	28	3.2	87	71	-69	216	29	-137	27	58	160	23
21/07/13	06:00	40.62	19.66	23	3.2	131	50	-57	266	50	-123	108	65	18	0
04/08/13	23:45	40.18	20.63	6	3.0	94	47	-15	194	80	-136	64	38	317	21
13/08/13	04:58	40.69	19.67	12	3.8	175	26	-85	350	64	-92	255	71	82	19
15/08/13	15:49	40.62	20.72	15	3.3	55	40	6	321	86	130	19	29	265	36
23/08/13	02:53	40.94	19.86	28	3.0	192	35	-81	2	55	-96	249	79	96	10
24/08/13	14:01	40.16	20.02	9	3.1	234	42	-17	337	79	-131	209	42	97	23
24/08/13	17:27	39.95	20.12	3	3.0	165	20	90	345	70	90	75	25	255	65
08/09/13	00:26	40.58	19.95	7	3.4	315	14	45	180	80	100	262	34	103	54
06/10/13	05:27	40.73	19.56	18	3.8	170	90	75	80	15	180	275	43	65	43
08/10/13	06:02	41.35	20.18	10	3.1	41	67	-68	175	31	-131	344	62	115	19
27/10/13	00:46	40.62	19.80	18	3.1	194	40	82	24	51	97	110	5	334	83
20/11/13	08:13	41.57	20.22	17	3.2	71	33	-62	219	61	-107	94	69	321	15
23/11/13	22:53	41.31	20.47	9	3.0	99	80	85	306	11	116	193	35	3	55
24/11/13	05:17	41.29	20.42	16	3.1	20	90	90	110	0	-0	110	45	290	45
04/12/13	16:43	40.70	19.67	10	3.8	27	40	0	297	90	130	355	33	240	33
13/12/13	03:34	42.03	20.58	7	3.9	89	35	-42	215	67	-118	88	58	326	18
17/01/14	19:42	40.78	20.66	12	3.1	237	30	-9	335	86	-120	217	42	90	34
20/01/14	06:00	41.38	19.48	28	3.5	345	46	76	185	46	104	85	0.1	176	80
20/01/14	07:15	41.38	19.56	29	3.3	210	71	69	80	28	136	316	23	91	59



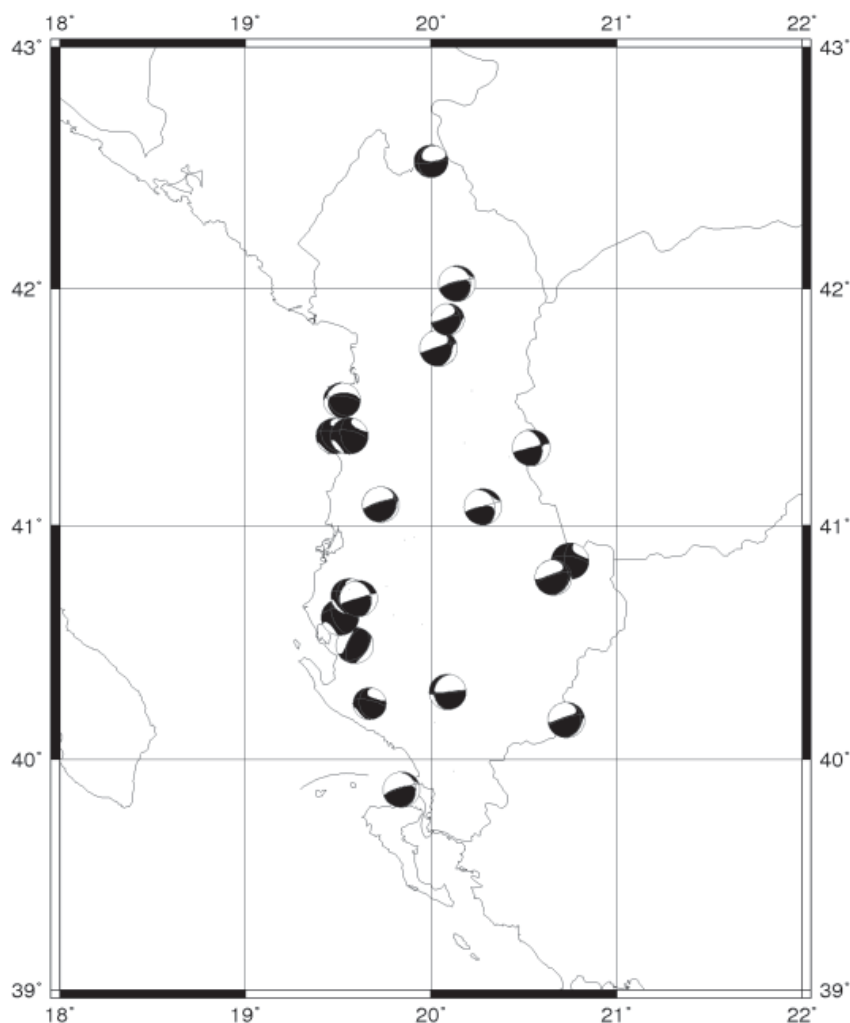
## Materials and Methods

To apply the above described method, a set of 39 moderate events ( $M \geq 3.0$ ) has been computed in order to determine their focal mechanism solutions. To achieve stable results the max number of stations per event is set as the primary criteria. First all the waveforms recorded for each pair *station component-event*, retrieved in Y-format (*Nanometrics Public Waveform Format*), were transformed to Seisan (*Nordic*) format. The next important step is the component association into respective events and event location. To optimize the location, data from regional stations from AUTH (Aristotle University of Thessaloniki Network) and INGV (Italian National Institute of Geophysics and Volcanology), are used and phase time errors are minimized. Mainly these errors results from the simple velocity structure assumed for local events. A *depth-rms* test has been used to approximate the depth range corresponding to the

lowest overall location *rms*, but also fixed depths have been used as well by taking into account parametric data from routine location. Location results are listed subsequently, (Tab. 1). Based on these broadband WF, both polarities and amplitude ratios are determined and used in computation of the focal mechanism. Seismic signals are corrected for free surface and attenuation effects based on the local model  $Q_C(f) = Q_a f^a$  ( $Q_a = 75 - 96$ ;  $a = 0.84$ ), in the seismic frequency range 0.25 – 14.5 Hz, (Dushi 2011, 2013). Obtained polarities and amplitude ratios are used as input in the FOCMEC program (Snoke 2003), implemented into Seisan ver. 10 environment (Ottemöller et al. 2013)

## Results and Discussion

Results for 39 earthquake focal mechanism solutions are listed in table 1, where values computed for primary plane (active plane) and auxiliary plane's geometrical parameters are given in terms of strike, dip and slip (rake) angles.



**Figure 1.** Types and distribution for the focal mechanisms, of local, moderate earthquakes in Albania ( $M \geq 3.0$ ), during the period 2012-2014.

In the case of the May 15, 2013 respectively at 14:54 (UTC), 15:52 (UTC) and 17:11 (UTC), representing events belonging to the same source (location), a compound focal mechanism solution has been attempted to optimize the number of input parameters. The results obtained generally agree with previous observations from different studies (Sulstarova 1986; Muço 2007; Aliaj 2012). The values for strike and dip angles, respective to P-axes and T-axes, representing the main directions of strain/stress, are determined as well. The obtained results are graphically demonstrated on the respective map, in figure 1.

### Conclusions

Broadband records are the bases for an overall source parameters computation and a better focal solution determination. Basically polarities of the first onsets could constrain good focal mechanism solutions for local and moderate earthquakes, which better fits the tectonic reality, and the usage of the amplitude ratio of primary and secondary body waves can improve this solution, checking its reliability as in the presented map (Fig. 1). Determination of fault plane mechanism is roughly based on the general radiation pattern from the focal sphere, thus using the amplitude ratio along with polarities is a strong tool to get more realistic results by correcting for radiation pattern, geometrical spreading and instrument's transfer function. Further the effects of free surface and attenuation, helps to get the optimum of this technique.

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## GENERAL SEISMOLOGICAL CHARACTERISTICS AND GEOLOGICAL SETTINGS FOR LESKOVIKU REGION (53 GEOLOGICAL MANIFOLD)

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### Abstract

The region comprised within the 53 geological manifold, where Leskoviku is situated, represents a rather complicated environment from geological point of view, where are spread different rock type formations which belong to Mirdita, Krasta, Kruja and Ionian tectonic zones (Fig. 1). The interaction between these zones is pure tectonic of thrust type leading toward west. The present seismic activity is mostly concentrated along the Barmash-Leskoviku allochthonous (Mirdita zone), as well as in the Ionian zone (the Berati tectonic sub-zone) (Fig. 1).

Based mainly on the instrumental data from the earthquakes occurred in Leskoviku region and surroundings, the seismicity has been characterized by an intense micro-activity, as an explicit demonstration of the young and very active tectonics of this region. Referring mainly to reports from the Albanian Seismological Network (ASN) as well as those from Aristotle University of Thessaloniki seismological network (AUTH), for the period 1998-2009, a number of 24 earthquakes with  $M > 2.0$ , occurred within the region under study.

The cumulative analyses of instrumental time series information ( $M > 2.0$ ) along with the areal distribution of hypocenters are plotted in the respective graph and are spatially mapped. Based on this analyses a periodic characteristic of seismic activity it is clearly evidenced. Accordingly, three characteristic periods are evidenced : 2000-2004 where an instant increase in the activity level is culminated with the 2001 earthquake ( $M_{4.7}$ ) ; 2004-2008 interval ; 2008 and on.

The evidenced periodicity express a characteristic closely related to the dynamic interaction of two main fault systems: the main active thrust faults lying to the SW-NNW flank and those of normal type with a E-W general orientation. Within this tectonic frame, this region is always under the mutual interaction of two different natural stress

fields, introducing an compressive deformation in the western side and an extension in the east and northeast. These natural fields are accommodated by the pre and post Pliocene seismic faults, where the thrust fault system gives the greatest contribution in the seismic energy release within 53 geological manifold.



**Figure 1.** Geological map and respective seismic activity distribution within the 53 Leskoviku manifold.

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## **TENTATIVE ANALYSIS OF THE HIGH RISE BUILDING VIBRATION ON THE MEASURED VALUES OF HVSR PARAMETER. A CASE STUDY**

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### **Abstract**

Environmental noise measurements have become popular in site – specific investigations and in microzonation studies. The advantages of HVSR method (horizontal to vertical spectral ratio of ambient noise recordings) are in estimating the fundamental resonance frequency of sediments without knowing the underground (geological structure or/and S wave velocity). HVSR is a low cost and simple method in application.

A series of measurements using HSVR method is completed along the main boulevard of Tirana City, including its historical part. The purpose of this study was the mapping of fundamental frequency of sediments in this part of the city. Problems were noted during the measurements due

to the high level of cultural noise and specifically, the probable influence of the high rise building vibration on the real HVSR measurements. HSVR measurements were performed near a high concrete structure to assess the effect in measurements and to establish a measurement procedure when surveying near structures. The instruments used for the measurements were portable “Trominos” produced by Micromed, Italy. Measurements are performed in 5 points, at 20 m starting from structure and going in line every 20m.

**Key words:** *HVSR, ambient noise, effect of structures, microzonation*



## ESTABLISHMENT OF SOIL PROFILES AND $V_{s30}$ PARAMETER FOR THE STATIONS OF ALBANIAN STRONG MOTION NETWORK

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### Abstract

The study of earthquakes is related to the solution of a number of problems, many of which are of engineering concern. Of specific importance is the study of soil and structures interaction during strong shaking that should be analyzed in detail for continuous improvement of seismic design and seismic codes. Related to the strong ground motion, the study of earthquake source mechanism, wave propagation path, effect of local topography, soil response at different soil conditions, site amplification factors etc. are important from seismological point of view. For this reason, apart the establishment of a modern seismographic network, attention is paid to the recording of the strong motion shaking during damaging earthquakes.

Ground motion at a particular site can be thought of as being influenced by three main elements: source, travel path and local soil conditions. The first one describes how the size and nature of the earthquake source controls the generation of earthquake waves, the second one describes the effect of the earth on these waves as they travel from the source to a particular location, and the third one describes the effect of the uppermost several hundred meters of rock and soil and the surface topography at that location on the resultant ground motion produced by the emerging or passing earthquake waves. In general, seismic waves and resulting ground motion are divided into two general levels; weak motion, or small amplitude motion from distant or small earthquakes, and strong motion, or large amplitude motion from nearby or large earthquakes. This kind of motion is of interest to engineers and those concerned with the effects of earthquakes on society. In contrast to most seismographs, which are designed to amplify very weak, otherwise undetectable motion from earthquakes, strong motion instruments are designed to make usable records of earthquake ground motion over an amplitude range from that barely felt by people to that which can destroy whole towns. Traditionally engineers have been interested in acceleration which is related to force and can be reliably measured. That explains why

the measurement of this parameter is so important on the context of the engineering seismology and earthquake engineering studies.

The strong motion network in Albania has been established for the first time on 1983. During a two years period, thirteen seismological stations of the Albanian Seismological Network (ASN) were equipped with SMA-1 analog accelerographs. The second phase begun in 1985 with the equipment of the major dams of the country with accelerographs and seismoscops of WM-II type. At the end of 1986, thirty SMA-1 accelerographs and fifty seismoscops were distributed around the country intended to constitute the base for future seismic hazard assessment studies, studies concerning the soil amplification, microzonation of major towns, soil-structure interaction etc. This network recorded the Tirana earthquake of January 9, 1988 ( $M_L=5.4$ ) with acceleration as high as 404.8 cm/sec on E-W component on sandstones of the Tirana seismological station.

The re-organization of Albanian Strong Motion Network (ASMN), already composed by 16 stations, came after a decade of absence of monitoring with the installation of the first digitally upgraded SMA-1 instrument in June 2002. Actually ASMN is composed of 23 digital stations: eight Guralp CMG-5TD standalone strong-motion systems, three Guralp CMG-5T strong-motion sensors and twelve digitally upgraded SMA-1 instruments. Some of them are co-located at our seismic stations, whereas the others are installed at the main towns in different soil ground conditions. The CMG-5T sensors are co-located with weak motions broadband sensors and are transmitting continuous real time data via VSAT, whereas the CMG-5TD accelerographs are transmitting via GPRS continuous real time accelerometric data at 100 sps rate. By the end of this year, the total number of strong motion sensors will be 30.

The paper we are presenting describes the work done for the presentation of the soil profiles over which these stations lie together with the determination of the  $V_{s30}$  parameter very important for the proper interpretation of these kind of data.

## SEISMICITY OF THE REGION OF ALGIERS . ANALYSIS AND SYNTHESIS OF CURRENT KNOWLEDGE

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### Abstract

In the western Mediterranean geodynamic context, the Algiers region is the consequence of the collision between the Eurasian-African plates. It is one of the regions in Algeria where deformations are slow and most of the activity is diffuse and moderate seismic magnitude is often not exceeding V degrees, but rarely strong earthquakes are produced. Thus, from the XIV century, several strong earthquakes of high intensity occurred (Algiers and its surroundings in 1365, 1541, 1673, 1716, 1755, 1924 Blida region in 1825 and 1716, Boumerdes region in 2003).

This seismic activity is mainly localized on the edges of the Miocene - Pliocene - Quaternary Mitidja basin and offshore.

Many researches in the fields of seismotectonics and seismology have identified the existence of some potential major seismogenic faults (Thenia, Boumerdes, Kair Eddine, Atlas Blidéen, Chenoua etc.) but the actual knowledge of their geodynamic evolution, depth or extension are inadequate and require further multidisciplinary research. These reverse faults and generally not particularly inclined are capable of generating earthquakes in the Algiers region.

**Key words:** *Algiers region, seismicity, slow deformations seismogenic faults, basin Mitidja*

## SEISMIC TOMOGRAPHY AND EARTHQUAKE MECHANISM IN ALBANIA

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### Abstract

The aim of this work was to study the seismic tomography structure of the Earth's lithosphere together with earthquake distribution and mechanism within the Albanian territory. The earthquake foci and some fault plane solutions are correlated with 3-D images of the velocity tomography. The results are discussed in relation to the stress field of the Shield and with other geophysical, e.g. geomagnetic, gravimetric, tectonic, and anisotropy studies of the Shield.

The earthquake data of the Albanian Shield has been extracted from the Albanian earthquake catalogue. Eight earlier earthquake source mechanisms are included in a pilot study on creating a novel technique for calculating an earthquake fault plane solution. Altogether, eleven source mechanisms of shallow, weak earthquakes are related in the 3-D tomography model to trace stresses of the crust in Albania. Earthquake mechanisms with NW-SE oriented horizontal compression (thrust faulting) dominate along the Adriatic collision confirm that the dominant stress field originates from the ridge-push force in the Albanian Earthquakes accumulation in coastal areas, in intersections of tectonic lineaments, in main fault zones or are bordered by fault lines. The Adriatic collision zone is the most seismically active zone in the country, which is represented by the Ionian-Adriatic coastal earthquake belt along the eastern margin of the Adria microplate (Sulstarova et al. 1980; Aliaj 1998, 2003).

Earthquake mechanisms with NE-SW oriented extension dominates behind them. The neotectonic geomorphology of the interior of the country has a horst-graben arrangement due to Pliocene-Quaternary normal faulting.

In the tomography model, the seismic velocities vary smoothly. The lateral variations are larger for  $V_p$  ( $V_p = 0.7 \text{ km s}^{-1}$ ). Elbasani-Dibra belts and their continuations at depth are associated with lower velocities in the granitoid areas. The tomography modeling suggests that the Albanian Orogeny was accreted from crustal blocks in cross-sectional area.

Thus, the tomographic model supports the concept that the thick Albanian crust was accreted from several crustal terranes, some of them hidden, and that the crust was later modified by intra- and underplating. In conclusion, as a novel approach the earthquake focal mechanism and focal depth distribution is discussed in relation to the 3-D tomography model. The schist belts and the transformation zones between the high- and low-velocity anomaly blocks are characterized by deeper earthquakes than the granitoid areas where shallow events dominate. Although only a few focal mechanisms were solved, there is a trend towards thrust movements inside outer areas. The normal fault and oblique strike slip type earthquakes are typical in the inner domain. Two near normal fault mechanism earthquakes occurred in the Elbasani-Dibra where low velocities were calculated.

**Key words:** 3-D tomography, earthquake, focal mechanism, low velocities

## SOME BASIC ASPECTS OF SEISMIC ACTIVITY IN ALBANIA DURING 2013

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### Abstract

Albania is characterized by intense micro-seismic activity, small and medium-size earthquakes and only seldom by large events. Seismic phases recorded by the Albanian network, integrated with other data of Thessalonicy (Greece), Montenegro and INGV (Italy) networks, are used to prepare the database for this year. The standard procedure uses the program Hypoinvers (Lee and Lahr, 1975) and velocity model Vel-Albanid (Ormeni 2007) for earthquake locations. We present here the results of the analysis in parameters of events and some features of seismicity that have occurred in Albania and surrounding area during 2013. The earthquake foci are concentrated mostly along some active faults: 1) Lushnje-Elbasan-Dibra transversal fault zone. From seismotectonic point of view, Lushnje-Elbasan-Dibra transversal fault zone belongs to a complex faulting environment, and according to the actual map of neotectonic zonation of Albania is located in the boundary between the two main tectonic zones characterized by compression and extensional. In the vicinity of Fieri was recorded a small series of earthquakes that have the same level of magnitude and supposed to be an induced seismicity. 2) Kurbnesh-Skavica seismogenetic zone. It lies in the area of Inner Albanides, along a depressional zone of faults extending nearly meridional and relatively narrow. 3) Ionian seismogenetic zone. It occurs in the tension stresses directed nearly east-west and is characterized by new differentiating movements of high gradients and by many and frequent earthquake epicenters. 4) Durres - Gjiri-Lazlit seismogenetic zone. It lies in the area of depressional zone which occurs in the tension stresses. Increased seismic activity was recorded nearby of southern Albania on the Greece territory.

**Key words:** *Earthquakes, Seismicity, epicenter, fault, focal mechanism*

### I. Introduction

Albania is situated in Alpine-Mediterranean seismic belt comprising the zone of contact between lithosphere tectonic plates of Africa and Eurasia. In Albania, the main geological structures are called the Albanides which are part of the Dinaric-Albanid-Hellenic arc of the Alpine orogeny. They are located between Hellenides in the south and Dinarides, in the north, which together form the Dinaric branch of the Mediterranean Alpine Belt. In the west, they are limited by the Apulia-Gargano foreland. The Albanides consist of magmatic and sedimentary rocks of Ordovician to Quaternary age according to the most recent studies (Aliaj et al. 2001). The Albanian orogeny and its surroundings are divided in two active tectonic domains: an external compressional domain constituting the Adriatic collision zone (Outer Albanides) and an internal extensional domain (Inner Albanides). The main cause of Albanian seismicity is the collision of Adriatic microplate with the Albanian orogeny. Albania is characterized by intense micro seismic activity and small and medium-size earthquakes and only seldom by large events. The earthquake foci is mostly concentrated along the active faults (Aliaj et al. 2001; Ormeni 2007). The typology of the earthquakes in Albania comprises all four primary and well-known types of earthquakes: earthquakes with main-shock followed by aftershocks, earthquakes with foreshocks and aftershocks, swarms and compound earthquakes (Ormeni et al. 2012). We present here the results of the analysis in parameters of events and some features of Seismicity that have occurred in the Albania and surrounding area during 2013. Compared with the two last years 2011 and 2012, the seismic activity is higher. The strongest earthquake occurred on October in the vicinity of Vlora town, in Southern Albania where the seismic activity reached an intensity of V-VI degrees on MSC-98 scale.



## II. Data and methods

In Albania and its surrounding territory, between 39°00'-43°00'N and 18°30'-21°30'E, 458 earthquakes were located with  $M_L=1.5-4.7$  (Richter). In the territory inside the Albanian boundary were located 370 earthquakes. Figure 1 shows the seismicity located for the year 2013. Statistics show an increase in seismic activity during 2013 compared with seismic activity during 2012. Seismic phases recorded by the Albanian network, integrated with data of INGV (Italy), Montenegro, Thessaloniki (Greece) and Kosovo networks are used to prepare the database for this study (Ormeni et al. 2013). The standard procedure uses the program Hypoinvers (Fred. W.Klein 2002) of the Atlas packet and velocity model Vel-Albanid (Ormeni 2007) for earthquake locations. Some formula for determination of the magnitude according to the time duration of the seismic signal is also used. For felt earthquakes of  $M_L > 3.5$ , questionnaires are distributed in the affected areas, in order to estimate the macro seismic intensity.

## III. Results and discussion

### 1. Some Feature of Seismicity

Moderate seismic activity was recorded within the transversal fault zones. The most of local earthquakes (about 92%) are distributed in depth between 0 and 25 km, with average depth of 9 km and maximum depth of 48 km. Depths maximum concentration is between 4 and 12 km. The earthquake foci during 2013 year is mostly concentrated in the active faults. The epicentral distribution of earthquakes shows that: Fieri-Elbasani-Dibra, Durres-Gjiri, Lazelit, Jonian and Kurbnesh-Skavic fault zones are more active (Fig. 2).

#### 1.1. The Fier-Elbasan-Diber seismogenic zone

On this transversal zone were located 146 earthquakes with  $M_L = 2.0 - 4.1$ , with average depth of 9 km and maximum depth of 25 km, and seismotectonic coefficient  $b=0.78$ . About 24 earthquakes have  $M_L > 3.0$  and one of them with  $M_L > 4.0$ . In the vicinity of Fieri was registered a small series of earthquakes having the same level of magnitude and supposed to be an induced

seismicity. Seismic events in this area seem neither to be a consequence of each other nor to be part of a unique seismic series. A moderate earthquake occurred on 21 of November at 19:45 (UTC), with a magnitude ( $M_L 4.3$ ). The focal mechanisms of this earthquake indicate normal faulting with a strike-slip component (Table.1). This region forms a roughly NE-SW-trending active seismotectonic zone in eastern Albania that continues in the western FYROM (Ormeni et al. 2013). From the seismotectonic point of view, the area belongs to a complex faulting environment and according to the actual map of nontectonic zonation of Albania is located in the boundary between the two main tectonic zones characterized by compressional and extensional movements. To this fault zone are related many geological phenomena. It comprises all four well-known types of earthquakes being seismoactive up today (Ormeni et al. 2012).

#### 1.2. The Durres-Gjiri Lazelit seismogenic zone

On this zone were located 21 earthquakes with  $M_L = 1.9-3.8$ , with average depth of 14 km and maximum depth of 39 km and seismotectonic coefficient  $b = 0.44$ . From them, 4 earthquakes are with  $M_L > 3.0$  and one earthquake is with  $M = 3.8$  (Richter) and occurred on 15<sup>th</sup> of May at 05:02 local time that has been felt by the population of Northwestern Albania. The focal mechanism of this earthquake indicates a thrust-oblique motion. This region forms a roughly NW-SE-trending active seismotectonic zone in western Albania. It is necessary to underline that Durres-Gjiri Lazelit is located in face of the orogeny front, in convergence with Adria micro plate and for this reason, here the compressional movements are strongest. This tectonic position and the active tectonic faults are the source of strong earthquakes that have stricken Durresi and the surrounding areas during the centuries.

#### 1.3. The Jonike seismogenic zone

On this fault zone were located 49 earthquakes with  $M_L > 1.5$  with average depth of 8 km and maximum depth of 26 km and seismotectonic coefficient  $b = 0.86$ , and 9 of them with  $M_L > 3.0$ . A moderate earthquake occurred on 22<sup>th</sup> of June at 08:22 (UTC) with magnitude  $M_L = 4.5$ . The focal mechanism of this earthquake indicates a thrust-oblique motion (Table 1). On the surfaces of these uplifts too, there are faults and flexures expressed

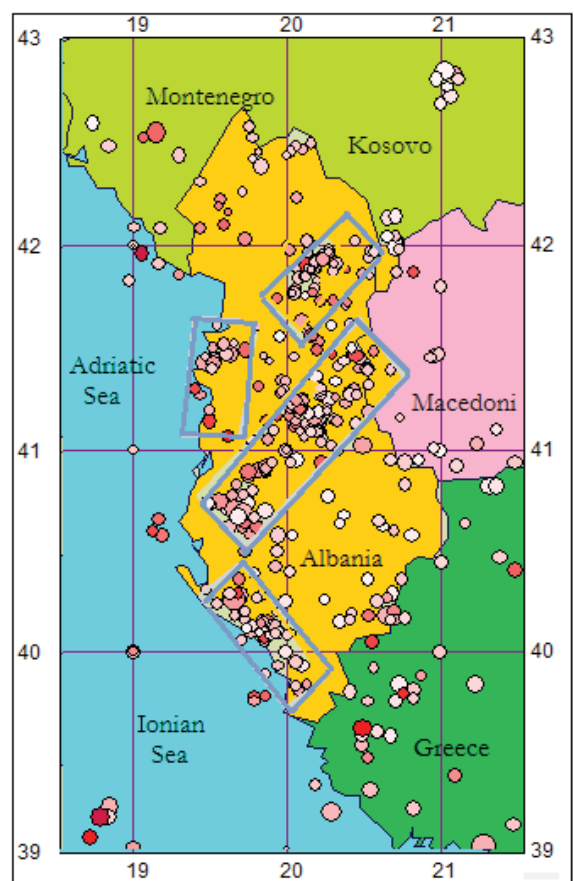
also with contrasts in relief; it appears very active in this year throughout its length. The Gjiri Ariut-Dukat transversal with east-southeast extension is a transtensive transversal with left compress and normal component. The left compress is evidenced by displacement of the mountain streams. A right compress is evidenced from Dukati to Brataj cutting Cika anticlinal with Tragjas anticlinal (Aliaj, 2001).

#### 1.4. The Kurbnesh-Skavic seismogenic zone

This transversal seismogenic zone with direction SW-NE is located in the inner side of folded Alpine orogeny with high mountains. During 2013 year were located 98 earthquakes with  $M_L > 1.6$  and 11 of them with  $M_L > 3.0$ . The earthquake that occurred on 25<sup>th</sup> of March at 07:20 (UTC) with epicenter coordinates 41.83°N; 20.15°E, the focal depth 21 km and magnitude ( $M_L = 4.3$ ). The solution of focal mechanism (Table 1) indicates an oblique strike-slip motion. This fault zone is characterized by a complex geomorphology and in addition, has been hit by numerous earthquakes during 2013.

Increased seismic activity was registered in the northern part of Greek territory near Albanian territory. One moderate earthquake occurred in the 1<sup>st</sup> of February at 01:26 (UTC), south of Leskovik town in Greece border with magnitude 4.1 (Richter). The strongest earthquake in this part of Greek territory occurred in June 1 at 00:01 local time, with magnitude of 4.7 (Richter).

The focal mechanism parameters of these



**Figure 1.** Epicentral map of earthquakes occurrence during 2013, for the Albanian territory and surrounding area.

earthquakes occurred inside Albania during 2013 ( $M_L > 4.1$ ) can be used to shed light on the seismotectonics of their areas and the current stress field. The focal mechanism of earthquake of 12 of April at 01 h 26 m, indicate oblique normal faulting.

**Table. 1** The focal mechanism parameters of the earthquakes

N	Date Y/m/d	Time h:m:s	RMS (s)	Lat	Long	Depth (km)	$M_L$	Nodal plane. 1 and 2			Type of Mechanism
								Strike	Dip	Rake	
2	13/03/25	07:58:14	0.2	41.83	20.15	13	4.3	129 241	48 08	31 134	
3	13/04/12	01:26:54	0.3	40.18	20.66	10	4.1	213 327	42 70	/31 -128	
	2013/06/22	08:41:08	0.1	40.26	19.65	13	4.5	314 224	90 10	80 180	
	2013/11/21	19:45:30	0.3	40.69	19.72	9	4.1	220 38	60 30	-89	

#### IV. Conclusions

The most seismic activity inside the Albanian territory analyzed in this work have been generated in an area with complex features from the neitectonic point of view. The local earthquakes are distributed in depth between 0 and 25 km, with maximum concentration between 4 and 15 km. The earthquake foci are concentrated mostly along some active faults. In the vicinity of Fieri was registered a small series of seismicity. Increased seismic activity was registered outside of Albania in the Greek territory.

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## SEISMIC VULNERABILITY ANALYSIS OF BUILDINGS IN NAINITAL CLUB WARD OF NAINITAL MUNICIPAL AREA USING RADIUS AND GIS TECHNIQUES

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### Introduction

The Himalaya is a young, dynamic and evolving mountain range that is the product of the eventual collision of Indian and Tibetan plates after consumption of the intervening oceanic crust. The north northeastward drift of the Indian Plate has not yet seized and it is responsible for intense seismicity of the region. In the past, the region has been jolted by four Great Earthquakes (Magnitude >8 on Richter Scale); 1897 Shillong Earthquake, 1905 Kangara Earthquake, 1934.

Bihar - Nepal Earthquake and 1950 Assam Earthquake apart from Kumaun Earthquake of 1720 and Garhwal Earthquake of 1803. Entire State of Uttarakhand falls in Zone IV and V of the Earthquake Risk Map of India with Nainital

similar structures here in the hilly terrains:. The earthquakes of Uttarkashi (1991) and Chamoli (1999) are the major events in recent past, in the region measuring 6 and 6.8 in magnitude in Richter scale.

### Study Area

The study area covers the Nainital Club Ward of Nainital town (29°24'9.0017"N to 29°23'34.4598"N 79°26'8.8643"E to 79°27'1.9278"E) covering an area of 0.659 sq km with the perimeter of 4.653 km. The population of the area is near about 5000. The study area lies in a very unstable steep slope of lesser Kumaun Himalaya. The altitude varies from 1980m to 2650m above sea level.



Figure 1. Study area of Nainital Club Ward

falling in Zone IV.

Some of the major earthquakes in the nearby region in the recent, past however, should be understood the estimated damage and behavior of the almost

### Zoning of the Area

Usually damage estimation is carried out by subdividing the area in question. That is why earthquake damage estimation is often called

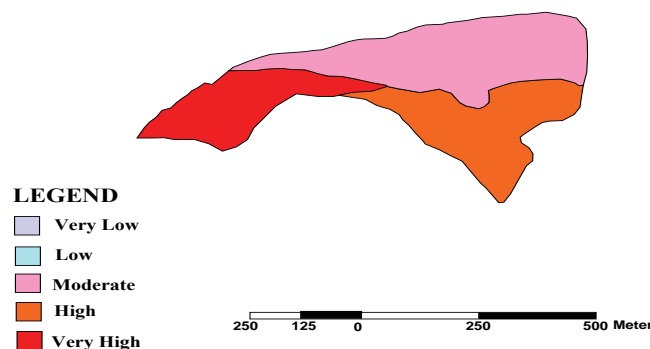


seismic microzoning. The RADIUS Tool introduces a simplified method to evaluate ground conditions. Subdivision of the area in question into mesh units or irregular shapes using GIS (Geographical Information System) is done. The zoning of area is done through the meshes created in the RADIUS program. The area is mainly divided into east and west zone on the simple basis of direction in the RADIUS program.

However for a better representation of data the area is further divided into hazard zones on the basis of population density and building types in the area.

that was of magnitude 6.8 on Richter Scale. It struck on the midnight of March 30, 1999 and about 100 people lost their lives and about 5 lakh people were affected in the districts of Chamoli, Rudraprayag and Pauri. The second is supposed to be intensity of Uttarkashi earthquake (with 6.6 magnitude) which rocked the districts of Uttarkashi, Tehri and Chamoli. This one came back in the night hours (02.53hrs.) of October 20, 1991. There was a death toll of about 750 with 5000 injured.

If such an earthquake strikes Nainital then what will happen? That's the major question. With the



**Figure 2.** Hazard zonation of the different areas in Ward Area (based on population density and building types).

### Hazard zonation of the different areas in Ward Area (based on population density and building types)

#### Data Analysis

The data analysis is done through RADIUS program with the input of the data collected. But before directly going into the analysis it should be better to see first that how this program works.

In this study the past earthquakes of Chamoli and Uttarkashi are chosen, assuming such earthquake to take place in the study area.

#### Estimated Building Damage

The estimated building damage for a hypothetical earthquake in Nainital Club Ward is calculated through RADIUS program. Here two hypothetical earthquakes are considered taking examples from past in the nearby areas. The first earthquake is supposed to be intensity of Chamoli Earthquake

collection of primary data regarding building types along with other information like soil type and then putting these data in RADIUS program, we got an estimation of the building type in Nainital club ward.

For an ease of study we divided Nainital club into east and west on the basis of direction with equal distribution of buildings on both sides. In total we surveyed 300 buildings on random sampling basis in the area, 150 in each area. For the eastern side we found out that out of 150 buildings, 85 buildings will be completely destroyed with the earthquake of same intensity as of Chamoli, with mean damage ratio (MDR) being 56.8. The same can be said for the western side where out of 150 buildings 88 are supposed to vanish completely with mean damage ratio (MDR) being 58.7. In total for 300 household 173 buildings are supposed to be damaged with a MDR of 57.7.

On the other hand, taking the magnitude of earthquake equaling that of Uttarkashi Earthquake of 6.6, we found out the damage of the buildings

to be 54.6 MDR. The total damage count is 164 buildings out of 300.

This is a very shocking result with more than half of buildings surrendering to the earthquake on both occasions. As there is a saying about earthquake, it is not the earthquake that kills people; it is the buildings that kill people. The reason for such a result is that the most of buildings in the area are sub-standard, not complying with the local code provisions, also there is no such major repairing done for the older buildings which are many in the area.

### Estimated Casualties

Casualties caused by earthquakes are main “damages” and their reduction is targeted in disaster planning and preparedness. Building collapse is a main cause of casualties during earthquakes. Therefore, information on the number of people inside buildings when the earthquake occurs is necessary for casualty estimations. Moreover, day and night populations are different.

The estimation of casualties is determined by putting the value of casualty coefficient into the data entered for the area.

The earthquake of the magnitude equaling Chamoli, would give the following results for our research area:

- For the total population 6% deaths are estimated. Out of 5000 people in the ward 316 are estimated to lose their life.
- Out of total population 25% are estimated to be injured, i.e. 1272 of 5000 people.
- The most damages are estimated on the western part with 665 injured and 166 deaths. Whereas in the eastern part the injured people are estimated to be 607 with 150 deaths.

Now, let's see the impact of earthquake equaling that of Uttarkashi:

- For the total population 5% deaths are estimated. Out of 5000 people in the ward 290 are estimated to lose their lives.
- Out of total population 23% are estimated to be injured, i.e. 1194 of 5000 population.
- The most damages are estimated on the western part with 625 injured people and 153 deaths. Whereas in the eastern part the injured are estimated to be 570 with 138 deaths.

This gives the clear idea how disastrous it can be

for the life of people. This data only implies to the casualties due to the damage to buildings, but the earthquake possibly can also cause landslide in this vulnerable unstable zone. So, the casualties could be lot higher in that scenario.

### Secondary Disasters

Nainital club ward is placed on a highly vulnerable unstable zone. Most of the settlements are on the steep slopes with Naina peak and Snow view peaks gazing all the time at the settlement. An earthquake in the area can lead to the chain reaction of the other secondary disasters. They can be categorized as following:

- 1. Landslide:** The earthquake can trigger the landslide from Naina peak which is already very unstable, that can be seen back in 1989 when this hill started weathering and the whole area had to be evacuated. The earthquake can only help this unstable hill on its way down.
- 2. Fire:** The highly densely populated settlement consists of some slum areas and wooden houses. Further there is many inflammable material in the houses such as LPG, wooden furnitures and garments. The short circuit, resultant of earthquake, can trigger fires in the region. Such fire can proliferate in the area and it will be very difficult to stop.

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## AMPHIPORA FACIES IN DEVONIAN SEQUENCES FROM THE MOESIAN PLATFORM (NE BULGARIA)

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### Abstract

The genus *Amphipora* includes branching stromatoporoids that are characterized by growth forms with very thin stems of spongiform skeletons and presence of axial canals. *Amphipora* floatstone facies occurs worldwide and is particularly common in calm-water lagoonal and back-reef Middle and Upper Devonian (mainly Givetian–Frasnian) carbonate complexes. This specific facies with *Amphipora* has not been distinguished and described in Devonian successions in Bulgaria until now.

Paleozoic rocks in the Moesian Platform (Northeastern Bulgaria) are known only from deep wells drilled for oil and gas prospecting. Predominantly shallow-marine carbonates and rare evaporites build up the Middle–Upper Devonian sequences. They are interpreted as formed in an arid low-energy ancient tidal flat with well distinguished shallow subtidal (lagoonal), intertidal and supratidal settings. The studied *Amphipora* facies represents a part of lagoonal successions and is recorded in several informal lithostratigraphic units with Givetian and Frasnian age: Carbonate-sulphate formation, Dolomite formation and Banded limestone formation. These sequences are composed predominantly of alternating dark brown and dark gray to black micritic or bioclastic limestones and light gray to brown fine- to coarse crystalline dolostones. White to light gray anhydrites and rare black shales are also locally presented.

Limestones and dolostones with *Amphipora* are distinguished within four deep well sections: Chreshovo 1, Nikola Kozlevo 24, Mihalich 2 and Marash 1. *Amphipora* facies consists of floatstones composed almost completely of abundant and mostly well-preserved stromatoporoid branches. In thin-sections, the rock matrix is micritic/microsparitic with high organic and clay content and is often characterized by dark brown colour. *Amphipora* branches reach a length up to 2 cm and are average 3.5–4 mm in diameter. Calcspheres, ostracods and palaeosiphonoclad algae are

also locally common. Massive stromatoporoids, gastropods, brachiopod shells and small solitary corals are only sporadically observed. Peloids are rarely presented scattered in the rock groundmass. The micritic matrix is locally replaced by fine- to medium-sized euhedral dolomite crystals. Some stromatoporoid branches are also partly or completely dolomitized.

According to different authors *Amphipora* was thought to be adapted to warm temperatures, intense light, elevated or fluctuating salinity and water depth between <1 m and 10 m. It is widely accepted that these stromatoporoid communities formed dense meadows over the shallow lagoon floor. The observed in studied carbonates monotonous fossil association (mostly *Amphipora* stromatoporoids, plus calcspheres, ostracods, and palaeosiphonoclad algae) also indicate deposition in a shallow subtidal environment with restricted or semi-restricted water circulation. The predominantly well-preserved fossil remains and micritic rock matrix characterize a possible calm sheltered setting with low-energy hydrodynamic conditions.

The *Amphipora* floatstones from investigated deep well sections occur in close association with other shallow subtidal facies (palaeosiphonoclad wackestones and packstones, ostracod mudstones and wackestones, and bioclastic-peloidal packstones and grainstones), also interpreted as formed in a lagoonal settings with restricted or semi-restricted water conditions.

The described *Amphipora* floatstone facies from the Moesian Platform (Northeastern Bulgaria) is very similar to others carbonate facies with *Amphipora* from Devonian lagoonal and back-reef successions recorded in Europe (the Ardennes in Belgium and France, Aachen in Germany, the Graz area in Austria, the Torbay Reef Complex in Southwest England, the Holy Cross Mountains and Malopolska Massif in Poland, the Moravia Karst in Czech Republic), the Urals in Russia, North America (Ohio, Alaska and Indiana in USA, Alberta and Saskatchewan in Canada) and the Canning Basin in Western Australia.

## STABLE C AND O ISOTOPIC COMPOSITION OF OLIGOCENE LAMINATED COCCOLITH LIMESTONES FROM THE OUTER CARPATHIANS AS PALEOCEANOGRAPHIC RECORD

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### Abstract

The final stages of deposition in the Outer Carpathian basin took place during the Oligocene and Early Miocene. Up to 2 km thick synorogenic flysch deposits were laid down in front of a prograding accretionary complex. This rapid and rather monotonous sedimentation of siliciclastic material produced the largest lithostratigraphic complexes in the Outer Carpathians, e.g. the Menilite and the Krosno formations which play a significant role in the Carpathian petroleum system as important source and reservoir rocks. There are, however, severe stratigraphic problems with dating and correlation even within a single structural unit, because these facies are diachronous, poor in biostratigraphically useful taxa and exhibit rather invariable lithology of alternating mudstones and sandstones. They are only interspersed with very thin, but distinctive layers of pelagic coccolith limestones which formed by intensive pelagic carbonate sedimentation induced by phytoplankton blooms. These blooms occurred within the entire Carpathian basin, so the coccolith limestones are widespread and represent isochronous horizons tracked over large distances up to 550 km. This makes them unique and very useful means for even basin-wide correlations. Nonetheless, there are still controversies concerning their origin and paleoceanographic conditions that persisted in the basin and favoured their formation. This is why we have undertaken a detailed research on these limestones employing field, biostratigraphic, petrographic and geochemical methods. Here, we present results of petrographic and stable C and O isotopic analyses of one of these limestones (the Tylawa Limestones).

Pelagic limestones usually constitute pristine sedimentary carbonate material because it is almost exclusively composed of biogenic carbonate represented by coccoliths. Consequently, stable C and O isotope measurements are often performed for reconstructions of major paleogeographic and paleoecologic conditions such as fluctuations of sea-level, primary productivity, temperature, salinity etc. provided that the limestones were not affected by significant diagenetic alterations.

We have analyzed the Tylawa Limestones from the Dukla and Silesian units of the Polish Outer Carpathians. They exhibit relatively broad range of  $\delta^{13}\text{C}$  values between -2.2 and 0.6 ‰ (mean -0.3 ‰, n=49), but still they fall in the range typical for primary marine carbonates. Microscopic examinations of these samples revealed that they are only slightly modified by diagenetic processes (occasional partial dissolution of coccoliths), contain little calcitic and dolomitic cements, and did not undergo recrystallization. Although these data indicate that the diagenetic overprint is superimposed upon the original marine signal causing variations in C isotopic composition, the overall C isotopic composition is primarily controlled by the isotopic ratios of biogenic components.  $\delta^{18}\text{O}$  values of these limestones are depleted in  $^{18}\text{O}$  by 3.7 to 6.2 ‰ relative to PDB standard (mean -4.8 ‰, n=49). Lack of clear correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  confirms that the isotopic composition was not significantly affected by diagenesis. Moreover, that low  $\delta^{18}\text{O}$  values cannot be related to disequilibrium isotope fractionation ('vital effects') during calcification of coccoliths. Therefore, O isotopic composition of these limestones is a primary signal indicating that the seawater was depleted in  $^{18}\text{O}$ . Large negative shifts in  $\delta^{18}\text{O}$  values of seawater are usually caused by large input of meteoric water typically having light O isotopic ratio. Coccolithophorid blooms are often related to seawater freshening and there are reports that the Carpathian basin was periodically isolated from Paratethys during the Oligocene. Furthermore, the Tylawa Limestones do not contain foraminifers which are frequently observed in the surrounding mudstones and other horizons of coccolith limestones. These facts and the isotopic composition herein reported indicate that the limestones formed during periods when the basin was isolated from Paratethys which impeded water exchange with the open ocean and caused the development of brackish-water conditions unfavorable for foraminifers.

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## **BASIN, DEPOSITIONAL AND LITHOFACIAL FEATURES OF THE MIDDLE TRIASSIC SEDIMENTS IN SOUTHERN PART OF THE CENTRAL NORTH BULGARIA**

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### **Abstract**

Triassic period marks the beginning of the Mesozoic evolution of the Bulgarian territories after the end of the Hercynian tectogenesis, denudation of the Hercynian orogen and the final formation of Late Permian arid plain. Triassic geological evolution took place in the geodynamic setting of the passive continental margin and deploying locally extensional processes. Failed rift systems are not fully developed and magmatic activity is found only in a few sites along the edge of the West Forebalkan (Chiren, Veslets, Golyamo Peshtane, Drashan, Varbitsa) and Moesian platform (Knezha, Pelovo).

Complete, well defined sedimentation and geodynamic cycle passed during the Triassic period in Northern Bulgaria. It began with continental sedimentation going through shallow marine settings with the formation of a carbonate platform (Paleo-Moesian platform) and ended with regression followed by inversion.

The main objective of the study is to restore the basin architecture and depositional conditions, linking the lithological composition of the sediments with a particular environment in the Middle Triassic. The lithofacial features are investigated in individual well sections and their relationships in the lateral direction are traced out due to the interpretation of regional seismic profiles.

The Middle Triassic section is relatively complete and preserved from erosion in the western part of the study area. Differences in thickness and in lithofacial characteristics of sediments are recognised on both sides of South Moesian fault. This main fault played important role in the separation of zones with different rates of subsidence and sedimentation conditions.

Geological development during Middle Triassic in the study area is determined in a first place by the sedimentation and tectonic features in the southern edge of the Moesian platform. At the end of the Early Triassic and beginning of Middle Triassic,

resulting in a gradual deepening of the basin and active transgression of marine waters from east, arose conditions for carbonate sedimentation within the broad shallow shelf. The Anisian marks the end of the transgressive and beginning of stable stage in the Triassic sedimentation. In the littoral and sub-littoral environments, while preserving arid climate, a considerable deposition and formation of a carbonate platform took place. In an epicontinental shallow basin in Anisian, there were favorable conditions for the deposition of thick carbonate sections presented by Doirentsi Formation. At the end of Anisian and the beginning of Ladinian, the platform was replaced by a shallow shelf with varied sedimentation. Ladinian stage is characterized by increased tectonic activity, interruption of pure carbonate deposition and periodic supply of terrigenous-clayey material. The outcome is the development of Mitrovtsi Formation, which continues its spreading in Early Carnian. Deposition then took place in the course of the steady stage of Triassic sedimentation. Middle Triassic basin was shallow marine, with subsided southern part. Lateral zonation of the sediments was a result largely of the bathymetry of the basin and the direction of the Triassic transgression.

In the study area there are separated 6 lithofacial complexes characterized by lithological diversity of the Middle Triassic rocks. The detailed observation show that the horizontal zonation is determined by the morphology of sedimentary basin, bathymetry, the supply of sediment material and the influence of the Iskar fault zone to the west. The common between complexes is that the lower part is build-up mostly of shallow marine limestone facies. The analysis of the middle part show also abundance of carbonates. These are limestones, locally fragmentar limestones seams, clayey limestones and dolomites, especially where the Dolni Dabnik member of Doirentsi Formation is present. The upper part dated as Ladinian includes mostly shales and limestone.

## GEOCHEMISTRY OF BADENIAN EVAPORITES AS A BASIS FOR MODEL OF SALT DEPOSITION IN THE CARPATHIAN FOREDEEP BASIN (POLAND)

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### Abstract

Badenian Salinity Crisis was one of the distinct changes of paleoenvironment in the Carpathian area. During that short period (13.8-13.4 Ma; de Leeuw et al. 2010), a complex of climatic, environmental and geological conditions caused the occurrence of continuous series of evaporate deposits on a large area. Badenian evaporites were accumulated in the Carpathian Foredeep area stretching from Upper Silesia in Poland to Doftana Valley, in Romania. Contemporaneous evaporites also were deposited in the Transylvanian Basin in Romania, the Transcarpathian Basin of Ukraine and the East Slovakian Basin. Determination of the geochemistry of these evaporates will be essential for understanding sedimentation in these highly restricted environments and allows us to explain the causes that led to the isolation of the basin from the open ocean. The goal of this presentation is to build a reliable model of the saline basin development. The western part of the Carpathian Foredeep (southern Poland) was selected for detailed studies (Bukowski 2011). The results of the bromine content in halite, chemistry of fluid inclusions, isotopic composition of stable isotopes of oxygen and sulphur from anhydrites occurring in the salt series and isotopic composition of oxygen and hydrogen in fluid inclusions were used for drawing conclusions on the origin of brine and access of continental waters as essential components of chloride facies evaporate sedimentation. Bromine content in halite indicates relatively low concentration of brine. Particularly low content of bromine recorded in some samples of halite, indicates that some of NaCl could be derived from the dissolution of previously deposited salts or leaching of older salt formation. This type of dissolution/leaching could occur both during periods of seawater inflow into basin as well by inflow of meteoric waters in periods of shallow-brine pan. Modeling made by Cendon et al. (2004) show very high proportion of

continental brine during salt sedimentation.

However, the presence of intercalations of clays within salts that contain bivalves, echinoderms, Lithotamnion and individual corals indicates a periodic inflow of seawater. Data on the chemical composition of primary fluid inclusions in the chevron halite crystals indicate that the brines were of the sulfate type and characterized by relatively low and stable concentration corresponding to the onset of the crystallization halite. The average value of isotopic composition (S and O) of anhydrites from salt series was similar to the isotopic composition of sulphate of marine origin. Based on those results and direct observations of the salt sedimentation, as well as experiments, a Badenian salt sedimentation model was developed (Bukowski 2011). Salt crystallization in the studied area was initiated in the sea basin containing water whose chemical composition was similar to present-day ocean water. During halite crystallization, the saline basin was supplied with seawater of normal salinity, as well as meteoric water (infiltration and surface water) mixing with basin's brine. The water entering the basin caused partial solution and redeposition of salt from shallow and marginal parts of the salt basin.

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## UPPER ORDOVICIAN DIAMICTITES FROM THE BALKAN TERRANE, WESTERN BULGARIA: A GLACIOMARINE RECORD OF THE GONDWANA HIRNANTIAN GLACIATION

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### Abstract

Hirnantian diamictites are exposed in the Paleozoic Balkan Terrane (western Stara planina Mts) which was an integral part of the Armorican Terrane Assemblage (s.l.). In terms of lithostratigraphy the rocks are referred to as Sirman Fm having thickness of 7-10 m. This unit overlies non-fossiliferous argillites of the Tseretsel Fm (Katian stage) and is covered by lydites and graptolite-bearing argillites of the Saltar Fm (Hirnantian-Telychian). The dark grey, massive, sandy diamictites contain single pebble-sized extraclasts derived from the Ordovician basement. The main microfabric constituents include quartz grains ( $\geq 80\%$ ), lithic fragments, intrabasinal shale clasts and silty-clayey matrix.

The combination of several rock characteristics indicates glaciomarine origin of the Hirnantian sediments: distinct stratification, poor sorting, presence of limestones (well preserved unstable lithic fragments), random arrangement of the clasts, lower gradational boundary and intercalation with dark marine shales, lack of evidence for glacial terrestrial deposition (e.g. abraded bed surfaces, faceted, striated or bullet-shaped clasts, specific landforms such as moraines, etc.). Moreover, these laterally persistent deposits show uniformity in thickness, colour, structures, composition, and texture. Another diagnostic feature is the occurrence of till pellets, e.g. unsorted debris identical to the rock matrix, but having diffuse boundaries, flattened shape and subparallel orientation to bedding. The ice-distal origin of the diamictites is emphasized by their relatively small thickness, common laminations, pronounced sandy (e.g. gravel-poor) character, homogeneous lithology of the extrabasinal clasts, and lack of ice-proximal and ice-contact facies (fining-up and coarsening-up units, rapid lateral facies changes, etc.).

The primary diamicts originated through rain-

out settling of clay-sized to sand-sized particles from turbid meltwater plumes and ice-rafted debris (IRD) reaching pebble size. The turbid plumes were emanated from the front of a distant grounded or floating glacier while the IRD were derived from seasonal ice or icebergs. Although distinction of those two sources for IRD is difficult in ancient successions, the heterogeneous particle size and shape, as well as the extrabasinal provenance of many clasts, imply far-travelled iceberg-related transport. The balance between transported material by meltwater plumes and IRD may have varied but the siliciclastic supply ultimately resulted in a regionally extensive, blanket-like diamict facies. The occurrence of slumps and load casts reflects high sedimentation rates and/or local steep slope with unstable substrate. The lack of high-energy depositional/erosional structures and the low degree of grain sorting suggest deposition in a weakly agitated, mid-shelf to outer shelf environment. Marine currents may have assisted in the distribution of clastic material across the shelf whereas intermittent reworking of semi-consolidated sediments is inferred from the commonly abundant intrabasinal clasts. While the glaciomarine sedimentation occurred mostly during glacier retreat forming a deglaciation sequence, the intercalated shales represent products of suspension settling during relatively short periods of interglacial highstand.

The abundant quartz grains and the ZTR heavy mineral association imply a low relief, granitoid-dominated sourceland with warm and humid climate. Extreme chemical weathering and erosion of the Gondwana interior related to intensive volcanic activity (e.g. a CO<sub>2</sub>-rich atmosphere) took place during the late Neoproterozoic and early Cambrian providing large volumes of mature quartz sands. The latter were transported by rivers and deposited as first-cycle sediments in Cambrian–Ordovician time on a vast shallow shelf along the northern continental margin. After a long-term coastal reworking the extensive ice-sheet growth

over part of Gondwana in the Hirnantian resulted in incorporation of those mature clastics and their subsequent release during the ice-sheet decay.

The regional geographic distribution of similar Upper Ordovician glaciogenic rocks in South/

Central Europe (Portugal, Spain, France, Italy, Germany, Czech Republic, Austria), Turkey and Iran is consistent with the existence of a broad belt of glaciomarine sedimentation along the north Peri-Gondwana non-glaciated shelf, e.g. beyond the outer ice-sheet limit, during the Hirnantian age.



## A GENERAL OVERVIEW ON THE GEOLOGICAL, GEODYNAMIC AND GEOENVIRONMENTAL UNIT OF THE ALBANIAN COASTAL AREA

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### Abstract

The aim of this work is to give an overview of the Albanian coastal area stretching along the orth-south direction for a length of about 454 km. This overview consists in lithological description of several coastline segments, their dynamics and genetical zoning of the area.

The lithological characteristic are based on the study from Geological Maps of Albania of different scales, site investigations etc.

The dynamics are based on the mapping of shoreline positions in different periods of time and the calculation of annual erosion and/or accretion rates. The rates of marine erosion (monitored in the last 20 years) in specific segments of the coastal area of Albania ranging from 100 m/year to 15-5 m/year indicate the necessity for monitoring and in-depth study of this phenomenon. As a result, the eroded and added areas are calculated.

The genetical zoning is based upon the following criteria: geotectonic evolution, geomorphology and physico-geography the sedimentological and oceanographical ones. As result, the map of genetical zoning of the geoenvironmental units for the coastal area of Albania, scale 1 : 200,000, 1:50,000 (geoenvironmental sub-units) has been compiled.

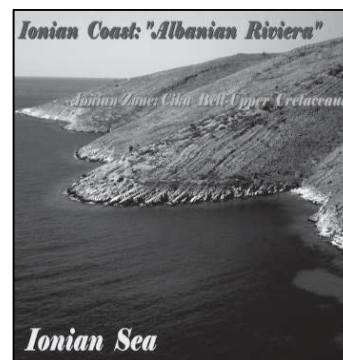
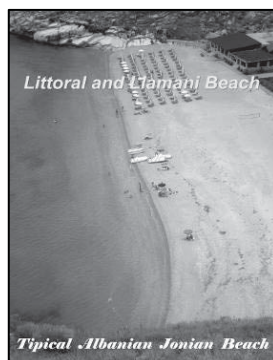
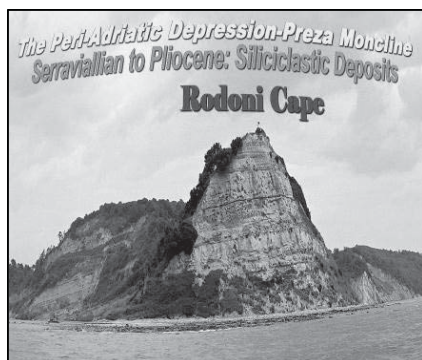
**Key words:** geological settings, Quaternary and present deposits, erosion, geoenvorinmental unit

### A. Lithological characteristics

The geological setting has conditioned the present configuration of the coastline. This coastline is characterized by the following rock types:

- Segments with a length of 194 km or 42 % of the entire coastline are composed of sandy beaches and river deltas, littoral cordons and arrows, sandy dunes;
- Segments with a length of 57 km or 12.5 % of the entire coastline, composed of molassic rocks (conglomerates, sandstones, clays) of Miocene-Pliocene age;
- Segments with a length of 153 km or 33.7 % of the entire coastline, composed of carbonate formations (Upper Triassic-Lower Jurassic dolomite limestones and Jurassic-Cretaceous-Paleogene cherty limestones);
- Segments with a length of 31 km or 6.8 % of the entire coastline, are alluvial fan deposits (gravel-sand) formed during the Quaternary period;
- Segments with a length of 19 km or 4.2 % of the entire coastline, consisting of Oligocene flysch;

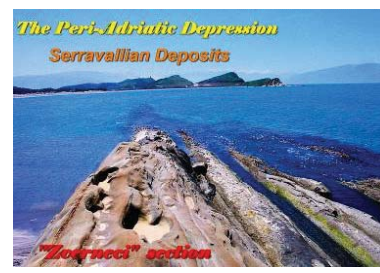
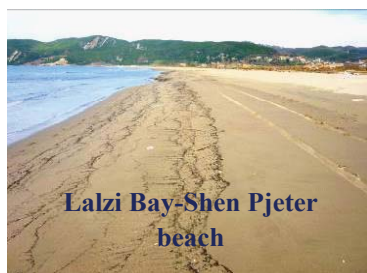
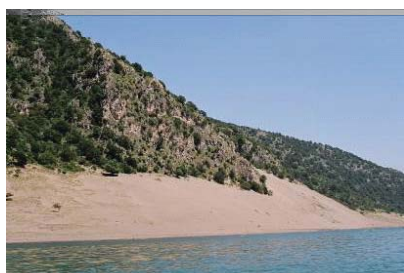
Quaternary and actual deposits extend along a south-north direction for a length of about 225-230 km or approximately 50 % of the Albanian coast. They mostly occur in Velipoja-Patok-Ishem depression, Lalzi Bay, Dures-Vlora depression, fan alluvial areas between Vlora and Saranda



coast (Orikum, Palase-Dhermi, Himare, Qeparo and Finiq-Vurg-Butrint-Murres-Xare lowlands. Sedimentological and geophysical studies of the Quaternary deposits are carried out in 5 sites of Albanian Coastal Area: a) Finiq-Vurg-Butrint-Murri-Xarra, b) alluvial fan of Borshi, c) Lalzi Bay-Durres, d) Ishem-Patok-Fushekuqe and e) Velipoje-Vilun-Rrjoll.

### 1. The marine and coastal area of the Adriatic sea

Coastal area of the Adriatic sea has a length of 251 km or represents 55.3 % of the entire Albanian coastline. An important role in the configuration and dynamics of this coastline is attributed to the river watersheds. Geomorphology, geometry, dynamics, the mouths of major rivers of Albania and their respective deltas are the main factors that affect changes in the pattern of coastline. The relief of this area is represented by hilly terrain, alluvial valleys, and also by the coastal plain with beaches, deltas, swamps, lakes and lagoons among the most typical. Geographically, this belt is part of the coastal plain with an extension of 250 km and a width up to 40-45 km in its central part (towards Tirana), but in the north direction towards Lezha, it becomes narrower to a few kilometers. Under the tectonic aspect, the coastal area from Vlora to Lezha is part of the Pre-Adriatic (or Adriatic) Plain and its northern part extends up to the area



of Kruja tectonic unit. The largest part of this area is formed at the end of Pliocene, especially during the Quaternary. The different tectonic sequences during this period have outlined the hilly chains on anticline and syncline structures that are raised during this period.

### 2. The mountainous coastal and marine-reef-the Ionian sea

Coastal area of the Ionian Sea has a length of 203 km or 44.7 % of the entire coastline of Albania. In this area, the configuration and geomorphology of

the coastline are mainly affected by the presence of mountainous ecosystem, where the hypsometry reaches up to 1000 m above the sea level in a short distance from the coastline. In general, the coastal area of the Ionian Sea during the neotectonic period is characterized by uplifts of high intensity. This is testified by the presence of several levels of erosive marine terraces (up to 4-5 levels) in Ksamili, Saranda, Kepi the Qefalit, Lukove, Porto Palermo, Uji Ftohte-Vlore, etc. and an elevation of 100-150 m above the sea level (Fig. 1).

In this area, there are several alluvial fans that make up the present specific natural ecosystems, such as alluvial fans of Orikumi, Palasa, Dhermiu, Ngjipe and the spectacular canyons of Jala, Himara and Potami, formed by the related mountainous streams, Qeparo, Borshi, Buneci (Sasaj), Kakome Gjiri Korzes.

### 3. Quaternary deposits (Holocen-Pleistocen) of the Albanian Coastal Area

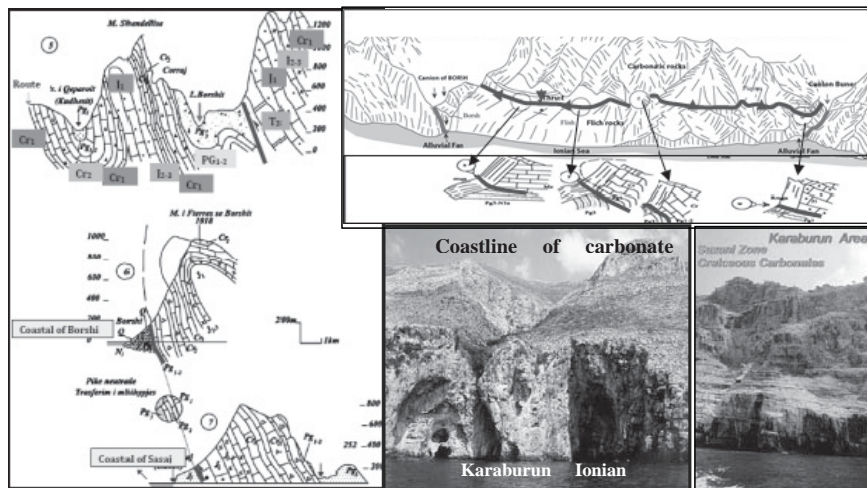
Based on geological morphological and sedimentological features of the present Quaternary basins, in the coastal areas two principal zones can be distinguished:

- Zone A - Preadriatic depression (from Velipoja to Vlora) and Graben depression of Finiq – Butrint – Xarre (Fig. 2).
- Zone B – abrasive rocky coast of the Ionian Sea

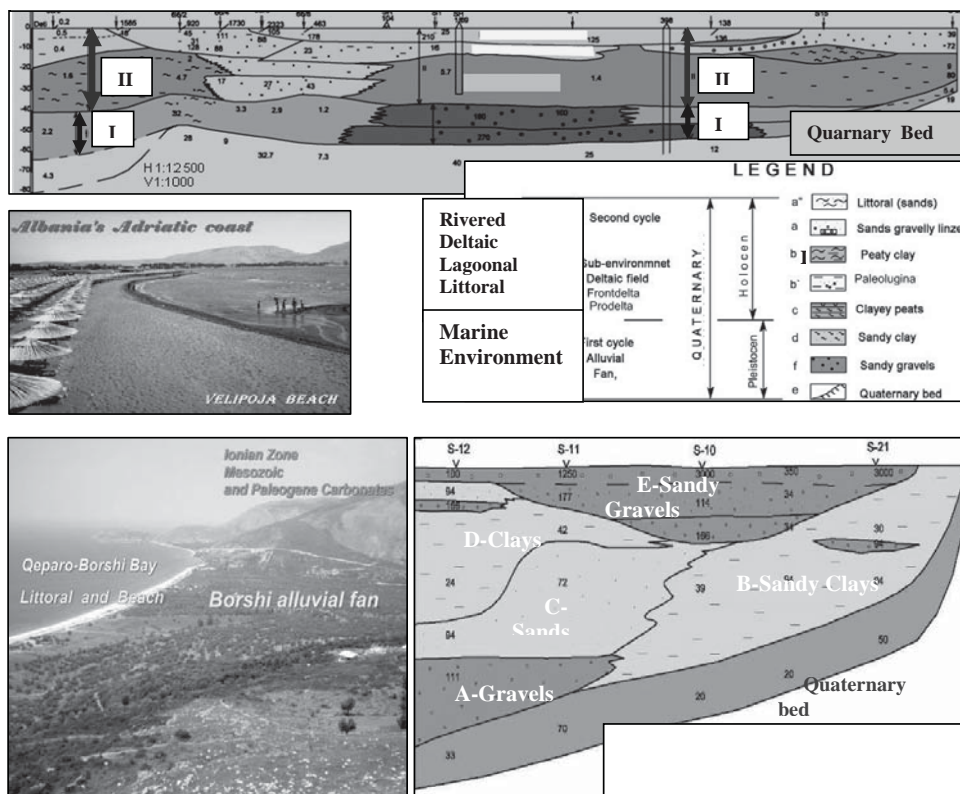
shoreline, with the presence of canyons and alluvial fans and quaternary beaches (Fig. 3).

The Quaternary deposits consist of: continental alluvial fans, relatively deep marine, fluvial, deltaic, lagoon – marshy and littoral ones. Their thickness varies from 20 to 200 m conditioned by the palaeogeography of the underlain formation that have undergone the folding phase at the end of Pliocene. Their highest thickness is encountered at the depression of the area Ishem – Patok – Fushkuqe (180-200 m). Two regional cycles (mega-sequences) can be clearly identified in all coastal areas.

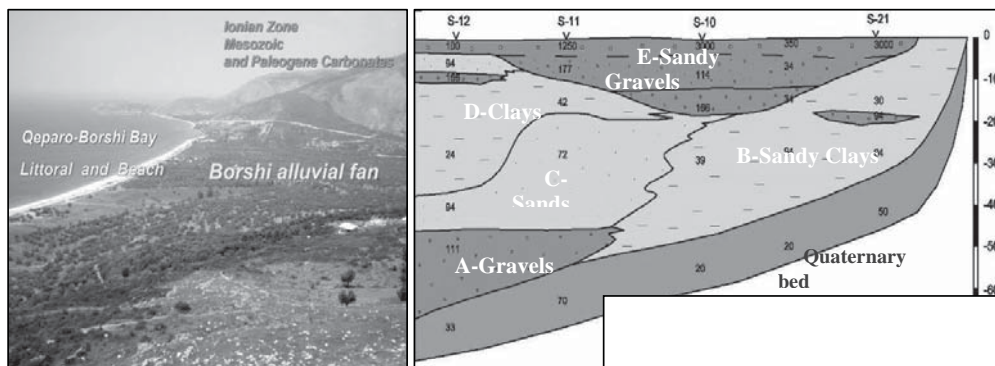




**Figure 1.** Geomorphological sketch: coastal area of Ionian Sea



**Figure 2.** Gjeophysic-Sedimentologic section: Velipoja region (Longitudinal section).



**Figure 3.** Geophysic-sedimentologic longitudinal section (Borsh region).

The first cycle of sedimentation formed during the Pleistocene is represented by intercalations of gravel-sand (alluvial fan) facies and marine clay ones. The second cycle formed during Holocene is represented mainly by intercalation of gravelly-sand, sand, sandy-silt, clay, peaty-clay and clayey-peat facies, formed in deltaic, river, lagoon and swamp, and littoral environments.

## B. Geo-Environmental Units Zoning of Albania coast 1:200,000 Scale (Figs 4,5)

Because the separation of the coastal areas in “units” for management purposes is a necessity of many countries with coastal zones, based on the

study of the basic elements of the natural ecosystems and related criteria, the genetical zoning of the coastal area of Albania, at a scale of 1:200,000 has been accomplished. The genetical zoning accomplished for this coastal area has distinguished 20 geoenvironmental units (Durmishi 2005) which constitute 20 % of the total area of Albania.

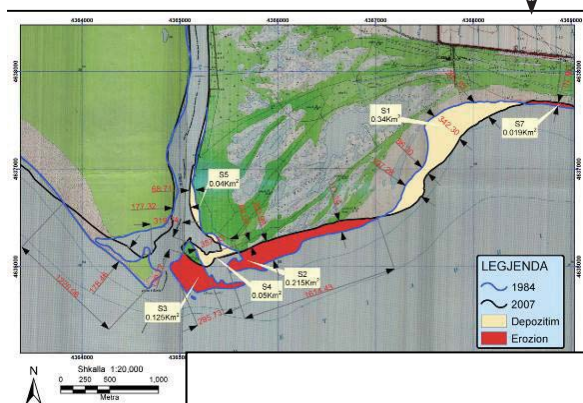
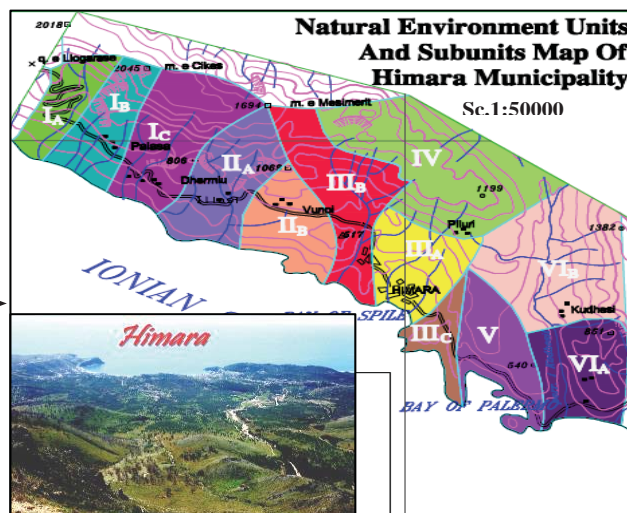
B. The dynamic change of shoreline of the Albanian coastal zone (Fig. 6). Interpretations of the dynamics of shoreline movement have been accomplished by comparing different maps made during the period 1937-1944-1950-1974-1985-1990, orthophotos of the year 2007 and field measurements and monitoring of the separated sectors during the years 2002-2012 (Fig. 6 a,b).



**Figure 4.** Geoenvironmental unit of Velipoja. Sc. 1:200,000

**Figure 5.** Natural Environments Unit and Subunit map of Himara Municipality.

**Figure 6.** (A,B) Shore line dynamics of the Buna river delta and Velipoja coastline.



In total, for the coastal area of the sandy littoral of the Adriatic Sea, the following areas with critical erosion are identified:

- Karpen – Qerret – Mali i Robit – Golem; the right flank of the Erzeni river mouth; Rushkulli – Hamallaj; Mouth of Buna River (the Franz Joseph Island has been eroded); Velipoje – Vilun – Rrjolle; South of Shengjini beach up to the south of Tale beach; the old mouth of Semani river and Semani beach; the present mouth up to south of the old mouth of Vjosa river; Cap of Triporti – old beach of Vlora – Skela. In total, the abovementioned sectors compose some 80-100 km length or about 28 % of the Adriatic sandy coastline, while the shoreline consisting of rock formations (Curila - Porto Romano – Kepi i Palit, Shen Pjetri – Kepi i Rodonit – Ishem, Kepi i Lagjit to Karpen, the critical erosion (erosion – slope sliding) represents a length of 33-35 km or some 14 % of the area.

## Conclusion

The numerous phenomena of the geological, morphological, geomorphological, sedimentological, neotectonic, oceanographic, movements of the

shoreline, relative raisings of the global sea level, the division of the coastal areas in “units” and “sub-units” are important factors to be integrated in the strategy of Integrated Coastal Zone Management (ICZM) of Albania.

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## PYROCLASTIC FLYSCH DEPOSITS (JURASSIC-CRETACEOUS TRANSITION) OF THE UKRAINIAN CARPATHIANS

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### Abstract

Pyroclastic flysch is very rare example among known world-wide turbiditic system of different age. Contrary to intercalations of thin tuffitic layers, which are popular in several flysch deposits, huge amount of pyroclastic material necessary to origin of pyroclastic turbidities indicates strong volcanic activity in source area and their proximity. The Outer Flysch Carpathians of the northernmost part of this arc is one of the biggest belt of stack of flysch nappes in Europe which occupied large part of central-European countries. This belt is almost exclusively constructed by siliciclastic flysch-type rocks represented by different kind of thin-, medium- and thick-bedded sandstones intercalated by conglomerates and shales. The ratio between such type of lithology constitutes different flysch sequences which correspond paleofacially to proximal and/or distal turbiditic system. In the Carpathians however, extremely sporadic are pyroclastic turbidites which are concentrated within Transcarpathian Ukrainian part of this flysch belt and occur in the Ukrainian-Romanian transborder zone (so-called Kaminnyi Potik Unit). In the frontal part of the Marmarosh Crystalline Massif of the Ukrainian Carpathians, this unit is represented by the Jurassic–Early Cretaceous Chyvchyn (up to 1000 m thickness) and Kaminnyi Potik (200 m) formations. This unit is composed by dark, thin-bedded limestones, black shales, sandstones and conglomerates containing latest Jurassic/earliest Cretaceous effusives of the basic type (including basaltic pillow lavas) and pyroclastic turbidites, which pass upward into thick-bedded psammites (thickness about 400 m). In Ukraine, the best places for study of this unit occur both in the Rahiv city vicinity (Kaminnyi stream – stratotype of the Kaminnyi Potik Unit) and on the Chyvchyn Mountain, the highest peak of the Chyvchynian Mountains. Here, this unit occupies the highest structural position in the flysch nappes, which firstly were investigated and published by polish geologists in XIX century and before II World War (by Hugo Zapalowicz and Zdzislaw Pazdro respectively). The Chyvchyn Mt showed that volcanic-sedimentary complex forms the four small tectonic scales which consist of: (a) thin-

bedded micritic limestones interbedded by coarse/fine-grained calcareous pyroclastic turbidites, (b) calcareous-pyroclastic breccias with blocks of the micritic and organodetritic limestones and basalts within volcanic/tuffitic matrix of submarine debris flows and (c) massive basalts of pillow lava. Such unique flysch-type rocks are usually developed as more or less thin intercalations both of coarse- and fine-grained calcareous pyroclastic beds within thin-bedded light and dark-gray micritic limestones sometimes with lenses of dark cherts. Sedimentologically is a distal-type of deep-marine lobes of turbiditic fans. On the other hand, more coarse-grained pyroclastic sandstones and fine-grained pyroclastic conglomerates could represent more proximal-type of turbiditic deposits. All these types of rocks have typical flysch-character features including sharp base of beds with clasts of allochthonous materials, fractionation of grains, cross-bedding ripplemark-type lamination and increase of pelagic character of the topmost part of beds (up to micritic limestones). The most proximal character has chaotic calcareous-pyroclastic breccia with blocks of micritic and organodetritic limestones and basalts (even as pillow lava fragments) which occur within volcanic/tuffitic matrix and represent most probably submarine debris flows. In our opinion, this facies has continued transition to proximal flysch-type facies in the same basin on the one side, and to flow of massive basaltic pillow lavas on the other side, which often co-occur with these debris flows. Full characteristic sedimentological structures (according to Bouma sequence) typical both for proximal and distal turbiditic fans of deep-marine lobes were observed. These rocks indicate strong volcanic activity in source area and their surroundings and could be one of the perfect arguments for better understanding of geodynamic history of the Carpathian basins in the northernmost part of the western Tethys Ocean. This volcanogenic-flysch-type sequences have been formed during the transition Jurassic/Cretaceous time in the Outer Dacide-Severinide part of the Carpathian basins.

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## SYNSEDIMENTARY-FAULT-CONTROLLED DOLOMITIZATION OF TRIASSIC BASINAL DEPOSITS, HUNGARY

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### Abstract

In the course of the spreading stage of the Neotethys Ocean, tectonically controlled extensional basins were developed near the margin of carbonate platform during the Carnian. The studied Upper Triassic successions are typified by cherty dolomite in the lower part and by toe-of-slope and basinal cherty limestone, in the upper part. Based on the results of petrographic, geochemical and fluid inclusion analyses, three dolomite types were distinguished: (1) microcrystalline to finely crystalline dolomite which have preserved microbial fabrics; (2) finely to medium crystalline dolomite which shows breccia or massive fabric or appears in partially dolomitized limestone; and (3) medium to coarsely crystalline baroque dolomite, which occurs as both massive replacement and fracture and breccia-related cement.

A specific unit of the underlying Middle Triassic dolomite formation mainly consists of medium and coarse-sized baroque crystals and exhibits multiphase breccia fabric. The formation of all these dolomite types is interpreted as being related to fluid expelled along synsedimentary faults. Pervasive dolomitization occurred within and near the fault breccia zone in the lower part of the basinal succession. Permeable beds and intervals channelled the fluid from the vicinity of fault upward and toward the basin margin where the fluid was capable of partial dolomitization. Thermal gradient is considered as a potential driving force for fluid flow. The fluid inclusion data obtained from the baroque dolomite cement compared to vitrinite reflectance and maturation data of organic matter suggest that the dolomitizing fluid was likely hydrothermal with respect to ambient host formation.

## CLAY MINERAL COMPOSITION AND SEDIMENT PROVENANCE OF HUKSAN MUD IN THE YELLOW SEA

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### Abstract

Huksan Mud (HSM, named for Huksan Island) Southeastern Yellow Sea Mud (SEYSM) is one of main mudbelt deposits located in the Yellow Sea, which is a typical epicontinental shelf located between Chinese mainland and Korean Peninsula. Huksan Mud or Southeastern Yellow Sea Mud is developed parallel to the southwestern coast of Korea with 20-50 km width and longer than 200 km length. The ultimate sources and budgets of SEYSM are still debated between two ideas; (1) The muds largely originated from Korean rivers and (2) Northern and southern parts of SEYSM have different in several respects, and have different source areas.

To clarify the origin of fine-grained sediments in HSM, we used relative clay mineral compositions based on semi-quantitative X-ray diffraction analysis. We used 52 marine surface sediments and 29 core sediments from HSM collected by KIGAM (Korea Institute of Geoscience and Mineral Resources) and 33 river surface sediments inflowed to Yellow Sea.

The clay-mineral assemblage in the surface sediments is composed of illite (56~69 %), chlorite (12~21 %), kaolinite (8~14 %), and smectite (3~23 %), in decreasing order. Smectite and illite content show negative correlations. Clay mineralogy of surface sediments in HSM is very similar to that of Korean rivers, therefore, we can estimate that the fine sediments in HSM are almost originated by Korean rivers. In the core sediments are always present illite, chlorite, kaolinite, and smectite in decreasing order. Ratio smectite:illite is decreasing with depth in P02 core sediments, however increasing in P07 and P10 core sediments. That ratio shows a relatively constant content and low value for middle depth area in P14 core sediments.

## TOARCIAN-AALENIAN SYNSEDIMENTARY TECTONIC EVENT OF THE WESTERN CARPATHIANS (PIENINY KLIPPEN BELT AND TATRA MOUNTAINS; UKRAINE, SLOVAKIA AND POLAND) – RIFT-RELATED EPISODE IN THE NORTHERNMOST PART OF THE WESTERN TETHYS

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### Abstract

During the whole Mesozoic evolution of the northernmost part of the Western Tethys, several tectonic events took place which resulted in different kind of sedimentary records in the Western Carpathians. Good evidences of such events occur in the Pieniny Klippen Belt in Ukraine (e.g. Priborzhavskoye quarry) in eastern Slovakia (e.g. Benatina quarry) and in the Tatra Mountains, in Poland (mainly Lower Subtatric-Krizna nappe) as well. One of such tectono-sedimentary events has been connected with Toarcian-Aalenian episode of rift-related movements. In the Ukrainian part of the Pieniny Klippen Belt, the oldest Jurassic rocks consist of different type of clastic sediments of widespread Alpine *Gresten*-like facies with spiriferinid brachiopods and grypheids, as typical Early Sinemurian benthic fauna of this facies. Overlying beds are represented by spotty limestones and marls of *Fleckenkalk/Fleckenmergel*-type facies of oxygen-depleted environments (Sinemurian-Pliensbachian) (almost 30 m in thickness). Still younger are condensed limestones (Uppermost Pliensbachian-Aalenian) with several omission surfaces, stromatolites, ferro-manganese crusts and oncoids, and iron-rich ooids in some places, and small neptunian dykes as well. These features indicate the reduced sedimentation rate and this very thin condensed limestone unit (maximum to 25 cm) indicates an important change in sedimentary regimes after thick sequence of pelagic limestones and marls. All discussed lithological units have perfect biostratigraphical control based on rich ammonite faunas.

The facies differentiation in Toarcian-Aalenian

time could reflect an episode of initial extensional, rift-related regime and desintegration and/or transformation of the original basin. Episode of condensation could be correlated with uplift effect of tilted blocks originated during first step of the rifting process. In the same time, in the Tatra Mountains condensed-type limestones full of large ferruginous oncoids and ferruginous-manganese crusts of the Toarcian age well dated by ammonites occurred. This unit is underlain by *Fleckenmergel/Fleckenkalk*-type spotty marls and limestones with spiculites (wackstones/packstones type). The Aalenian deposits are missing here, the most probably due to rifting uplift and non deposition effect. In the eastern part of the same basin, (Krizna) in the Tatra Mts more basal facies (*Fleckenmergel/Fleckenkalk*-type with radiolarites) were dominated, as equivalent of the Toarcian condensed deposits. On the other hand, the Aalenian is represented by black, marly shales with sponge spicules. Some calcareous turbidite-type intercalations occur in this facies due to downslope transport from shallower zones. In the Tatra Mts, similarly as in the Pieniny Klippen Belt (Ukrainian and eastern Slovakian part), the big contrast between pelagic sedimentation of *Fleckenkalk/Fleckenmergel*-type facies and the overlying condensed deposits resulted from the isochronous rift-related movements, known as the Devin rifting phase, in the local Carpathian nomenclature. In both cases the submarine swells originated in independent basins, but generally in the same northernmost part of the western Tethys realm and its passive margin under rift-related control.



## SEISMOGENIC SOFT SEDIMENT DEFORMATION STRUCTURES IN THE UPPER OLENEKIAN–ANISIAN SUCCESSION FROM THE TATRA MTS. (SOUTHERN POLAND)

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### Abstract

Soft sediment deformation structures (SSDS) were described in the Upper Olenekian–Anisian carbonate rocks from the Polish Tatra Mountains (Western Carpathians). The sediments were accumulated on a carbonate ramp developed in Fatricum and Tatricum domains (palinspastic units). In Triassic time they were located in the northern part of the Central Carpathian Basin. These domains correspond to latitudinally arranged Sub-Tatric (Križna) and High-Tatric tectonic units, respectively. Two complexes containing horizons with SSDS were recognized. The first one was found in the Upper Olenekian interbedded dolostones, limestones and calcareous mudshales of the Križna nappe, whereas the second one within Anisian interbedded limestones and dolostones of the Giewont nappe (uppermost nappe of the High-Tatric Unit). The Upper Olenekian complex comprising levels with SSDS is approximately 200 cm in thick and its lateral extent reaches ca 250 m. The following structures can be observed in it: recumbent folds, faults, fractures of sediments and breccias occurring within the lower (about 100 cm thick), dolomite part of the complex as well as faults and breccias passing upward into homogenized sediments in the upper, limestone part of the complex (also appx. 100 cm thick). Anisian complex containing levels with SSDS in the western part of Giewont nappe is cca 60 cm in thick. It is composed of several levels of calcilutites with sigmoidal structures (2.5 to 25 cm in thick) sandwiched between limestone strata (commonly laminated) devoid of such deformations. However, small, synsedimentary faults (throw up to 3 cm) are developed in some laminated limestones.

Although the quality of outcrops do not allow to investigate beds with sigmoidal structures on a long distance, they can be observed in a few outcrops, away from each other, up to several kilometers. Described horizons with sigmoidal structures can be correlated with sigmoidally deformed fine-grained limestone bed (about 10 cm in thick), which occurs 6 km to the east (eastern part of Giewont nappe) in the same stratigraphic position. Both complexes comprising SSDS described above, meet the most of criteria proposed for deformations, which were seismically induced. These are as follows: (I) deformations might be traced or correlated over relatively large area, (II) their top and bottom are bounded by undisturbed beds, (III) they are vertically repeated (IV) they are similar to structures described from certain earthquake-affected layers. Moreover, there is lack of indications for any other causal mechanisms (eg. rapid sediment loading, wave action, flood surges) which can be deduced from sedimentological features and sedimentary environment of described sediments. Establishing of some concrete active seismic fault zone, being the epicentre of earthquakes, which resulted in formation of structures described above is difficult, due to later tectonic movements during Alpine orogeny, which largely masked the Triassic tectonic pattern. Nevertheless, during Late Olenekian and Anisian time, investigated area was a seismically active region. Seismic-induced deformation structures in Lower and Middle Triassic were also reported from the other parts of the Central Western Carpathian region. Seismic activity of that area was closely linked with tectonic movements induced by fragmentation of the Central Carpathian Basin related to the initial stage of development of the western Tethys.

## CENOMANIAN-TURONIAN CARBONATE BLACK SHALES WEST OF THE CRIMEA PENINSULA, UKRAINE, AS A PROSPECTIVE SHALE OIL AND GAS PLAY

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### Abstract

To known shale gas in Ukraine which now are under active evaluation, it would worth to add another prospective area in the Southern region located within the petroleum-prone basin characterized by this date with minor discoveries of conventional hydrocarbons. The geological setting of the formation reveals direct analogies to the Eagle Ford–Woodbine petroleum system and corresponds to the OAE-2 anoxic global event.

This potential play for unconventional hydrocarbons occupies the western part of Crimean Peninsula and stratigraphically belongs to upper part of the Belogorsk suite, topmost part of Cenomanian stage, deposited in rather deepwater euxinic environment. Likewise the Southern Texas, in the Mountainous Crimea it is observed a gentle unconformities related to sub-phases of the Subhercynian tectonism. The history of volcanic activity in the region resembles the one from the South Texas as well. The prospective area is totaled to ca. 2100 sq.km embracing onshore part of the Karkinit-North Crimean graben (Odessa-Dzhankoy paleo-rift) within a 20-km wide belt stretching WSW-ENE from Cape Tarkhankut towards Dzhankoy town.

Net thickness of the marly shale interval (1-3 % TOC in average, 3.84 % max) varies from 15 to 30 m within the transition series of 100 m thick mainly composed by carbonate rocks (marly shales, marls, and limestones). Higher thicknesses of this carbonate black shales with very characteristic gamma-ray log response signature are revealed to the northwest under the waters of the Karkinit Bay and Gulf of Odessa. A lateral analog of the rocks is outcropped to the south, near Bakhchisaray town in the Crimean Mountains where TOC in the condensed Aksu-Dere section (0.7 m) of the black shales with high REE content reaches as much as 7.2 %. Rather intense intra-formation fracturing is characteristic of that interval demonstrating low permeability and matrix porosity above 3 %.

The depth to target interval within the potential play is 1700-3000 m. The rocks are occurred within MK<sub>1</sub>-MK<sub>2</sub> thermal maturity zone of main hydrocarbon generation (oil window) and characterized non-reservoir and semi-reservoir properties. There is several small and sub-commercial gas and oil field discovered in the terrigenous (silts and volcanoclastic sandstones) varieties of the Cenomanian-Turonian transition sequence and fractured Senonian carbonate formations (Austin Chalk analog) in the region, plus frequent oil and gas manifestations while drilling through the shales are reported (32 wells in total). Shale gas resources of the play in place are estimated as much as 1 Tcm, excluding gas condensate.

The presence of the OAE-2 carbonate black shales south of the Kalamit swell beyond the West Black sea sub-basin paleoshelf break is rather questionable issue yet, however, if so, this could add another source rock level should be taken into account while evaluating hydrocarbon potential of the whole mega-basin.

The territory of this potential shale gas play is a steppe terrain characterized by rather dry temperate continental climate, moderate agriculture and relatively low population density. Though the area lacks freshwater resources there is a possibility to use marine water of the Karkinit Bay for fracking.

The preliminary feasibility study of the exploration program for the prospective area has revealed rather high geological risks due to ambiguity of the available data interpretation so further investigation of the issue should be done.

## GEOTECTONIC SIGNIFICANCE OF THE LATEST JURASSIC–EARLIEST CRETACEOUS VOLCANOGENIC UNITS OF THE CHYVCHYNIAN MOUNTAINS (UKRAINE CARPATHIANS)

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### Abstract

The Ukrainian Carpathians form a connecting link between the West and East Carpathians, but the structure of this connection is disputable. Accumulation of the ancient accretionary prism, which turned into the Flysch Carpathian nappes – was caused by the subduction of the Carpathian Flysch Basin basement beneath both the ALCAPA and Tisza-Dacia terranes. Outer Carpathian Flysch is divided into inner and outer Flysch nappes. Inner Flysch Nappes of the Outer Western Carpathians (Fore-ALCAPA Magura-Dukla prism) were built in the foreland of the ALCAPA terrane during the Paleogene times. Inner Flysch Nappes of the Outer Eastern Carpathians (Fore-Marmarosh flysch prism) was formed in the front of Tisza-Dacia terrane during the Cretaceous-Paleogene times. The Kaminnyyi Potik, Rakhiv and Burkut suture units (Transcarpathian Ukraine) were developed in the frontal part of the Marmarosh basement nappes (Crystalline Massif) of the Central East Carpathians and correspond to the Outer Dacides-Severinides. The Kaminnyyi Potik Unit forms most probably the prolongation of the Black Flysch Unit of the Romanian Carpathians. Volcano-sedimentary complex of the Chyvchynian Mountains is represented by (i) basalts and volcanic breccias of the lower(?) part of the so-called Chyvchyn Formation, (ii) upper(?) part of the Chyvchyn Formation represented by debris-flow sedimentary and volcano-sedimentary breccias with blocks of the limestones, basalts, small fragments of red radiolarites within volcanic/tuffitic matrix and coral limestones with basalt fragments and pyroclastic intercalations, and (iii) the Kaminnyyi Potik Formation represented by thin-bedded micritic limestones with cherts interbedded by coarse/fine-grained calcareous pyroclastic turbidites (flysch). It is assumed that these three rock associations are genetically related and they can be attributed to the Kaminnyyi Potik Unit (Nappe). These associations probably were formed in the Late Jurassic–Early Cretaceous times generating several different parts of the Outer Dacides-Severinides Carpathian basin.

They can be considered as a facies. These facies have continual transition from very proximal type of debris flows through flysch-type facies of coarse- and fine-grained pyroclastic turbidites up to flow of massive basaltic pillow lavas on the other side in our reconstruction. The present stage of investigations provide arguments that the volcanogenic formation of the Chyvchynian Mts was formed on the presumable oceanic crust and can be attributed to the Fore-Marmarosh suture zone (?Outer Dacides-Severinides). The trace of the Jurassic–Cretaceous (sub)oceanic basin (part of the embryonic Outer Carpathian Basin) existed between the Tisza-Dacia terrane and Eurasia. From wider geodynamical point of view, mentioned above volcanogenic-sedimentary units is small part of the Severin-Moldavidic Basin developed within the North European Platform as rift and/or back-arc basin. Its basement is represented by the attenuated crust of the North European plate with perhaps incipient oceanic fragments. The sedimentary cover is represented by several sequences of Late Jurassic–Early Miocene age belonging recently to various tectonic units in Poland, Czech Republic and Ukraine Carpathians. The Silesian Ridge is an uplifted area, originally part of the North European platform separating the Magura and the Severin-Moldavidic basins during Jurassic–Early Cretaceous times. It is known only from exotics and olistoliths occurring within the various allochthonous units of the Outer Carpathians. The shallow-water marine sedimentation prevailed on the Silesian Ridge during Late Jurassic and the earliest Cretaceous times. The carbonate material was transported from such uplifted zones toward the Severin-Moldavidic Basin during this time. Generally, it was wider effect of the Pangea break-up and origin of the Alpine Tethys, which constitutes important paleogeographic elements of the future Outer Carpathians, developed as an oceanic basin during Jurassic–Early Cretaceous.

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## MAJOR AND TRACE ELEMENT GEOCHEMICAL VARIATIONS OF DEEP-SEA SEDIMENTS FROM EASTERN CLARION-CLIPPERTON ZONE (NE PACIFIC)

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### Abstract

In the present study we have determined major and trace elements in the subsurface deep-sea sediments from three stations from eastern Clarion-Clipperton zone of NE Pacific. Our data are similar to those for pelagic clays, but are lower than most of those reported for CCZ and metalliferous sediments. Ba is the only one element that shows elevated values. Down the core profiles, in two of the stations sediments show some common peculiarities as clear enrichment of Cu, Zn and Pb in the surface samples (depth of 0-3 cm). As for the third station, clear maximum content for these elements has been acquired in samples at 3-5 cm depth (in the middle of “the geochemically active layer”). Based on some element ratios we suggest that the source rocks are rather intermediate than felsic in composition and kaolinite as prevailing main clay mineral and indicator for continental source rocks. Geochemical features of the studied sediments imply a deposition at well oxygenated waters. The geochemical associations outlined based on correlation coefficients are typical for marine sediments and confirm the polygenic genesis of the sediments

**Key words:** major and trace elements, deep-sea sediments, eastern CCZ

### Introduction

Mineralogy and geochemistry of sediments in the Fe-Mn ore field of Clarion-Clipperton Zone (CCZ) have been studied sporadically, mainly as a subject of scientific interest. Recent interest has arisen after publishing the work on REE and Y distribution in deep-sea mud in the Pacific Ocean (Kato et al. 2011) suggesting that deep-sea “mud constitutes a highly promising huge resource” for rare-earth elements. So, we have been provoked to study the major and trace elements signatures for deep-sea subsurface sediments. We have published

our preliminary data on bulk mineralogy, REE and Y geochemistry and metalliferous characteristics of the deep-sea sediments (Milakovska et al. 2013). The mineralogical and geochemical features suggest that the sediments have complex genetical record reflected on REE distribution. We submit now data on major and trace element characteristics in the sediments and interpret them in terms of tectonic and morphological position and as a part of the dynamic system of coexisting sediments, Fe-Mn micronodules and nodules.

### Geological setting

The eastern CCZ (to the east of 125° W) is a part of Paleo East Pacific Rise which main bottom morphologic element is a system of linear ridges and valleys that are approximately perpendicular to the bordering fractures. The bottom sediments in the area comprise end members (carbonates, red-brown clays, siliceous sediments) and mixtures of them (Kotlinski et al. 2009). The east-west increase in water depth favors siliceous sediments persistence, since carbonate minerals become unstable with hydrostatic pressure increase. Siliceous-argillaceous oozes/clays deposited in the area studied belong to the Quaternary level of Clipperton formation (Cl<sub>IV</sub>). The sediment profile reveals a distinct top layer (geochemically active layer, ca. 15 cm of thickness) of siliceous argillaceous ooze which down the profile, grades into lighter-colored sediments with a mottled appearance.

### Sampling and analytics

Sixteen samples studied were collected from three (2267, 3001 and 3017) stations during InterOceanmetal (IOM) 2009 cruise with 0.25 m<sup>2</sup> box corer equipped with SONY DSC-V1 digital camera. Sampling includes the following core intervals 0-3, 3-5, 5-10, 10-15, and 15-20 cm. In the laboratory samples were imaged, dried at 30 °C and split. Major and trace elements content was



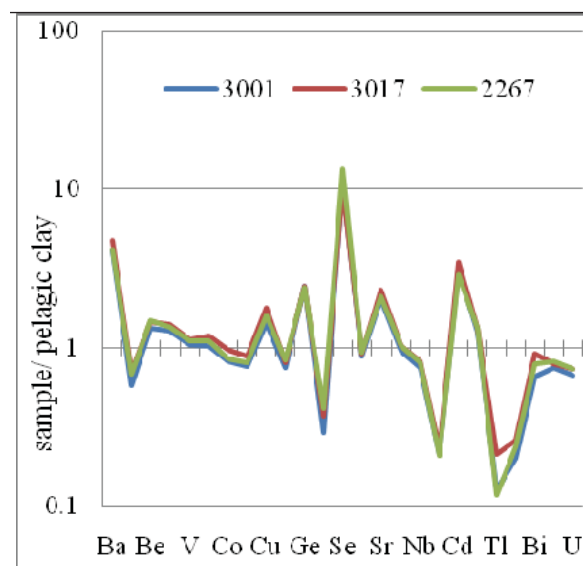
determined by ICP-OES and LA-ICP-MS.

## Results and Discussion

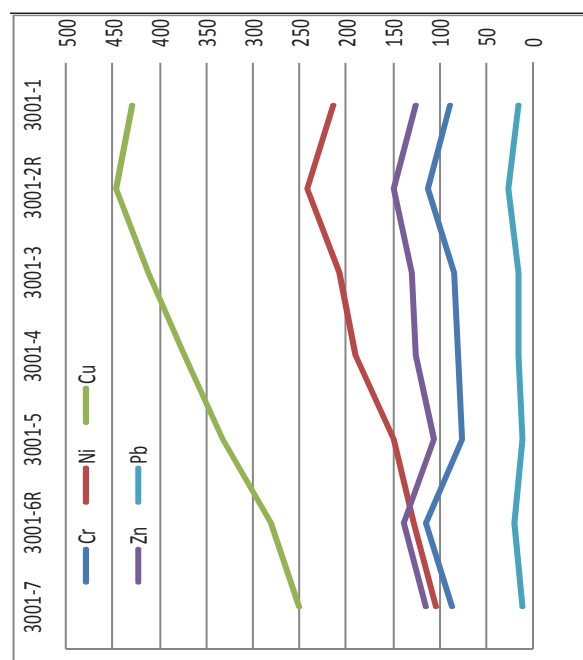
**Sedimentological description.** Stations 2267 and 3017 have been located within terraces at a depth of 4369 and 4419 m, and station 3001 - on the bottom of a depression at a depth of 4457 m. On the bottom surface, traces of animal activities (station 2267) and different nodule distribution (patchy or random) and quantity (ca. 18-24 %) have been observed. The topmost layer (thickness of 7-8 to 12 cm) of sediment core consists of brown homogenous clay of massive structure and a consistence changing from liquid-plastic to soft-plastic, i.e. this layer is the “geochemically active layer” as its chemical, physical and geotechnical parameters are substantially different from those of the underlying sediments. The quantity of micronodules varies from scarce (station 3017) to remarkable and up to 0.8 mm in size (station 2276). The contact with the underlying layer is gradual through increasing mottle presence and pale coloration. This layer (7-20 cm) is brownish-yellow in color, mottled in structure, soft-plastic in consistence within the interval of 7-15 cm grading into plastic in the interval of 15-20 cm. The patches are pale brown, 0.5 to 2 cm in size, of various form and orientation (frequently rounded isometric or elongate), well to poorly distinguishable among the sediment matrix; patch to matrix ratio is 2:3. Traces of sediment-feeding organisms are abundant in this layer for stations 2267 and 3017, and of bioturbation - for station 2267.

**Major and trace elements characteristics.** The average major and trace element contents in each station were normalized to those for pelagic clays (Li and Schoonmaker 2007) (Fig. 1A,B). The pelagic clays have been considered as being representative for the average composition of deep-sea sediments.

Mean values for major elements in sediments studied, are in general rather close to those for pelagic clays (Li and Schoonmaker 2007), Pacific red clays (Bischoff et al. 1979 according to Dekov et al. 2010) and deep-sea sediments of the North Pacific (Calvert and Price 1977) and are lower than those for CCZ reported by Stoffers et al. (1981). The low values could be explained by bioturbation processes and lack of organic matter on one hand, and Fe-Mn nodules and micronodules formation that gain a big portion of the elements on other



**Figure 1.** Pelagic clays normalized patterns of trace elements in the sediments studied from CCZ.



**Figure 2.** Some trace elements distribution down the core of station 3001.

hand. One exception is Ba - its values are always higher than in the reference sediments. Our data for the moment is not sufficient to argue which of the possible materials that could contribute Ba in the marine sediments (barite, Fe-Mn (hydr)oxides, carbonates and organic matter) plays a major role in our case. Clayey sediments studied show high Si content varying in a short interval that is consistent with the presence of biogenous opal-siliceous debris. Aluminum shows low concentration. The amount of aluminosilicate impurities can be estimated from Al content, since Al is not

associated to a large extent with the (hyd)oxide fraction of pelagic clays, so we can assume faint terrigenous input. Iron content in the sediments is close to or lower than those for red clays and CCZ sediments and much lower than those for pelagic clays. Manganese values are higher than those for red clays and much lower than those for pelagic clays and CCZ sediments. There are not any clear and strong differences between the major elements values among the stations although they are remote and from morphologically different areas. The lowest concentrations of major elements are measured in samples from station 3001. The major elements distribution down the sediment core does not show any clear variations. Iron and Mn show tendency slight decrease in depth. Aluminum content stays almost constant down the cores. For cores from stations 3017 and 2267 silicon values have similar trends of distribution, and they are different for core for station 3001.

Mean values for Co, Ni, Zn, Mo and Pb are close to or lower than those for pelagic and red clays and CCZ sediments, are very slightly elevated compared to those for V and Cr (especially for samples from stations 3017 and 2267). Strontium and Cu show values higher than those in red and pelagic clays, but lower than those in CCZ sediments. Chromium behavior is close to those of Si - similar for samples from stations 3017 and 2267, and opposite - for station 3001. Bismuth, Ge and Pb follow trends of Al and Fe distribution and one can suggest an isomorphic substitution in aluminosilicates and/or a sorbed form on Fe hydroxides surfaces. Down the core profile, barium, Ni, Co, Cu, and Pb show clear tendency of depletion. Manganese, Zn and V do not show any clear trends of distribution down the core. It is worth mentioning that Cu, Zn, Pb, Cr, Ni (Fig. 2) and Ba are enriched in samples at 3-5 cm depth interval (in the middle of "the geochemically active layer") from station 3001 (positioned on the bottom of a depression) for. As for the other stations, clear maximum content for Cu, Zn and Pb has been measured for the surface samples (depth of 0-3 cm).

Provenance and paleoredox conditions. The values for  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio for samples studied vary between 4.31 and 5.32. These values are much higher than the values for pure montmorillonite and kaolinite, so we can assume that they indicate kaolinite as the prevailing clay mineral and detrital (continental) source rocks. The range of

values for  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratio is 21.39-22.78. This ratio is informative for source rock composition. We suggest a source rock composition rather close to the intermediate rocks than to the felsic igneous rocks (Hayashi et al. 1997) for the studied samples. The values for characteristic ratios –  $\text{Fe}/(\text{Al}+\text{Fe}+\text{Mn})$ ,  $(\text{Fe}+\text{Mn})/\text{Ti}$ ,  $\text{Al}/(\text{Al}+\text{Fe}+\text{Mn})$  and  $(\text{Fe}+\text{Mn})/\text{Al}$  - are lower than those required for metalliferous sediments, although on the triangular diagram of Bonatti et al. (1972). They fall in the field of hydrothermal metalliferous sediments.

Ratios of some trace elements (e.g. Ni/Co, V/Cr, U/Th) have been used as paleoredox indicators (Jones and Manning 1994). In sediments studied from eastern CCZ these values are lower than 5, 2 and 1.25 respectively and suggest a well oxygenated environment of sediment deposition.

Geochemical associations based on correlation coefficients. On the correlation matrices we have chosen the values higher than 0.75 as statistically significant and will discuss some of the most characteristic of them. Aluminum shows high values of correlation to Ti, Rb, Cs, Pb and U, that are typical for aluminosilicates and clays, especially. Silicon does not show any significant correlations probably because of both biogenic and lithogenic main types of presence. Manganese closely correlates to Co, Ni and Cu on one hand, and to Ba and P - on the other hand. These relations are most probably connected to Mn (hydr)oxide precipitates mainly and to an authigenic phosphate (Dubinin 2004) and/or barite phase. Iron correlates mainly to Ti and Cu as well as to Ca, P, Ba and Sr. The first relation is probably connected to co-precipitation/adsorption on Fe (hydr)oxide phases, and the second one to a carbonate-fluor-apatite phase and/or barite. The high degree of correlation between the P and Fe contents of Fe-Mn nodules has been ascribed to the adsorption of P by hydrous ferric oxides or to the formation of a ferric phosphate phase and probably could be applied to the hosting sediments. Another specific geochemical association outlined by the significant values of correlation is Ca to Sr, Ba, P, V, Co, Ni, Cu that could be related most probably to authigenic carbonate-fluor-phosphate (apatite) and barite. As a whole, we can conclude that most of trace elements determined have very "dispersed" correlations - some of them are lithogenic/terrigenous, some - biogenic, others - authigenic, that is another conclusion to the polygenic origin of the deep-sea sediments studied.

## Conclusions

The following main conclusions could be drawn as a signature for the major and trace elements in the sediments from eastern Clarion-Clipperton Zone:

- deep-sea subsurface sediments have major and trace elements average content that does not exceed the average for pelagic clays and is lower than most of those reported for some elements from metalliferous and CCZ sediments;
- down the core sediments show some common peculiarities, despite the processes of bioturbation - clear enrichment for samples at 3-5 cm depth (in the middle of "the geochemically active layer") for station 3001 for Cu, Zn, Pb, Cr, Ni (Fig. 2) and Ba. As for the other stations, clear maximum content for Cu, Zn and Pb has been acquired for the surface samples (depth of 0-3 cm);
- the values for some element ratios are geochemically characteristic for rather intermediate than felsic source rocks and kaolinite as prevailing main clay mineral and indicator for continental source rocks; the sediments show geochemical features of deposition at well oxygenated waters;
- the geochemical associations outlined based on the correlations coefficients are typical for marine sediments and confirm the polygenic genesis of the sediments.

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## SEDIMENTOLOGICAL EVALUATION OF QUATERNARY AND RECENT DEPOSITS ON GEOENVIRONMENTAL UNIT OF BUTRINTI REGION

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### Abstract

Butrinti region is located on the western part of the Ionian zone, SW of Albania. The Quaternary deposits are formed in the typical graben depression where an important role on its geomorphology, besides the neotectonic movements, belongs to the phenomenon of diapirism. From geological point of view, the Butrint graben is composed of Pliocene-Quaternary sediments. Quaternary deposits basement, as well as defining and preparing of geo-electrical maps of deposit thickness. Two regional cycles (mega-sequences) can be clearly identified in all coastal areas. The first cycle of sedimentation formed during the Pleistocene is represented by intercalations of gravel-sand (alluvial fan) facies and marine clays. The second cycle formed during Holocene is mainly represented by intercalations of gravel-sand, sand, sand-silt, clay, peat-clay and clay-peat facies formed on deltaic, river, lagoon marshland and littoral environments

The basic characteristics of Butrinti lagoon water and surface sediments were assessed in June 2004, using in situ (CTD, O<sub>2</sub>) and laboratory (grain size, element geochemistry) methods. The water column was evidently divided in two layers: (a) the upper layer, in which dissolved oxygen ranges from 9 mg/L on the surface to zero at the depth of 7.5-8 m; and (b) the lower layer, in which there was no oxygen. The bottom sediments were clay within the lagoon and muddy sands in Vivari channel.

The maximum concentrations of some heavy

metals in sediments were relatively high (e.g. Cr: 497 ppm, Mn: 3096 ppm, Ni: 308 ppm, Pb: 21.5 ppm, and Zn: 156 ppm) and the combined contamination index values (w) indicated that the environment was slightly polluted. The contamination was probably due to the human activity, such as the enhanced use of fertilizers and pesticides in Vurgu and Vrina plains and the intense mussel cultivation in the Lagoon.

The coastal area of Saranda region, according to genetic division of geo-environmental units of the Albanian Coastal Area of 1:200,000 scale (Durmishi et al. 2005), is composed by three units (total area of 426 km<sup>2</sup>). The geo-environmental sub-units zoning division is crucial in helping urban planners for an sustainable integrated management territory plan and for a control on development of territory avoiding the uncontrolled and isolated initiatives. The division into geo-environmental sub-units and an assessment of natural ecosystem resources of the region is essential element before that urban planning to be start up.



## RECORD OF THE MSC IN PERCHED BASINS (ADRIATIC BASIN), GEODYNAMIC CONSIDERATION AND EROSIONAL CONSEQUENCES.

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The Mediterranean Sea (including the Adriatic basin) is the place of intense controversy concerning the sedimentary dynamics and paleogeographic evolution during the Neogene time, especially during the Messinian salinity crisis (5.96 to 5.33 Ma) (CIESM 2008). Following the various interpretations, this basin was totally disconnected or connected to the deep basins during the Messinian Salinity Crisis (Bache et al. 2012 vs Roveri et al. 2006).

One of our concerns is: What would be the impact on the sedimentary transfers of the presence (or not) of a sill separating these perched basins from the Central Mediterranean basin? What are the influence of the tectonic inheritance and evolution on (1) the paleogeographic evolution and (2) the stratigraphic markers of the messinian crisis?

Several qualitative approaches (seismic, well study from Videpi database and field data) on the sedimentary filling around the Gargano peninsula are used to highlight the tectono-stratigraphic evolution of these basins:

For the Adriatic basin characterization of the upper Miocene and Pliocene-Quaternary units by well and seismic study show a different paleogeographic evolution on either side of the Gargano Peninsula (Central Adriatic). North of this peninsula messinian units show a relatively flat topography marked by regular deposit thickness (reworked Gessoso Solifera fm. (~0.1 stwt) and thin post-crisis Colombacci formation (~0.2 stwt). South of the Gargano peninsula, the tortono-messinian units show a gentle deepening to the South-East associated with the development of a huge turbiditic unit partially linked to the Gessoso Solifera fm. The following Pliocene-quaternary infill would reflect an existing paleo-topography during the Messinian.

On land, mapping Tortono-Messinian to Pliocene deposits also highlights the paleogeographic evolution of the region. A short field trip on both side of the Gargano Peninsula was done in March 2014. At first sight, the Messinian peripheral gypsums have been similarly deposited (1<sup>st</sup> step of the Messinian Salinity Crisis) then eroded (2<sup>nd</sup> step of the Messinian Crisis). We can notice in the southern part that the low presence of primary evaporites is associated with a strong deformation phase before and/or during the deposition of reworked evaporites. North of the Gargano peninsula (Apennine foredeep), the reworked evaporites deposits are followed by the deposition of more than 1.5 km turbidite layers marked on the roof by the clayed-limestone of Colombacci fm., then sealed by blue clays (Argille Azzurre) of the lower Pliocene. South of the peninsula (Apennine wedge-top basin), the reworked evaporites deposits are eroded and sealed by sand to conglomerate formations then blue clayed formation, marking a shallow to proximal paleoenvironment (region Savignano Irpino). The total thickness of the preserved units does not exceed 300 m.

From these first elements, different sediment dynamics on both side of the Gargano peninsula seems to have taken up shortly after the reworked evaporites. These works will be complemented via (1) study of depositional environments (dinocyst analysis) and (2) analysis of drilling along the deformation front of the Apennines belt. Associated with seismic surveys, these studies will help to clarify the paleogeography and subsidence evolution during the messinian and Pliocene-quaternary in this region. From these observations, we will discuss the importance of geodynamic processes on sediment dynamics around the Gargano Peninsula.

## FORMATION MECHANISM OF HALOTURBATION STRUCTURES: EXAMPLES FROM THE UPPER DEVONIAN STIPINAI FM. (MAIN DEVONIAN FIELD, LITHUANIA)

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### Abstract

Calcareous silty arenite from the lower part of the Frasnian Stipinai Formation (Main Devonian Field, northern Lithuania) comprise a wide range of haloturbation structures, which disturbed its primary sedimentary features (e.g. planar lamination and asymmetrical wave-ripple cross lamination). Discussed silty arenite (up to 4 cm thick) is sandwiched between dolomitic marlstones. It is composed of quartz, feldspar and mica grains cemented by poikilitopic calcite. Mentioned haloturbation structures are halite crystal casts as well as sink-hole and dewatering structures. Well-preserved casts of halite crystals (with protuberance up to 6 mm) occur on the lower surface of the bed, while on the upper bedding surface, poorly-preserved casts (with protuberance less than 1 mm) are present. The casts of halite hopper (more than 10 mm wide) occur individually or as intergrows of two or more crystals, while casts of small halite cubes cover densely and evenly whole lower surfaces of the bed. Individual casts show variable morphology and orientation. There are casts of: three crystal faces (type A); one complete face and incomplete three, two or one another faces (type B); only one face (type C); crystal edge or a corner only (type D); one slightly depressed crystal face with elongated corners (pagoda-like halite skeletal crystals; type E), and twinned (two or more) cubic and/or hopper halite crystals (type F). Faces of cubic halite crystal casts are flat, while casts of halite hopper crystals show slightly to deeply stepped cubic faces with steps descending to the centre of the face. The casts are filled with structureless silty arenite. Rare, poorly preserved casts on the upper surface of the bed are visible as cubic shallow depressions or low elevations, all without steps. In cross section perpendicular to bedding planes occur sink-hole structures, developed as funnel-shaped sediment disturbances. Sink-hole structures over

the larger casts affected whole layer thickness and they often compose of two adjacent or partly overlapping funnels. The structures pierce the bed and manifest on the top surface as shallow conical depressions. Halite crystal casts are also related to water-escape structures filled with homogenous arenite. The water-escape structures cause up-wrapping of disrupted lamina sets along the pipe. The discussed cast-bearing bed is relatively coarser-grained and more permeable than under- and overlying sediments. In this bed halite hoppers precipitated from NaCl-over-saturated pore waters, when the sediment remained in the marine phreatic zone. Formation of skeletal hopper crystals take place when supersaturation reaches a critically high point. It resulted in rapid growth of corners and edges of crystals. Such fast crystals growth did not disturb primary sedimentary structures. The subsequent dissolution was caused by the influx of marine water, undersaturated with respect to halite, which resulted in formation of unstable caverns in sediment. The process took place before the sediment cementation. Scale of subsequent deformations depends on the primary size of the halite crystal as well as its location in respect to the lower bed boundary. If the halite hopper grew on the interface of the silty arenite and dolomitic marlstones, more of the overlying sediment is involved in collapsing into space after dissolution of the crystal. Water-escape structures also originated as a consequence of crystal dissolution which caused a disturbance of state of equilibrium between grain framework and pore waters in silty arenite bed. Moulds which formed between the top of silty arenite and overlying cohesive mudstones were filled by local quick sand flows. In that way could originated elevated casts on the upper bedding surface. Haloturbation structures described above originated as the result of syn- or post-dissolution sediment collapse and fluid escaping that disturb primary sedimentary structures.

## FACIES AND MICROFACIES ANALYSIS OF THE UPPER CRETACEOUS (EARLY CAMPANIAN) DEPOSITS FROM THE BORIZANA SECTION, KRUJA ZONE (ALBANIA): PRELIMINARY APPROACH.

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### Abstract

This work presents the preliminary data of the facies and microfacies study of the Upper Cretaceous (Early Campanian) deposits outcropping along Droja valley, close to "Titan" Quarry, from Borizana section (Makareshi structure, Kruja Zone). The Upper Cretaceous Formation, in Makareshi structure mainly consists of limestones, dolomitic limestones and different levels of dolomite intercalations. For the first time in the studied section (from all of scientific studies carried out until now in this area by different authors) the presence of a siliciclastic lithofacies is identified, composed of three main facies: sandstone, and clay. The presence of siliciclastic lithofacies is distinguishable at several levels, overlying hard ground surfaces. Petrographic analysis shows that the sandstone facies essentially contain quartz, a small percentage of micas set in a carbonate mud and iron oxides matrix. The quartz composition of this facies holds great interest for further interpretations regarding source area because Kruja zone is delimited to the east by Krasta-Cukali and to the west by Ionian tectonic zones which during this period have represented basins, respectively. The presence of hard ground surfaces observed in the field is another phenomenon present in this section. These surfaces are often associated with boring organisms, large mineralized zones with iron oxides and tidal channel carbonate deposits. The hard ground characteristics (morphological, mineralogical, sedimentological) may highlight a sedimentological phenomenon like the frequent emersion of the Kruja platform during this period. It indicates also sediments deposition in a platform interior (intertidal to shallow-deep subtidal) environments. Detailed work in the field and in the laboratory revealed that it contains microfacies forming SMF zones and exhibits frequent peloidal and bioclastic packstone/grainstone microfacies that constitute a predominant part in this section. Different types of fauna, observed in the formation, include algae, bivalves, ostracods and benthic

foraminifera (miliolidae).

**Key words:** Upper Cretaceous, carbonate facies, siliciclastic facies, hard ground

### Introduction

The study area is situated in Makareshi structure and is part of Kruja Zone, located in the center of Albania which extends towards south with Gavrovo Zone in Greece and it represents a platform (Korovesi et al. 1999, Heba 2008, etc). In the Makareshi structure, the Santonian-Campanian-Maastrichtian deposits are represented by limestone, dolomitic limestones and thick layered dolomites containing remnants of different organisms. Our study is focused only on Upper Cretaceous (Early Campanian) carbonate succession.

### Materials and Methods

During field work, a systematic sampling as well as simultaneous photography of textures and sedimentary texture has been carried out. A total of 60 rock samples was collected and facies were studied along the layers trend, according to similar characteristics. Based on distinct lithological and textural variations, more than 50 thin sections were prepared from the formation and were studied under a polarized microscope (Nikon Eclipse SQ/POL). The classification of carbonate and siliciclastic followed the nomenclature of Dunham (1962) and Pettijohn et al (1987) respectively. Whereas for the determination of the depositional environments, the Standard Microfacies Types (SMF) and Facies zones classifications, after Flugel (1972) and Wilson (1975), were used.

### Results and Discussion

#### Facies and microfacies analysis.

a- Two are the determined lithofacies groups (Plate I):

1. Carbonate lithofacies group;

## 2. Siliciclastic lithofacies group (limited lithofacies distribution).

### 1. Carbonate lithofacies

Based on characteristic lithology, texture, fossil content, sedimentary structures, color etc, the most important distinguished facies in this section are as follows (Plate I):

- Bioconstructed limestone facies (F3, Heba 2008) (Plate I, Fig. 12);
- Brecciated limestone facies;
- Coquina limestone facies (F2, Heba 2008);
- Dolomite facies (with desiccation cracks figures, ripple marks (F8, Heba 2008) (Plate 1, Figs. 8 and 9);
- Laminated limestone facies (F1, Heba 2008) (Plate 1, Fig.10);
- Limestone with debris of rudists facies (F4, Heba 2008) (Plate 1, Fig.11);
- Tidal channel limestone facies. (Plate 1, Fig.1, 2);

### 1/1- Microfacies analysis.

Six microfacies are recognized in the succession studied (Plate 2,):

- MF-1 Mudstone. (Corresponds to SMF 23, FZ8, Flugel 1972 and Wilson 1975);
- MF-2 Bioclastic wackstone. (Corresponds to SMF 18, FZ8, Flugel 1972 and Wilson 1975);
- MF-3 Non laminated peloidal packstone/ grainstone. (Corresponds to SMF 16, FZ8, Flugel 1972 and Wilson 1975);
- MF-4 Bioclastic grainstone. (Corresponds to SMF 18, FZ8, Flugel 1972 and Wilson 1975);
- MF-5 Bioclastic dolomitic wackstone;
- MF-6 Laminated stromatolitic mudstone. (Corresponds to SMF 20, FZ8, FZ7, Flugel 1972 and Wilson 1975);

### 2. Siliciclastic lithofacies

This facies mainly consist of siliciclastic and other detrital grains which are made up of quartz and reworked carbonate grains. This facies group sometimes exhibit sedimentary structures such as horizontal lamination, and normal graded bedding. The most important facies types are as follows:

- Sandstone facies (Plate I, Figs. 5 and 7a; Plate

II Figs. 2 c,d).

- Calcareous sand facies. (Plate I, Figs. 5 and 7b);
- Clay facies (Plate I, Figs. 5, 7c and 8c);
- Dark blue clay facies with oil (syndimentary) signs (Plate I, Figs. 9e,f,g,h).

### 3. Hard ground surfaces.

Important hard ground surface has been observed in the Borizana section (Plate I, Figs. 1, 2, 3, 4, 5 and 6). Stratigraphers and sedimentologists often use the hard ground as indicators of sedimentary hiatus and transgressive events. Hard ground and their faunas may also represent specific depositional environments like the tidal channels (Wilson et al. 2005). Various features confirming hard ground surfaces in the Borizana section occur as surface having ferruginous pits, spots and films on uneven beds are well visible and bioturbated and burrowed bed, bored by a shallow variety of a trace fossil called Trypanites, burrows filled by secondary yellow colored material forming patchy look.

### Conclusions

The presence of compilation of field and petrographic data achieved until now revealed that the formation was deposited in facies belt 7, 8 (FZ7, FZ8) "restricted and open platform interior" under SMF types 16, 18, 20, 23 according to the facies classification of Wilson (1975).

Siliciclastic facies have been identified for the first time within Upper Cretaceous carbonate platform deposits of the Kruja zone (Albania).

Several hard ground surfaces and tidal channels facies are well exposed in this study area.

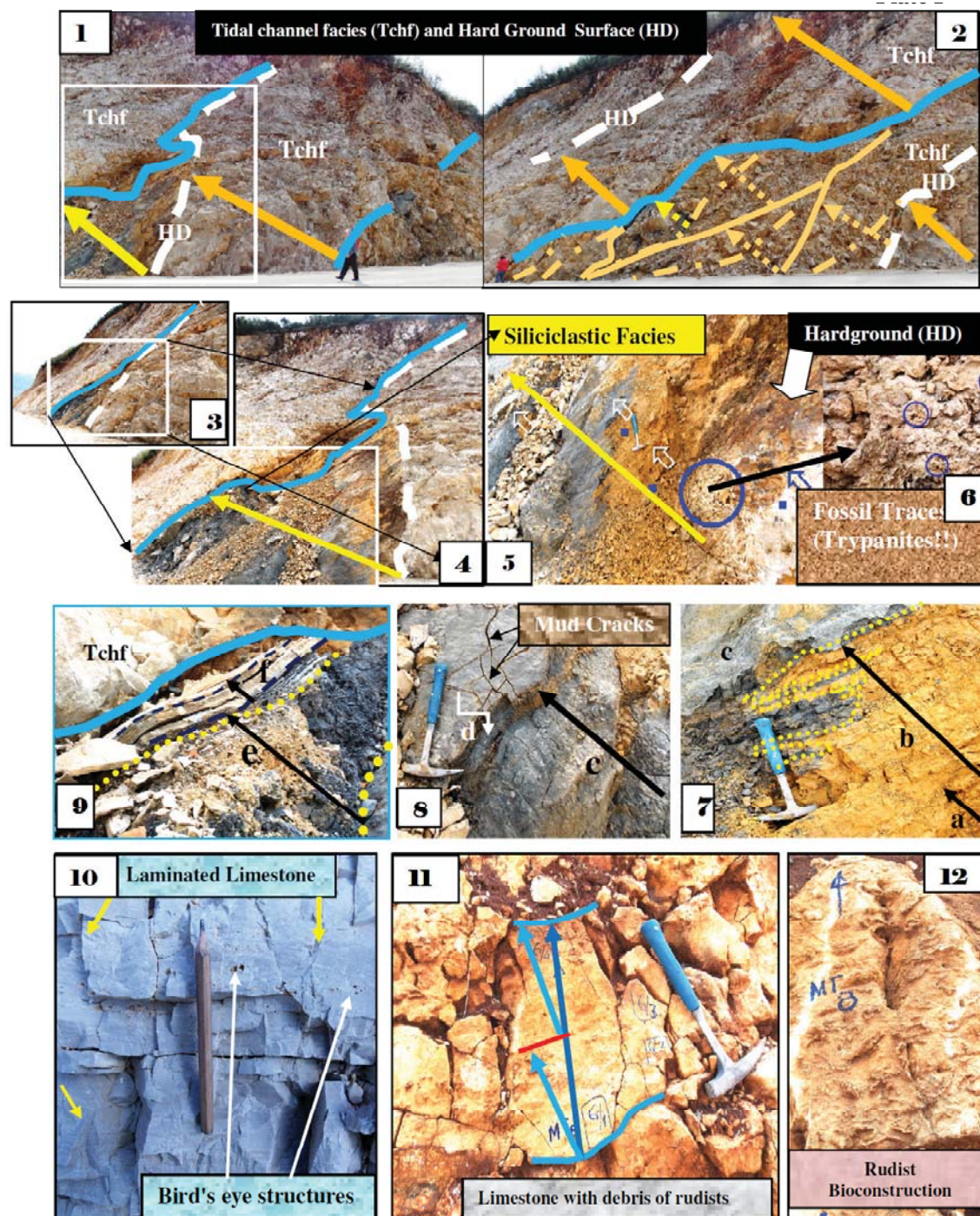
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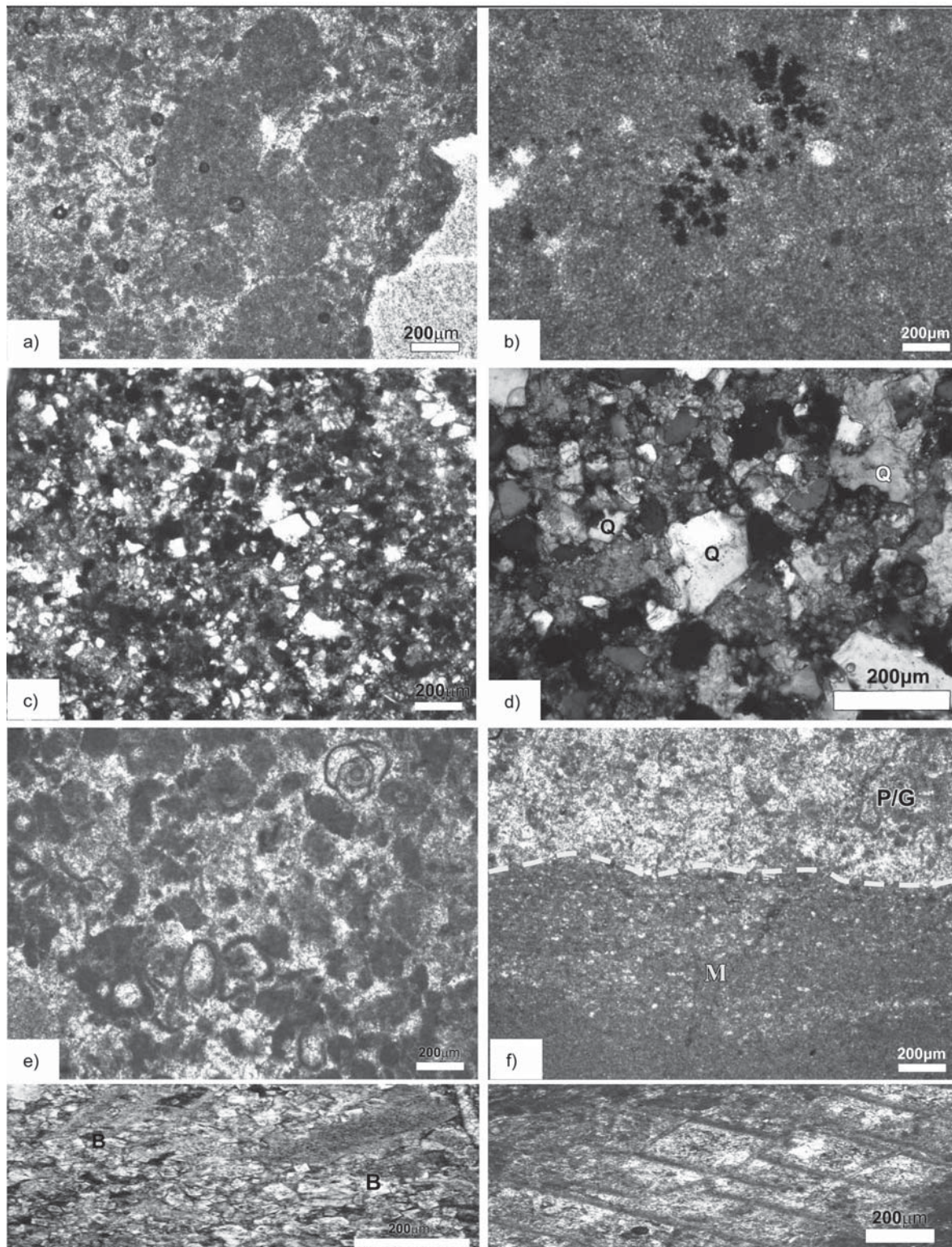
## PLATES

### PLATE I





## PLATE II



**Figura 2** a: Peloidal packstone to grainstone b: Mudstone with oil signs c, d: Sandstone facies, note the angular shape of quartz grains (Q) cemented by calcite and iron oxides e: Peloidal Bioclastic packstone to grainstone f: Laminated limestone due to the intercalations of mudstone (M) with packstone/grainstone (P/G) g: Bioclastic dolomitic wackstone (B- rudist clast) h: A longitudinal section of a rudistid bivalve showing their characteristic internal structure.

## DISSOLUTION OF APATITE GRAINS DURING ALLUVIAL STORAGE: AN EXAMPLE FROM HOLOCENE SEDIMENTS OF THE SKOLE NAPPE (POLISH FLYSCH CARPATHIANS)

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### Abstract

Many species of heavy minerals are relatively resistant to mechanical abrasion during transportation but not to chemical alteration during weathering and burial diagenesis. Less stable minerals are dissolved faster and progressively disappear at relatively shallow burial depths; more stable minerals are dissolved slower and disappear last. Investigations of chemical dissolution of heavy minerals revealed that severe dissolution affects not only unstable minerals, such as amphibole, pyroxene or olivine, but also tourmaline and even zircon. Contrary to that, apatite is relatively resistant to burial diagenesis tending rather to develop overgrowths than to dissolve. However, some investigations have shown that this mineral is sensitive to alluvial storage, which may lead to its total disappearance from heavy mineral assemblages in weathering profile, which may result in misinterpretation of heavy mineral provenance. Microtextures on mineral surfaces are visible symptoms of mineral dissolution, allowing to judge whether and to what extent minerals have been modified by post-erosional processes. Although there is a growing number of papers dealing with mineral dissolution, in case of apatite the investigations are often restricted to soil profiles or modern sediments in humid tropical climate. The data presented here refer to dissolution of apatite during storage in the Holocene fresh-water alluvial environment after erosion of the Campanian-Maastrichtian Ropianka Formation flysch sediments in temperate climatic conditions. The study endeavours also to explain the almost total lack of apatite in Oligocene sediments of the Menilite Formation, which is supposed to represent sediments eroded partly from the same source as the older Ropianka Formation, but stored for a long period in the Skole Basin foreland prior to deposition in the basin. In order to avoid contamination with minerals derived from various sediments, heavy minerals from the Holocene alluvia of streams eroding only one sedimentary flysch formation (Ropianka Formation) have been examined and

compared to heavy minerals occurring in this formation. The research was conducted in the Husówka catchment, in the northern part of the Skole Nappe in the Polish Flysch Carpathians. Sandstones of the Ropianka Formation contain considerable amounts of apatite (up to 8% of translucent heavy minerals), what was confirmed in previous studies. The Carpathian flysch basins remained in a temperate climatic zone during the Late Cretaceous and Oligocene, although during the Cretaceous the climate was relatively warmer than during the Oligocene. The analyses revealed that there is no significant difference in the apatite content between the Ropianka Formation and the Holocene alluvia, which may be attributed to relatively short period (about 0.117 Ma) of apatite storage in fresh-water environment and/or secondary heavy mineral concentration in stream deposits. However, it was noticed that many apatite grains display microtextures revealing their dissolution. They include mostly hacksaw terminations and surface lamellae. The degree of dissolution is diverse varying from initial to very deep, leading to development of skeletal texture of apatite grains. Such features are not visible in apatite grains from the Ropianka Formation, which are often euhedral to rounded with smooth edges and surfaces. Therefore, it is obvious that the apatite dissolution took place after erosion from the Ropianka Formation during storage in the Holocene sediments. In the light of the obtained data, it seems probably that the lack of apatite in the Menilite Formation (Oligocene) may be the effect of long-lasting storage of sediments prior to the final deposition in the Skole Basin. Taking into consideration that the investigated apatite dissolution features developed in Holocene deposits during a relatively short time (about 0.117 Ma), the long-lasting storage (about 50 Ma) of apatite may lead to its total disappearance from heavy mineral assemblages, as in case of the Menilite Formation.

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## RANK COALIFICATION OF THE LIGNITE OF SW SIBOVCI DEPOSIT, KOSOVO.

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### Abstract

Based on the studies carried so far in the coal basin, the geology of the basin, the chemical composition and technological characteristics of coal and coal reserves have been defined.

The study of the coal section consists of: field observations in the exploitation sectors of coal deposit, sampling in coal section and drillings, their chemical, petrographic and technologic analysis and interpretation.

There are studies about the petrographic composition of coal, known as macerals analysis, these being necessary for the analysis of the coal basin. This study completes the range of studies of this kind and the compiling of the atlas of the coal basin of Kosovo will be a recommendation for the future. Firstly, this study is accomplished only for Kosovo basin and later it will continue for other coal basins, as well. The coal samples are collected in the context of the geological studies and mining operations carried out in this coal deposit. The study is accomplished employing the petrographic study of coal and organic matter present in the coal basin. the type of organic matter depends on the type of deposition (autochthonous or allochthonous) and the peat – forming plant communities.

The coal basin contents three forms of organic matter:

1. In concentrated form that is represented by coal
2. In the form of coal shale
3. In the form of distribution or dispersive in sedimentary section of the basin.

The petrographic study carried out by optical-microscopic devices being supported by the reflected light, or macerals analysis, allows a morphological-chemical classification, in which the biological criteria is of second importance. In the lower

stages of maturity (peat stage, brown coal, lignite coal), identifying biological criteria of macerals is of special importance. It is the basic method of study for coal included in peat stage.

Studies by reflected fluorescent lights enables the identification of the main components rich in hydrogen, represented by liptinites. By this method, the organic diffused part of the coal that is closely linked and coupled with rock can be distinguished.

In the study of Kosovo coal basin, the methods of reflected light and fluorescent light are used.

The coal rank is defined by chemical (contents of C, H, S, N and O) and technological features (moisture content, calorific power, volatile substances, ash content) of coal. Coal characteristics are not affected by maturity, because the coal is not mature. The characteristics of coal are affected by the environment of sedimentation.

**Key words:** *huminite's reflectivity, calorific power, volatile matter, ash*

### Introduction

Based on the revaluation of petrographic studies on peat coal in the Kosovo coal basin, by their investigation with new microscopy methods, an analysis and generalization of geological studies has been accomplished. The prepared coal samples underwent the petrographic investigation on the coal composition. Three main groups of macerals have been separated: huminite, liptinite, neritinite and mineral matter. Pyrites are clearly distinguished because they are formed from anoxic condition within the coal basin. Vitrinite's reflectivity and the chemical and technological analysis did not show for the rank coalification.

### Materials and Method

Samples are taken from Kosovo coal basins in conformity with guidelines:

1. From coal seams in situ



## 2. Core samples of a seam.

There are standards or guidelines for sampling in different countries. They contain specifications on the technique of sampling as well as on the weight of increments or of mean samples, depending on the grain or the lump size. Correct sampling is essential for the reliability of the subsequent analyses and for the well interpretation of the results. Vitrinite's reflectance is specified in macerals

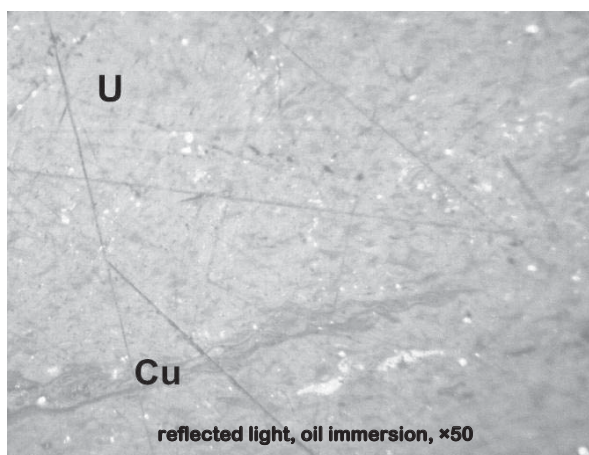


Photo 1. Maceral of Ulminite (U)

of textinite and ulminite (Photo 1), where darker textinites have reflectance about 0.14 to 0.18 %, light textinite have reflectance 0.19 to 0.22 %, while ulminite presented with higher reflectance up to 0.34 %. Chemical and technological samples are collected by the ISO European standard (Durmishi 1993; ICCP 1993; Stach 1982).

## Discussion

Description of macerals will relies only for predominant ones. Huminites are the most frequent ones and accordingly the most important maceral group occurring in peat coals. Huminites are subdivided on the basis of morphologic and reflectance criteria and they represent 15÷86 % of coal. Textinite is the main component of coal, occurring in thicker layers, having the normal reflection characteristic of the peat coal and it might be called huminite A. Some huminites occurring in the same seam in layers, are characterized by a somewhat weaker reflectance and a somewhat higher hydrogen content than normal huminite. It

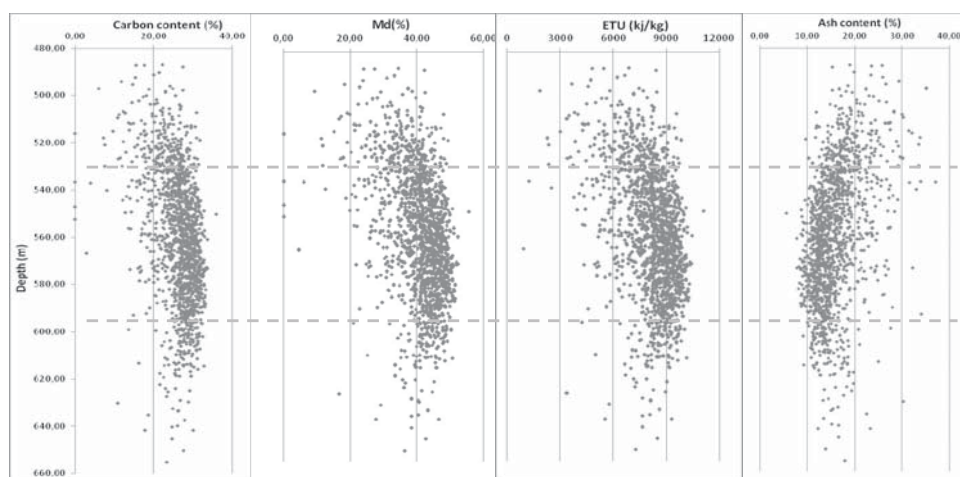


Figure 1. Position of coals from Kosova (lignite of SW Sibovci) basin in rank coalification.

Coal Types and Peat				Total Water Content (%)	Energy Content a.f.* (kJ/kg)	Volatiles d.a.f.** (%)	Vitrinite Reflection in oil (%)
UNECE	USA (ASTM)	Germany (DIN)					
Peat	Peat	Torf		35	6,700		
Ortho-Lignite	Lignite	Weichbraunkohle		35	16,500		0.3
Meta-Lignite	Sub-bituminous Coal	Mattbraunkohle		25	19,000	220	0.45
Sub-bituminous Coal		Glanzbraunkohle		14	25,000	45	0.65
Bituminous Coal	High Volatile Bituminous Coal	Flammkohle			103	40	0.2
		Gasflammkohle				5	0.5
	Medium Volatile Bituminous Coal	Gaskohle				35	1.0
		Fettkohle				28	1.2
	Low Volatile Bituminous Coal	Eßkohle				19	1.6
Anthracite	Semi-Anthracite	Magerkohle				14	1.9
	Anthracite	Anthrazit		3	36,000	10	2.2

Figure 2. Chemical and technological features of coal vary in wide limits.

is called "huminite B". These degrees of reflectance of vitrinite can be distinguished in low-rank coals using oil immersion.

Chemical and technological parameters have the following variations: total moisture (or water content) is 45 %, organic carbon content ranging 7.3-34 %, volatile matter ranging from 12 to 52 %, calorific power varies in the range 2,200 to 10,365 kJ / kg , while the ash content ranges from 8 to 34 % (Fig. 1).

The quality of coal increases when the carbon values are higher and the content of mineral material is low. This belongs to the interval 530-595 m of the coal section (Fig. 2).

Chemical and technological features of coal vary in wide limits. This is not a result of the maturity of coals, but of the environment of sedimentation that has limited reports of organic matter with minerals.

These changes are due to different original plant materials and to different degrees of preservation from biochemical reaction of the plant substance. While different degrees of thermal maturity have not taken place, because there is not any burial history of coal basin. So coal in Kosovo are positioned on the border between peat and lignite (Fig.1).

## Conclusions

1. For the definition of the rank (coalification stage) of the coal formation of Kosovo basin, the data on the basic parameters have been considered: values of C, H, S, N and O, calorific power, volatiles, ash and moisture. The determination of reflectance value of Vitrinite, has been used, as well.
2. The obtained data show that the rank of the coalification stage of Kosovo basin (SW Si-bovci) agrees with the range of type peat – lignite, according to the classifications: UNECE, USA (ASTM), Germany (DIN).

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## MACROSCOPIC LITHOTYPE AND PETROGRAPHIC CHARACTERIZATION OF THE LIGNITE OF SW SIBOVCI DEPOSIT - KOSOVO

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### Abstract

The work presents data on the macroscopy lithotype and petrographic composition of Neogene lignites from Kosovo. As a sedimentary rock, lignite – particularly its fragmental pattern – can be described in terms of the properties of sedimentary rocks as e.g. defined by Griffiths (1967) (from Skaberne 1980). According to this concept, lignite may be axiomatically defined as an aggregate of its constituent elements, therefore having properties according to the following Griffiths's (1967). Petrographic heterogeneity of coals is macroscopically studied in terms of lithotypes, microlithotypes and macerals. Composition of the SW Sibovci lignite was investigated on the basis of five vertical sections in open-pit mines in central Kosova. According to the ICCP (1993) recommendations and with some specific supplements, the SW Sibovci lignite can be also described by the following features:

- Ratios between fine-detrital matrix and xylitic fragments;
- Size, shape, orientation and arrangement of coal components;
- Degree of gelification;
- Structural characteristics (lamination, bedding, banding);
- Colour, fissuring, fracturing, jointing, hardness, brittleness, toughness.

Finally it has been decided to introduce the concept of fragmental lithotype components termed as:

- Detrite Lignite (DL)
- Xylo-Detrite Lignite (XDL)
- Detro-Xylite Lignite (DXL)
- Xylite Lignite (XL) - differentiated into three size classes (XL, XXL and XXXL)

and

- Fusite Lignite (FL).

During the microscopic studies of the lignites

from Sibovci deposit there have been observed almost all macerals of the three maceral groups - Huminite, Liptinite and Inertinite, as well as some mineral admixtures.

**Keywords:** Kosovo lignites, macroscopic lithotype, petrographic composition

### Macro-petrographic lithotype characterization of the SW Sibovci lignite

The coal formation has a thickness of about 70 m and depending on the sedimentation conditions, four main facies can be distinguished: lignite facies, carbonatic facies, volcanic ash facies and lignite clays facies. Typical feature, vertically and laterally, is the cyclic repetition of the beds of lignite and carbonatic facies, this conditioned by the "season climatic effects" or by the interaction of sedimentary environments: lagoon – lacustrine – deltaic ones.

Macroscopic characterization and macro-facies study of the SW Sibovci lignite involved two kinds of study objects: lignite in the exposure of the open-pit mines and lignite cores from boreholes. In our case, the fragmental pattern of lignite is macroscopically described by the size of different macroscopic constituent elements, by their composition and by their shape, orientation and packing. At the early beginning of petrographic studies, a question arose how to describe the very wide size range of different lithotype constituent elements – especially with regard to the description of ratios between lithotype terminology. The lignite material is built by the these lithotypes:

- Detrite Lignite (DL)
- Xylo-Detrite Lignite (XDL)
- Detro-Xylite Lignite (DX)
- Xylite Lignite (XL)– differentiated into three size classes (XL, XXL and XXXL)
- Fusite Lignite (FL).

Detrite Lignite lithotype and maceral groups of

huminite are the ones that dominate and display also the role of a matrix for the rest lithotypes.

Because the lignite of SW Sibovci has a striking fragmental character of its composition and texture, the scale of UDEN (e.g. in Selley 2000; Tucker 2001; and in many others) is applied to define the size limits of the lignite-forming constituent elements. On the basis of the UDEN scale, the size criteria for constituent elements of the lithotype components. For the largest wooden pieces it was not possible to find a name different from "xylite", therefore these are termed as xylite XX and xylite XXX. They can be regarded as referring to tree branches, stumps and trunks. Field experience shows that four letters are enough for the basic description of the lignite structure. Appropriate lower-case letters for the structure of lignites are: m (for massive), h (for horizontally stratified), g (for gelified), and d (for deformed). Deformed lignite can be coded by two extra letters (between brackets) to indicate the type of deformation: (fr) for fractured, (fa) for faulted, and (fo) for folded ones.

### Maceral Composition

The microscopic studies of the lignites from SW Sibovci deposit have individuated almost all macerals of the three maceral groups: huminite, liptinite and inertinite, as well as some mineral admixtures (carbonate, pyrite). From the data it is apparent that leading role in the composition of lignites is played by the macerals belonging to the group of huminite followed by those of ofliptinite group, while inertinite and the minerals are considerably lower in content. The first results of petrographic analyses indicate a predominant huminite maceral group (60-80 %) with a content in liptinite (5-10 %) and lower in inertinite (0-7 %). Maceral subgroup in Huminite group: Humotelinite, Humodetrinite, Humocollinite and Maceral: Texinite, Ulminite, Attrinite, Densinite, Corpohuminit, Cutinite, Liptodetrinite, Semifusinite, Fuzinit, Sclerotinite, Inertodetrinite. The mineral material consists of: clays, carbonates, pyrite and volcanic ash. Pyrite is found mostly in the form of framboidal pyrite.

### Conclusions

SW Sibovci is an important Neogene coal deposit (lignite deposit) in Kosovo, formed within an intramountainous basin, generated by the

neotectonic activity within this area. The age of this basin is defined by the fossils belonging to the Upper Miocene (Pontian) up to the beginning of Pliocene.

The lignite-bearing sequences are marked by matrix-dominated lithotype or by mixed xylite-rich/matrix lithotypes and xylite horizons and constitute the main characteristic of the SW Sibovci lignite deposits. Detrite Lignite Lithotype and maceral groups of huminite is the one that dominates and displays also the role of a matrix for the rest lithotypes. Peat was accumulated in a wet forest swamp under telmatic to limno-telmatic conditions and increased inorganic influx of clay and carbonates minerals which prevail in all the samples.

The combination of mineralogical composition and the plant communities identified in the studied area, suggests a humid and warm climate conditions during the SW Sibovci peat accumulation (Oikonomopoulos et al. 2007).

The presence of lignified wood fragments of various sizes is well known in this coal deposit as fragments of branches of various size, stems with well-preserved tissue. The macroscopic observations provided evidence about sedimentological structures.

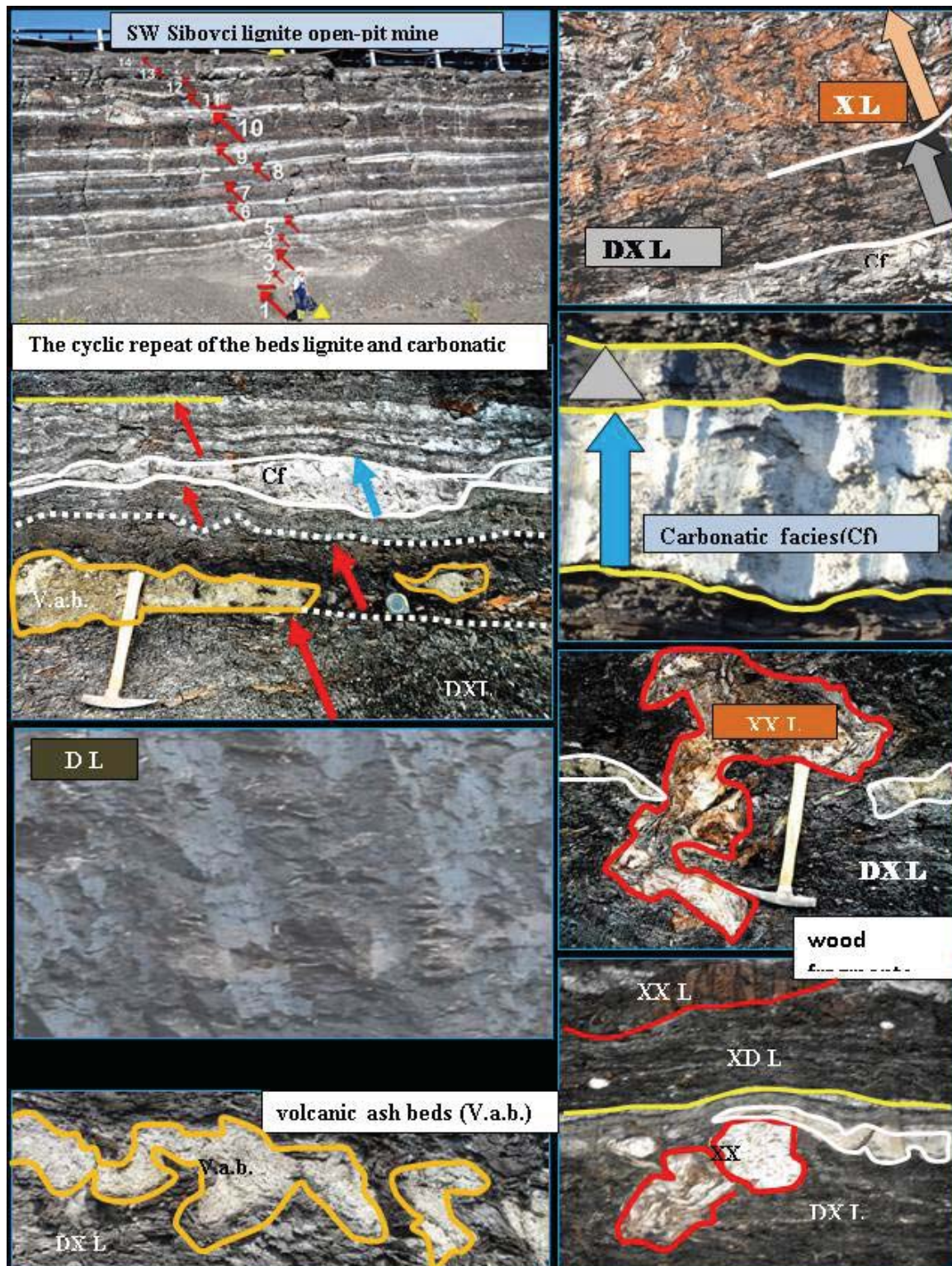
The recent underway research has evidenced the rhythmic deposition of lignite and carbonate and the distinction of sedimentary cycles that are in correlation with probably forced orbital - Cycles of Milankovitch (Oikonomopoulos et al. 2007).

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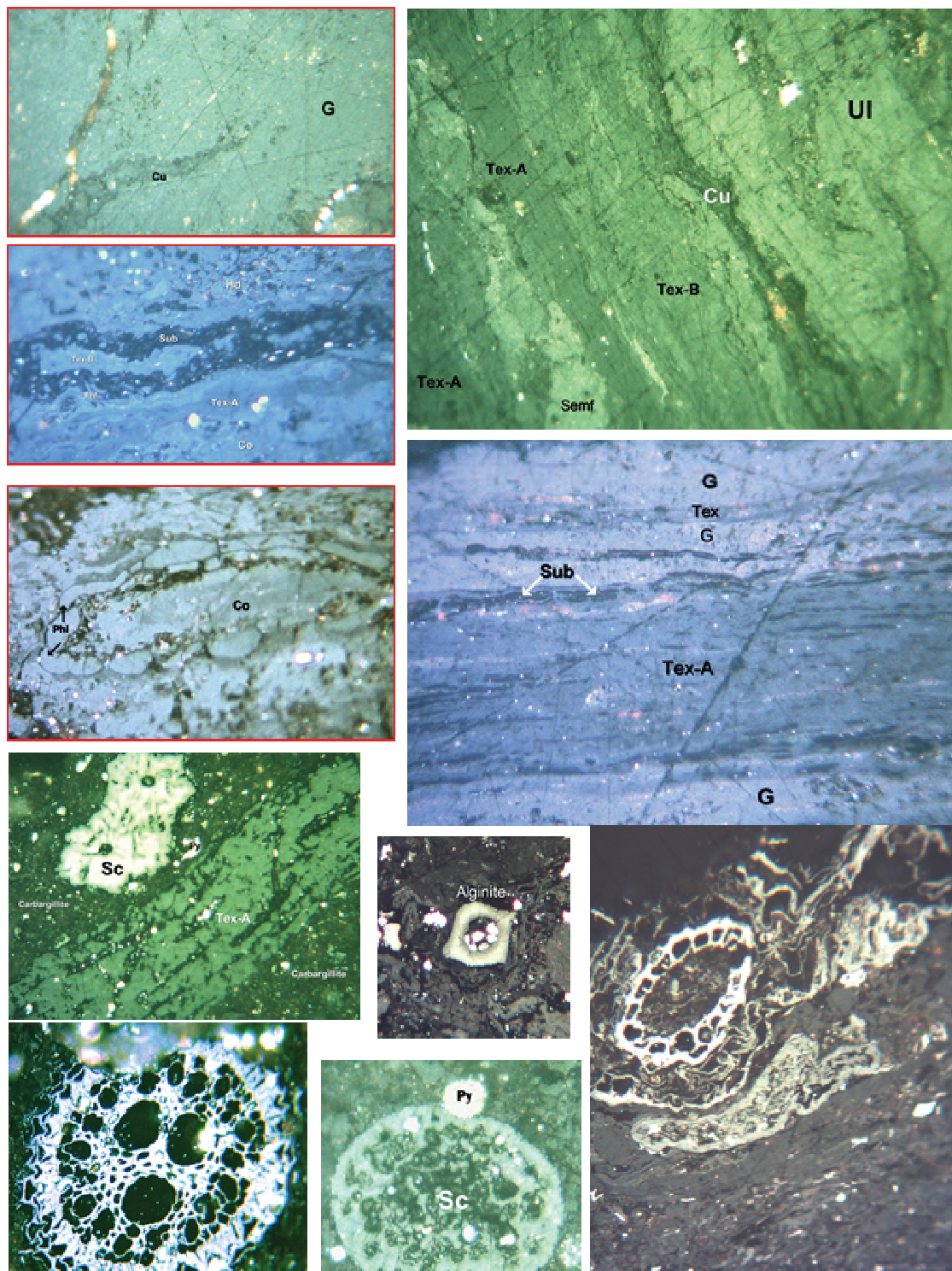
## PLATE I



**Plate I.** Macroscopic lithotype characterization of the SW Sibovci lignite: Detrite Lignite (DL) Xylo-Detrite Lignite (XDL) Detro-Xylite Lignite (DXL) Xylite Lignite (XL) - differentiated into three size classes (XL, XXL and XXXL), VOLCANIC ASH BEDS, Carbonatic facies (Cf). The macroscopic observations provided evidence about sedimentological structures



## PLATE II



**Plate II.** Macerals under reflected light, oil immersion, x50; Lignite of SW Siboci

Humidine maceral group: Textinite: Tex- A (dark), B (brigh), Ulminite: UI, Humodentrinite: Hd., Corpohuminide: Co., Phlo-  
 baphinite: Phl, Lipinite maceral group: Cutinite: Cu.

## COASTAL DYNAMICS OF VJOSA RIVER DELTA (ALBANIA)

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### Abstract

The Adriatic coastline (from Buna to Vlora) consists of several delta river systems and sandy beaches that exert a major control on the configuration and dynamics of the coastline. The area of this study represents a lowland coastal area that is characterized by an intensive erosion of the shoreline, affected by the activity of the Vjosa River flows and wave activity of the Adriatic Sea from the Pliocene period until today, mostly affecting the river mouth and abandoned tributaries. The combination of the physical character of the coastline and geotectonical, sedimentological, geomorphological and oceanographic processes, explain the frequent displacement of the river delta during the recent years. The Vjosa River stretches from the Hoxhara artificial channel in the north to the molasse hills of Zvernec and Narta lagoon, in the south. Geomorphology and geometry of Vjosa River Delta have been conditioned by the tectonic orientation of the Panaja and Frakulla neogenic molasses hills. Based on the classification of deltas systems, since the beginning until present, the Vjosa Delta can be classified mainly as fluvial dominated delta, even that sometimes it passed into a wave dominated delta. In Vjosa River Delta two old tributaries were identified, a southern one abandoned in 1918 and a northern one corresponding to the actual position of the Hoxhara Channel. The study area is characterized by sandy banks, mud flats, salt marshes, reedbeds, small lagoons, and temporary marshes. The studies carried out so far on the dynamics, evolution, erosion, accumulation, as well as the movement of the coast line and the Integrated Coastal Zone Management represented by the coastal zone, lead to the conclusion that this zone is continuously in evolution. The calculation of deposition and erosion phenomena is analyzed in GIS using the information of the maps available for different time periods.

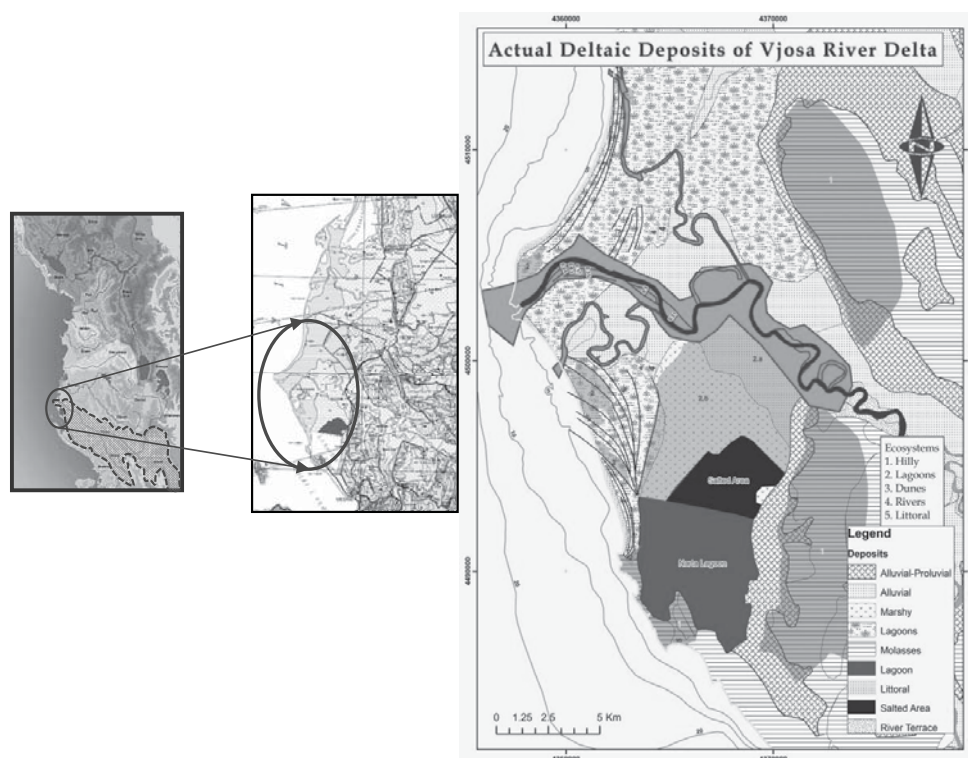
**Keywords:** *Vjosa River, Narta Lagoon, Coastal Dynamic, Evolution, GIS*

### Introduction

The Adriatic coastline (from Buna to Vlora) consists of several delta river systems and sandy beaches that exert a major control on the configuration and dynamics of the coastline. The area of this study represents a lowland coastal area that is characterized by an intensive erosion of the shoreline, affected by the activity of the Vjosa River flows (the active fluvial unit is composed of 30 km<sup>2</sup>) and wave effects of the Adriatic from the Pliocene period until today that mostly affected the river mouth and abandoned tributaries. The Vjosa River is an important river of southern Albania, with its source located in the Pindus Mountains in Greece. The surface occupied by the delta of Vjosa is 317 km<sup>2</sup>. It stretches from the Hoxhara artificial channel in the north, to the molasse hills of the Zvernec and Narta lagoon in the south with a drainage basin surface is 6700 km<sup>2</sup>. The geomorphology and geometry of Vjosa River Delta has been conditioned by the tectonic orientation of the Panaja and Frakulla neogenic molasses hills (Fig. 1). The geometry of this delta represents a coastal area up to 12.6 km toward the south and ~9.5 km in northern direction. Based on the classification of delta systems, since the beginning until present, the Vjosa Delta corresponds mainly to a fluvial dominated delta, even that sometimes it passed into a wave dominated delta. In Vjosa River Delta two old tributaries were identified, a southern one abandoned in 1918, and a northern one corresponding to the actual position of the Hoxhara Channel. The Vjosa River Delta segment (22 km) consists of sandy sediments. Several small beaches are formed as the results of movement dynamics of the Vjosa River mouth during the Holocene Period. The study area is characterized by sand banks, mud flats, salt marshes, reedbeds, small lagoons, and temporary marshes. The morphology of the coastline is closely related to the alluvial deposits brought by the rivers. Due to

the presence of a river mouth, the alluvial deposits are concentrated at locations along the coast, which leads to the building up of a sediment lobe. On either side of these lobes, sand bars are built up under the effect of the long shore drift. As soon as a river mouth is abandoned, the accumulation process of the sediments stops. The process of the straightening of the coastline then starts, which leads to rapid regression of the coastline around the abandoned mouth.

geomorphology. Also lagoons and coastal marsh deposits, as well as alluvial deposits occur in some places along this littoral area. The main lagoon included in this area is Narta lagoon, which is situated north of Vlora, between the Vjosa river mouth to the north and the city of Vlora to the south, covering a surface area of 41.8 km<sup>2</sup> of which as much as 1/3 are Skorofotina salt pans. The average depth of the lagoon is 0.8 m. A strip of alluvial land composes the northern part of the lagoon area, and the



**Figure 1.**

Geomorphological - Sedimentological map of actual deposits of the Vjosa River Delta.

This is documented on the evolution of the coastline from 1870 to 1990. It is evident that, within the geomorphological context of a low, sandy coast with bars and spits, the evolution of the littoral is rapid and very susceptible to variations in the sedimentary deposits, especially when a river mouth is abandoned. This area is formed by alluvial and marine deposits of Quaternary age with a thickness of ~200 m. The alluvial deposits mainly consist of gravels, sands and clays often intercalated with peat formed in small lakes on the flood plain. The marine deposits occupy most of the coastal zone and mainly consist of sands and silts with local gravel intercalations. The fluvial unit forms a passage that follows the rivers covering 30 km<sup>2</sup>. It is delimited by channels, which has poor vegetation and is rarely cultivated. The deposits in this delta are characterized by fine grained and well-sorted sediments. The Albanian Adriatic coastline has many beautiful sandy beaches, with different

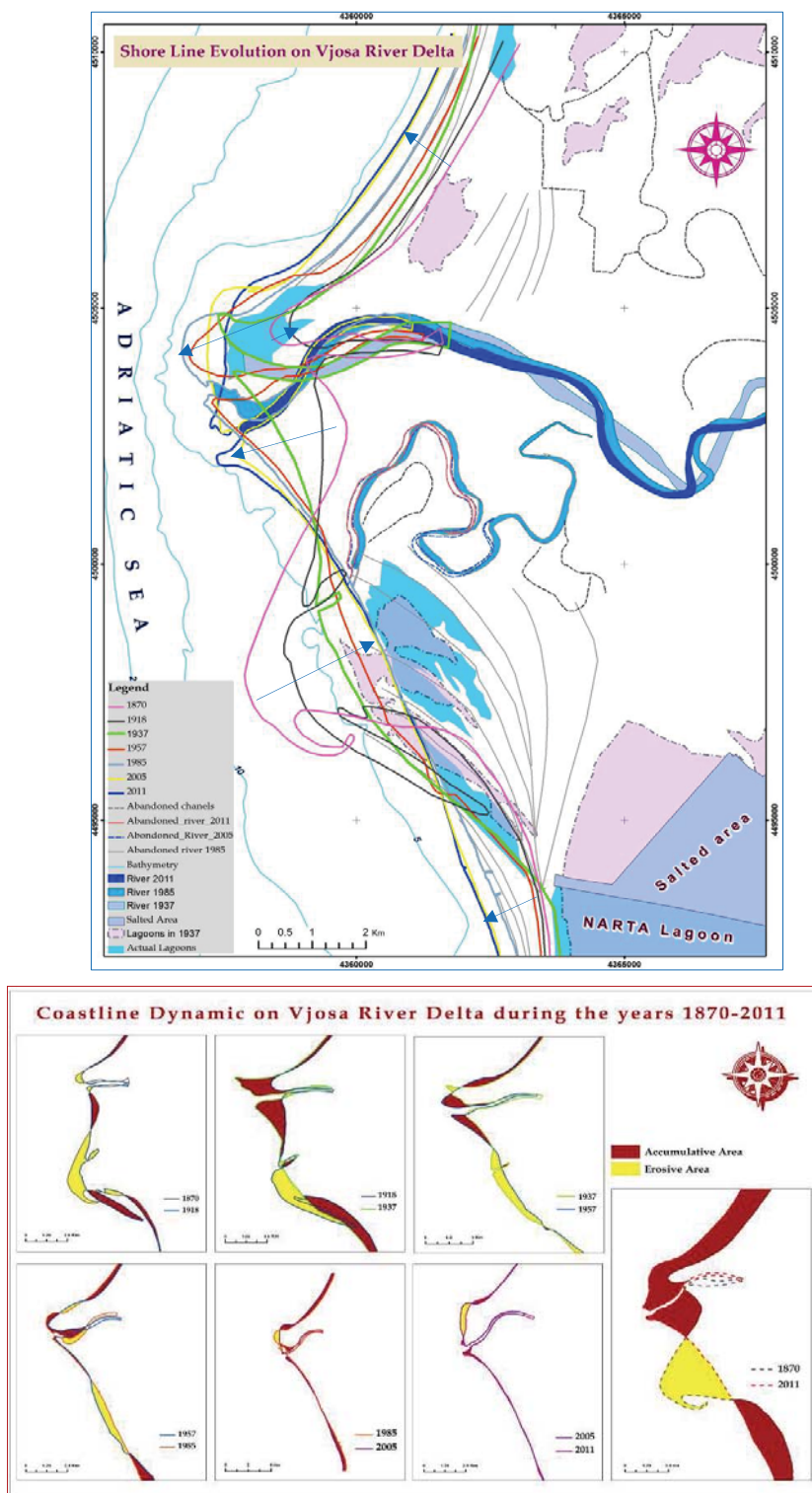
rocky sandstone and conglomerate coast in the southern part separates the lagoon from the sea, the only connection being a channel.

### Methods and Materials

Maps made over a period of more than one century are used to study the coastline and dynamic evolution of the Vjosa River. These studies are important for the master plans of touristic development, construction and infrastructure. The coastal dynamics as well as the coastline changes has been reconstructed using the information over the years of cartographic maps of Albania, consulting aerial photographs, previous studies, and satellite images taken over a several year time span. The calculation of deposition and erosion phenomena is analyzed using GIS software. The coastal dynamic is studied using the information of maps from different times (for the years 1870,



- Evolution of the constituent elements of the Vjosa River Delta (from 1870 to 2011).



**Figure 2.** Evolution of the shoreline and the mouth of the Vjosa River Delta.

1918, 1937, 1957, 1985, 2005, 2011). The region includes the main coastal lagoons, such as Narta as well as other small lagoons. In the map below, it is well distinguished that the shape of the lagoons and their surface area has changed through time.

## Results

Geographic data on the Vjosa River, Narta lagoon, shore lines, other lagoons, abandoned tributaries and abandoned channels, are presented in Fig. 2a. The environmental evolution can be identified during time. To calculate eroded and accumulation surfaces over the years, these areas are digitized as

unique surfaces (Fig. 2b), then the total surfaces are calculated for each two lines. The study and the observations of maps made over time (from the years 1870, 1918, 1937, 1957, 1985, 2005, 2011), comparing with the oldest map, show that the coastline was not stable. The total of eroded and accumulation area during the years is shown in the Figure 3. In total, from 1870 to 2011 the dynamic processes resulted in an accumulative surface of about 19.04 km<sup>2</sup> and an eroded surface of about 7.26 km<sup>2</sup>. The shoreline configuration of the area is conditioned by the interaction of the dynamics of the river, the type of the delta and the oceanographic factors of the Adriatic Sea. The advancement of the Vjosa mouth in years is presented in Figure 2a,b.

years. The most intense erosion of the shoreline is directly conditioned by wave activity and occurs at the river mouths and abandoned tributaries. Following abandonment of a river mouth, the littoral becomes straighter (i.e. the old tributary in 1918). The deltaic mouths disappear first and the coast retracts, until a new balance is reached. During 1870 to 1937, the mouth of the river has advanced with 1300 m to the west. The shoreline of the right side of the estuary has advanced 400 m to the west, while the left side has been eroded and has advanced with 1500 m to the east. The shoreline near to the Narta lagoon, as shown in the Figure 2, has advanced with 1 km to the west. During 1937 to 1985, the mouth of river has advanced again with 1km to the west. The shore of the right side

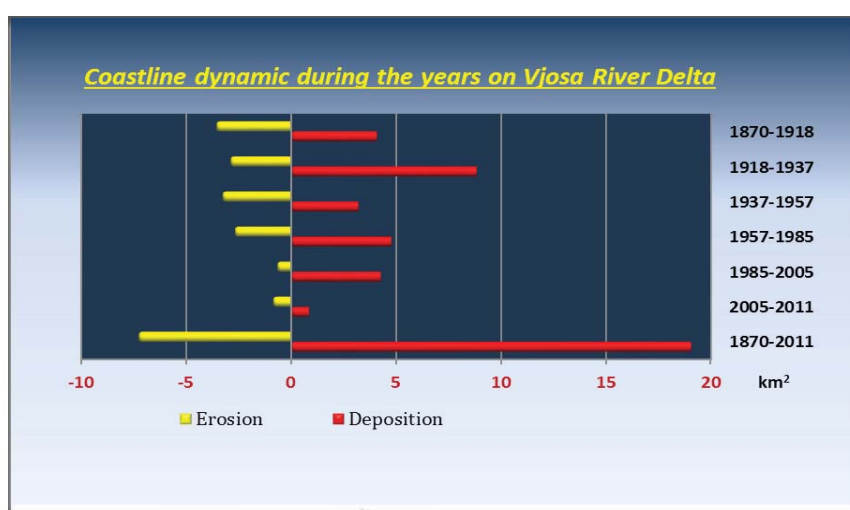


Figure 3. Coastline dynamic during the last 140 years on Vjosa River Delta.

## Conclusion

In the configuration of the study area and along the shoreline of Vjosa River Delta, continuous changes have occurred over time. These phenomena occur as a result of the combination of the physical characteristics of the coastline, as well as geotectonical, sedimentological, geomorphological, oceanographical processes such as erosion and sediment accumulation that explain the regular displacement of the river delta over the last 140

has advanced 400 m to the west, and

850 m to the east in the left side. During 1985 to 2011, the mouth of river has advanced with 700 m to the south - west. The shoreline of the right side has advanced with 350 m to the west, and 70 m to the west on the left side. While near to the Narta lagoon the advancement changes to the east with 100 m.

## TRACE ELEMENTS IN SOILS AND VINE FROM TIKVES AREA-FYR OF MACEDONIA WITH PARTICULAR REFERENCES TO NICKEL DISTRIBUTION

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### Abstract

This study presents the research of the presence of trace elements as Al, Ba, Ca, Cu, K, Mg, Mn, Na, Sr, As, Cd, Co, Cr, Ni, Pb, Zn in the soil of the Tikves area and the wine produced from the grapevine grown on this soil. The determination of the presence of trace elements is made according to the method ICP-AES, ETASS. Due to the quantity in the graphic interpretation (maps of correlation between wine/soil), only the graphic interpretations for the elements NI, are presented.

**Keywords:** wine, soil, elements in traces, Tikves

### Introduction

Vineculture and wine in Tikves area have a rich historical past and long tradition. They constitute the core industries of the population of the whole region.

The history of wines in this region goes back to more than two millennia, and that something can be seen from the numerous remnants of the past (archaeological artifacts in archeological sites such as: Stobi Eudarist, Belgrade, Antigone, Demir Blackberry etc. ), written documents, photographs, stories, as well as folk songs, customs and other works (Cvijich, 1906).

Today, when we talk about viticulture in Macedonia, it immediately reminds us of the Tikves area, the Tikves grapes and wine which are mentioned in numerous native Macedonian folk songs. Today the Tikvesh wine area is one of the most important, both in Macedonia and the Balkans.

Results which refer to the determination of the trace elements in the wine produces in in Tikves area, as well as in the rest of the wine regions in Republic of Macedonia can be found in the papers of Cvetkovic et al. (2001, 2002), Karadjova et al. (2004, 2007), Tašev et al. (2004, 2006, 2005), Stafilov and Karadjova (2009).

Also, the results which refer to the geological,

pedo-genetical and geo-chemical characteristics in the region Tikves and its surrounding can be found in the papers of Boev et al. (2005) and Stafilov et al. (2008).

### Materials and Methods

The field research methods are very important research activity of which depends greatly on further research results, and of course the performance of the final conclusions. In this Master work these methods are renamed in full in order to:

- detailed insight on the field that is the subject of research;
- drafting outreach activities;
- sampling of soils with their GPS location, packaging and labeling samples;
- photographing the developed profiles in soil horizons from which the samples are collected;
- record owners of vineyards whose grapes are collected soil samples and samples of wines;
- sampling of wines which are produced at home, packing labeling.

The collection of soil samples was done in accordance with generally accepted methodologies for work, as the methodology FOREGS (methodology for the geochemical map of Europe).

The following methods of laboratory research were applied:

- Preparation of soil samples for geochemical and wine pursuits representation macroelements and trace elements (ISO-14507);
- Preparation of samples of soil and wine, according to ISO-11466;
- Determination of the macroelements and trace elements by applying the methods of ICP-AES

and ETASS.

The researched elements are analysed by applying the atomic emission spectrometric method with double plasma (AES-ICP) and the method of electrothermal spectrometric atomic absorption (ETAAS). With the method of AES-ICP, the following elements were simultaneously measured: Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Zn.

The concentration of As, Cd, Co, Cr, Ni и Pb in the samples of wine were lower than the limitations of detection of AES-ICP and therefore they were analysed ETAAS. The instruments like: Varian 715-ES Series ICP Optical Emission Spectrometer (Varian, USA) and Zeeman ETAAS Varian SpectrAA-640Z were used for the analyses.

### Results and discussion

The results for the presence of trace elements in soils are shown in Table 1 (minimum, maximum and average values from 33 individual probes).

In the very same manner, the results for the presence of trace elements in wine are shown in Table 2 (minimum, maximum and average values from 33 individual probes).

**Table 1.** Concentrations of the trace elements (in mg/kg) in the soil of Tikves area.

Probe	Min	Average	Max
Al	17978	30854	44972
As	1,2	15,1	83
Ba	145,1	315,2	717,7
Ca	9140	40790	88862
Cd	0	0,1	0,5
Co	11	16,8	37,6
Cr	30,6	99,9	442,4
Cu	11,3	24,6	46,3
K	4187	12031	19038
Mg	3769	9751	23195
Mn	397	568	794
Na	3385	7003	13975
Ni	24	78,7	528,5
Pb	1,9	14,1	24,9
Sr	40,9	129,5	401,6
Zn	33,2	48,7	72,4

The results indicate an increased prevalence of correlativity between Ni in soils and wine (Fig. 1). The correlation with the contents of Ni in soils and wine can be explained by the large contamination of soils with nickel due to metallurgical activity in the region.

### Conclusion

From the surveys on the presence of trace elements in soils and in the wine of Tikves region

**Table 2.** Concentration of the trace elements in vine from Tikves area . Al, Ba, Ca, Cu, K, Mg, Mn, Na and Sr in mg/l; As, Cd, Co, Cr, Ni, Pb and Zn in µg/l.

Probe	Min	Average	Max
Al	0,1	0,71	4,93
Ba	0,06	0,2	0,47
Ca	19,77	49,64	105,16
Cu	0,009	0,196	1,389
K	323,5	835,9	1626,4
Mg	23,92	85,06	130,52
Mn	0,46	1,32	3
Na	1,05	8,9	63,91
Sr	0,15	0,99	2,88
As	1,28	46,91	128,74
Cd	0,09	1	5,32
Co	0,18	2,56	10,57
Cr	1,37	11,98	99,53
Ni	6,71	43,92	313,83
Pb	6,02	58,53	289,79
Zn	0,04	0,35	0,9

winery expressed correlative relationships among elements Ni, can be concluded.



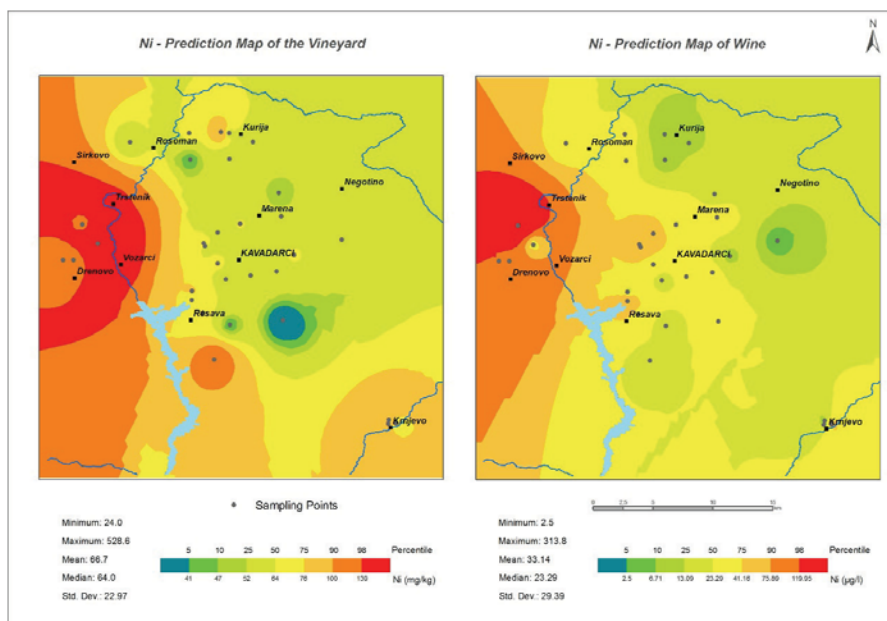


Figure 1. Map distribution of Ni in the soil/wine.

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## CO<sub>2</sub> SEQUESTRATION INTO SHALE BEDS - ŞIRNAK COAL MINES

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### Abstract

CO<sub>2</sub> capturing, transport and sequestration by pressurized water dissolution and reacting by natural alkali lime and magnesite or other sources becomes an industrial advantageous sequestration option. Resulting in green waste solutions or solid fines, Mg and Ca containing minerals are reacting with CO<sub>2</sub> to form carbonates. Various types of hot water sources may react with CO<sub>2</sub> to form carbonate regarding brine composition and reaction parameters. Mineral sequestration of CO<sub>2</sub> will also allow using the products in cement industry or as cement material in constructions with low cost.

The CO<sub>2</sub> will be delivered by truck in liquid phase, temporarily stored at the well site, and conditioned before injection. The project proposed plans to inject the CO<sub>2</sub> at the well head in gaseous phase at a slightly supercritical pressure and slightly supercritical temperature. The anticline at Şirnak-Silopi was used for gas storage in the past in a shallower depth interval in Şirnak-Silopi pit mine field, which also is an mining industry partner in CO<sub>2</sub> sequestration and will be responsible for the CO<sub>2</sub>-injection operations.

This study discussed progress on reactor achieved by tests and search for fast reaction methods using exhaust gas containing waste sulfur and carbon gases at the stack of Power Stations. Other alkaline sources containing calcium, magnesium and magnesium salts, supercritical CO<sub>2</sub>, water slurry, and additives were searched for optimum sequestration methods and also in order to enhance mineral reactivity; and in analyzing the structural changes to identify reaction paths and potential barriers. Carbonation liquid and gaseous products may change to near 20%–45% yield performances by time increase from 1hr to 6hr.

**Key words:** carbon sequestration, saline water utilization, mineral carbonation, mineralization, shale bed

## NATURAL RADIOACTIVE ELEMENTS, CHARACTERISTICS AND THEIR STATUS IN GEOENVIRONMENT OF ALBANIA

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### Abstract

This research aims to analyse the disintegration of natural radioactive elements, based to the results of radioactivity mapping performed in Albanian the territory of Albania. During field surveys, a proper attention was paid to determination of the integrate assessment of alpha ( $\alpha$ ), beta ( $\beta$ ) and gamma ( $\gamma$ ) radioactivity, which is issued by different radioelements, especially the series of uranium, radium, actinium, and thorium. Except them there have been also observed the radioisotope of stable chemical elements as potassium, rubidium, samarium, etc. As a result of radioactive decay in the environment, is also quite artificial radioisotope different life length as  ${}^5\text{C}^{137}$ ,  $\text{Co}^{60}$ , etc.  $\text{Zr}^{95}$ , whose survey has been in our attention. It is also estimated the presence of radon, the inert radioactive gas formed by the decay of radium alpha ( $\text{Ra}^{226} \rightarrow \text{Rn}^{222}$ ). For that reason, the length of these radioisotope ( $T_{1/2}$ ) was 3.8 days, it spread around the environment through diffusion. We paid attention to the presence of cosmic radiation, which is characterized by low intensity but high energy (Skende and Dodona 1978; Dodona 1987, 2002; Tashko and Dodona 1991)

This mapping has been conducted because the radioactive radiation protection is a duty and a special care for the preservation of human health,

because some of them have carcinogenic effects. In addition, they are also used for curative effects. Most leading radio-elements are presented in Table 1, Adams and Gasparini 1970.

### Decay scheme of Important Radioactive Elements in the Earth

Data provided relate specifically to radio-elements (radioisotope) of stable natural elements like potassium (K), rubidium (Rb), indium (I), samarium ( $\text{Sm}^{50}$ ), tellurium ( $\text{Te}^{52}$ ), latin ( $\text{La}^{57}$ ), neodymium ( $\text{Nd}^{60}$ ), lutetium ( $\text{Lu}^{71}$ ), and rhenium ( $\text{Re}^{75}$ ). These elements have radioisotopes that emit gamma ( $\gamma$ ) radiation, alpha ( $\alpha$ ), beta ( $\beta$ ) and K absorption during their decay, which ends in to the stable elements (Table 2).

### Natural radio-active elements that don't include in radioactive stuff

Determination of some natural radioelements in soil and rocks and their radio spectrometry performed in the framework of the project on geochemical mapping of Albania (1993-1998), and some separately radiometric studies results are analyzed and presented in the research (Table 3, and Map 1). The above mentioned studies present radio-geochemical, environmental and technological values, leading in this way to

Table 1

Element	Parent isotope	Percent of natural elements	Decay mechanism	Stable daughter	Decay Constant ( $\text{ye}^{-1}$ )	Half-life (yr)
Uranium	${}^{238}\text{U}$	99.274	$(8\alpha + 6\beta)$ series decay	${}^{206}\text{Pb}$	$1.55125 \times 10^{-10}$	$4.468 \times 10^9$
			Spontaneous fussion	Various		
	${}^{235}\text{U}$	0.720	$(7\alpha + 4\beta)$ series decay	${}^{207}\text{Pb}$	$9.8485 \times 10^{-10}$	$9.8485 \times 10^8$
			Neutro-induced fussion	Various		
Thorium	${}^{232}\text{Th}$	100	$(6\alpha + 4\beta)$ series decay	${}^{208}\text{Pb}$	$4.9475 \times 10^{-11}$	$1.401 \times 10^{10}$
Rubidium	${}^{87}\text{R}$	27.85	$\beta$ emission	${}^{87}\text{Sr}$	$1.420 \times 10^{-11}$	
Potasium	${}^{40}\text{K}$	0.1167	11.% k-electron capture	${}^{40}\text{Ar}$	$(\lambda_k) 0.581 \times 10^{-10}$	$1.25 \times 10^9$
			89 % $\beta$ emission	${}^{40}\text{Ca}$	$(\lambda_\beta) 4.962 \times 10^{-10}$	
Carbon	${}^{14}\text{C}$	$1.6 \times 10^{-10}$ (atmospheric $\text{CO}_2$ )	$\beta$ emission	${}^{14}\text{N}$	$1.209 \times 10^{-4}$	$5.73 \times 10^3$

**Table 2**

Element (Symbol)	% in natural equivalent	Half-life Decay Period T	Decay type	Radiation energy, in Mev		product that is created (stable element)
				Particles Mev	$\Gamma$ rays Mev	
$_{19}^{40}\text{K}$	0.0119	$1,31 \cdot 10^9$ Y	$\beta^-$ (88%) K absorption (12%) $\gamma$	1.325	1.450	$_{20}^{40}\text{Ca}$ $_{19}^{40}\text{Ar}$
$_{32}^{87}\text{Rb}$	27.85	$6,18 \cdot 10^{10}$	$\beta^-$	0.275	0.394	$_{38}^{87}\text{Sr}$
$_{49}^{115}\text{In}$	95.77	$6,10 \cdot 10^{17}$	$\beta^-$	0.63	--	$_{50}^{115}\text{Sn}$
$_{50}^{124}\text{Sn}$	6.11	$>1,5 \cdot 10^{11}$	$\beta^-$	1.5	0	$_{51}^{124}\text{Sb}$
$_{52}^{130}\text{Te}$	34.11	$1,4 \cdot 10^{21}$	$\beta^-$	--	--	$_{53}^{130}\text{I}$
$_{57}^{138}\text{La}$	0.089	$7 \cdot 10^{10}$	$\beta^+ \beta^-$ K absorption $\gamma$	1.0	0.355 0.807 1.39	$_{56}^{138}\text{Ba}$
$_{60}^{150}\text{Nd}$	5.60	$5 \cdot 10^{10}$	$\beta^-$	0.011		$_{61}^{150}\text{Pm}$
$_{62}^{147}\text{Sm}$	15.07	$6,7 \cdot 10^{11}$	$\alpha$	2.11		$_{60}^{143}\text{Nd}$
$_{71}^{176}\text{Ln}$	2.60	$2,4 \cdot 10^{10}$	$\beta^-$ $\gamma$	0.215 0.40	0.180 0.270	$_{72}^{176}\text{Hf}$
$_{75}^{187}\text{Re}$	62.93	$4 \cdot 10^{12}$	$\beta^-$	0.040		$_{76}^{187}\text{Os}$

(Skende and Dodona 1978; Dodona 1987, 2002; Tashko and Dodona 1991):

1. Mapping of the respective natural radio-elements of K, Rb, Ln, etc.

2. Tracking the radio-spectrometric characteristic of these natural isotopes.

3. Multi-element correlation encountered in representative samples (Tables 1 and 2) Map 1.

**Table 3**

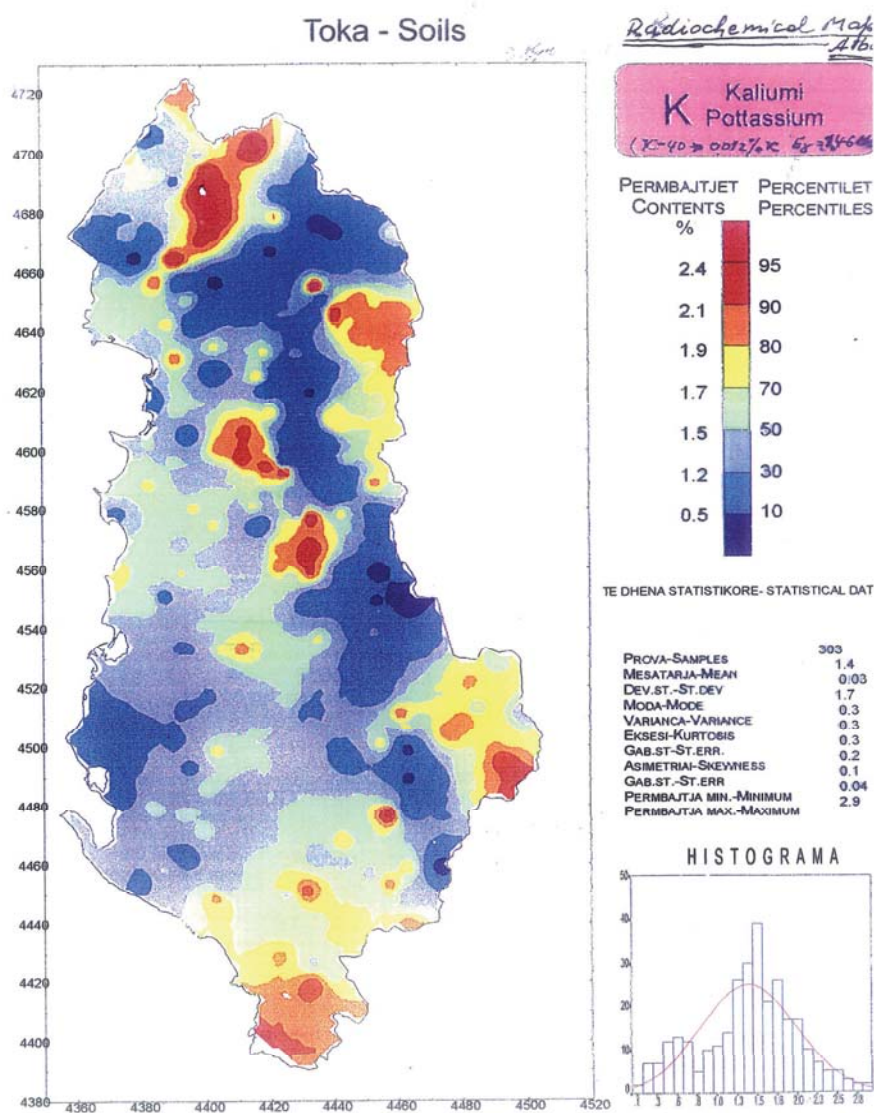
a) Analytical results for rock's samples- Korrabi Zone Gamma spectrometric analyzes.

Nr.	Nr. proves	eU <sub>Σ</sub> ppm	eU <sub>Ra</sub> ppm	eTh ppm	K %	Th U	Th K	KU Th	Δ	ΣTR ppm
1.	G-002	30	5.3	48	1.8	9.1	27	0.20	D	1124
2.	G-006	37	5.6	56	2.5	10.0	22	0.25	D	1387
3.	G-011	19	4.4	24	4.0	5.5	6	0.73	*	967
4.	G-017	33	8.5	42	2.3	4.9	18	0.47	D	1135
5.	G-023	36	9.0	61	1.3	4.8	47	0.19	D	1300
6.	G-024	36	13.0	45	2.5	3.5	18	0.72	D	1395
7.	G-033	53	7.7	96	2.3	12.5	42	0.18	D	1413
8.	G-034	20	4.7	12	12.8	2.6	1.2*	5.0*	*	555
9.	G-045	52	12.0	85	2.8	7.1	30	0.31	D	1203
10.	G-052	52	15.0	86	1.8	5.8	48	0.31	D	2496
11.	G-061	106	34.0	17	1.6	5.0	106	0.32	*	502
12.	G-065	54	17.0	78	1.2	4.6	65	0.26	*	11
13.	G-070	27	8.6	29	5.3	3.4	5.5	1.57	*	261
14.	*	*	*	*	*	*	*	*	*	*



b) Chemical-spectrometric analyzes.

Nr (pr*)	ΣTR ppm	Ce ppm	Dy ppm	Tb ppm	Nd ppm	La ppm	Y ppm	Sm ppm	Pr ppm	Gd ppm	Lu ppm	Yb ppm	Er ppm	Ho ppm
1.	1124	35	6	15	230	200	20	50	120	50	1	8	8	1
2.	1387	600	12	20	250	100	100	80	150	50	5	10	9	1
3.	967	450	15	15	130	120	80	40	60	*	2	8	5	1
4.	1135	500	7	20	200	150	100	40	100	*	3	10	4	1
5.	1300	600	8	20	220	150	80	50	100	50	3	8	8	2
6.	1395	600	7	40	260	200	150	50	100	50	30	15	8	2
7.	1413	600	10	35	28	300	150	80	150	50	3	15	8	2
8.	555	160	2	5	100	150	80	15	30	*	1	8	4	*
9.	1203	300	8	20	200	300	120	35	150	50	2	10	8	*
10.	2496	700	10	50	400	600	200	100	300	100	5	15	10	1
11.	502	200	2	10	100	150	30	15	80	*	*	3	2	*
12.	11	*	*	*	*	*	10	*	*	*	*	1	*	*
13.	261	65	*	3	50	70	50	*	20	*	*	4	1	*



Map 1.

**Reference**

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## USING OF NOVEL SECUENCING BATCH REACTOR FOR NITROGEN REMOVAL FROM DOMESTIC WASTEWATER IN THE TERRITORY OF AGRICULTURAL UNIVERSITY OF TIRANA, ALBANIA

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### Abstract

At present, the wastewater treatment practices can be significantly improved through the introduction of new treatment technologies. To meet increasingly stringent discharge standards, new applications and control strategies for the sustainable removal of ammonium from wastewater have to be implemented. Partial nitrification to nitrite was reported to be technically feasible and economically favorable, especially when wastewater with high ammonium concentrations or low C/N ratios is treated. For successful implementation of the new technology, the critical point is how to maintain partial nitrification of ammonium to nitrite. Partial nitrification can be obtained by selectively inhibiting nitrite oxidizing bacteria through appropriate regulation of the system's DO concentration, microbial SRT, pH, temperature, substrate concentration and load, operational and aeration pattern, and inhibitor. For this reason a pilot scale sequencing batch reactor (SBR) was constructed and operated to remove organic substance and nitrogen from the domestic wastewater.

The wastewater contains high concentration of organic substance (300-800 mg/l COD) and nitrogen (30-80 mg/l N). The pilot-scale SBR operates in an 8-hour cycle with 3 pairs of aerobic/anoxic phase and 1:2 A/AN ratio succeeded a biological nitrogen removal through by pass of nitrates and completely removal of soluble COD. The removal efficiency of COD, NH<sub>4</sub>-N and TP respectively were up to 80, 99.5 and 85 %. Nitrate concentration remained close to 0 throughout the cycle, whereas nitrites at the end of the cycle were close to zero. This represents then an actual demonstration of PND – process at a pilot – scale confirming our laboratory results. All effluent characteristics are within legal requirements, respectively NH<sub>4</sub>-N < 0.05 mg/l, NH<sub>3</sub>-N < 1.0 mg/l, NO<sub>2</sub>-N 0.02 mg/l, P-PO<sub>4</sub> < 2mg/l and COD 40mg/l.

**Key words:** sequencing batch reactor; partial nitrification-denitrification process, different forms of nitrogen (NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N)

## ENVIRONMENTAL ASSESSMENT OF THE REPS MINE DUMP SITE, MIRDITA (ALBANIA)

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### Abstract

The mine dumps of Reps, a major ore processing site in the Mirdita District, worked as collectors of tailings deriving from the adjacent copper processing plant. The Reps milling and concentration facilities operated until 1994, producing several tons of waste and tailings, mostly stocked in two main piles alongside the Fan river. The sulphide-rich nature of the waste material, the location and the unstable conditions of the piles are issues of environmental concern. The aim of this work is to outline the heterogeneous characters of the stocked materials and evaluate the release of potentially toxic elements (PTE) in the local environment through a geochemical survey of the two main piles, respectively named *Reps1* and *Reps2*.

We collected 60 solid samples from the two dump bodies, and 17 water samples representative of the upstream flow, drainage and downstream delivery. The physical characters of the solid materials were investigated through particle size distribution analyses, pH measures and in situ permeability tests. The mineralogical study was conducted by optical transmitted and reflected light microscopy and X-ray diffraction (XRD) investigations on representative samples. Quantitative data on major and trace elements were collected using inductively coupled plasma (ICP) mass spectrometry techniques. Furthermore, we undertook electron microprobe spot analyses (EMPA) on single grains of sulphide minerals and associated sulphates. The physical and chemical parameters of the water samples have been investigated through pH-Eh measurements and atomic emission spectrometry (AES). The acid drainage production and the neutralising capacity were evaluated for a set of samples through the Acid Base Account (ABA) test.

The comparison between the pH analyses on solid samples revealed a stronger acidity of the waste materials of the *Reps2* dump (pH = 2.4-3.7), with respect to *Reps1* (pH = 3.2-4.3). The mineralogical investigations reveal that such a difference is to be attributed to a higher content of pyrite, marcasite, sphalerite, chalcopyrite and minor enargite in the *Reps2* samples. The mineralogical composition of these samples is also reflected in the considerable concentrations of S and hazardous metals such as Cu (aver. 4430 ppm), Zn (aver. 1970 ppm), and As (660 ppm). The drainage water samples show very low pH values (2.3-2.7), with respect to the upstream waters (pH = 6.7-7.8). This acid character is associated to a high concentration of ions, the highest values being the ones of Zn (up to 100 ppm), Cu (up to 20 ppm) and Mn (up to 20 ppm). Our preliminary results on the potential acid drainage production include a total H<sub>2</sub>SO<sub>4</sub> release of 588.087t and a predicted buffering time of 230 000 years.

Preliminary investigations at Reps show that this site undergoes a general widespread pollution due to the storage of sulphur and PTE-rich fine grained material in strong disequilibrium with the local morphology and adjacent to a main river that works as a collector of highly acid PTE-rich drainage water. In such frame a detailed knowledge of local differences between the two main dumps and heterogeneities within the same dump is fundamental for any possible remediation planning.

**Key words:** Tailings, acid rock drainage, sulfides, potentially toxic elements, Mirdita



## WATER CLASSIFICATION OF THE AMYNTEO HYDROLOGICAL BASIN, NORTHERN GREECE

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### Abstract

The chemical composition of the water of a region is directly linked to the mineralogical composition of rocks that dominate in the particular region; water quality is greatly affected upon contact with the minerals, both on the surface of the soil and in the groundwater aquifers. An important role in the quality of water may be played by other factors such as the residence time of water in the aquifer, the presence of other compounds and human activities. The determination of hydro-chemical characteristics of groundwater and surface water may give significant information related to water resources quality, the relationship between them, the mixing pattern of different types of water supply areas and aquifers. This study deals with the examination of the hydro-chemical conditions in the Amynteo's hydrological basin, which belongs to the Florina-Ptolemais-Kozani coal-bearing basin and includes several water resources.

The determination of the quality of groundwater and surface water of the study area took place through extensive sampling during 2010. Water samples were collected from two lakes (Zazari and Cheimaditida), from one torrent (Sklithro torrent) and from a canal connecting Cheimaditida and Lake Petron. Groundwater samples were collected from eighteen wells. Water samples were analysed for the determination of the following parameters: pH, EC, Eh, TDS (in situ), anions including  $F^-$ ,  $Br^-$ ,  $Cl^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $PO_4^{2-}$ ,  $SO_4^{2-}$ , and the cations  $Li^+$ ,  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ , using an ion chromatograph. The following results were deduced by the analysis of the water samples.

The pH of Zazari lake water was ranging from 6.96 to 8.20 while for Cheimaditida was between 6.26 and 7.60. The nitrates content in both lakes was below the upper limit values foreseen by the guidelines, although for Zazari lake, nitrates were marginally above the drinking water limits of 50 mg/L. The waters of Zazari lake are ranked as

soft according to Sawyer – McCarty and very soft according to Hem. The waters of Cheimaditida lake are ranked as moderately hard to very hard. A high positive correlation was found for Zazari lake, between the ions  $Na^+$  and  $Ca^{2+}$ , and between the ions  $Ca^{2+}$  and  $Cl^-$ . For Cheimaditida water, a statistically significant positive correlation was found between the ions  $Ca^{2+}$  and  $Mg^{2+}$ ,  $Mg^{2+}$  and  $SO_4^{2-}$  and  $Ca^{2+}$  and  $HCO_3^-$ . Additionally, according to the Durov diagram, the prevailing cations in the borehole, canal and surface waters are  $Ca^{2+}$  and  $Mg^{2+}$  and in some cases  $Na^+$ , while the dominant anions are  $HCO_3^-$  and  $SO_4^{2-}$ .

Groundwater pH varied from 6.60 to 8.20. Groundwater was slightly more alkaline than the surface water. Mean concentrations of nitrate in alluvial aquifer ranged from 6.32 to 199.36 mg/L; these values are apparently low for such an intensively cultivated area. The presence of manganese in groundwater samples was attributed to the composition of geological formations corresponding to sedimentary and metamorphic rocks, particularly rich in mica and hornblendes. The average hardness of the water of the alluvial aquifer was characterized as very hard, according to Sawyer – McCarty and Hem. From the Piper diagram, it appears that waters can be characterized as calcium-magnesium rich. No significant changes were found in the water quality, according to the Piper diagrams; The basin water (surface water and groundwater) in general, exhibited a rather stable hydro-chemical character. Based on the Durov diagram, the waters of the study region are refreshed very quickly and water quality is very satisfactory.

## THE REDUCTION OF SOIL EROSION BY IMPROVING THE FORESTRY SPACE IN ALBANIA

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### Abstract

Many studies have been carried out in the region of Albania on soils, but only few of them have measured the real erosion and sedimentation scale throughout Albania during the last 20 years. They hardly have offered databases on soil erosion and sedimentation both in depth and surface. However, they have laid down the foundations for the evaluation and conservation of natural systems from landcovering, landusing and environmental point of view. The actual features of Albanian watersheds shows their degraded state and strong erosion indicating simultaneously the economical and environmental consequences. In the period between 2006-2010, an enormous work has been done by the government, by implementing new forest spaces, forest improvement, pasture enhancement, forage cultivation, establishment of plantations with fruit trees, vineyards and olive groves in order to have a minimum scale of erosion in a near future and after. The methodology consists in the calculation of actual erosion scale before afforestation and after the forestry improving (new forest spaces, forest systematization, built mountainous dams, etc). In order to calculate the soil erosion reduction, the group is based on measurements of the new trees crown in years, as well as in accumulated sediments per year by dams. In Albania, land (soil) loss through erosion is a widespread phenomenon in the whole territory of the country, in fields, hills, mountainous terrains and it covers all land resources such as: agricultural land, woodland, pastures, river, non-productive surfaces. Based on field data and a great deal of measurements as well as in our calculations applying the erosion equation, we draw out some results and here they are shown as erosion examples in order to calibrate the model. In Albania, land loss due to erosion is 2-3 times higher compared to other Mediterranean countries. Following the regional studies, which have been carried out in Albania, the level of erosion varies

through average limits of 25-40 ton/hectare/year. Nevertheless, on highly inclined and bare areas, under the impact of intensive rainfall, it reaches 180 ton/hectare/year. In approximately 25 % of the territory, the potential risk of erosion is high, reaching the limits of 60-180 ton/hectares/year. According to the data on the map of erosion's intensity in our country, it results that non-degraded or no-erosion territories cover approximately 48 % of the country; territories with small amounts of degradation (erosion intensity up to 300 ton/km<sup>2</sup>/year) cover 16 % of its surface; territories with average amounts of degradation (300-1200ton/km<sup>2</sup>/year) cover 12 %; territories with great amounts of degradation (erosion 1200-6000 ton/km<sup>2</sup>/year) include 14 % of the country and territories with extensive amounts of degradation up to desertion (6000 - 18000 ton/km<sup>2</sup>/year) cover 10 % of our territory. The database is not complete for indicators of soil loss calculation from erosion and also for the reduction of erosion rate from the implementation of works. The works will be more effective by implementing complex measures in the area as (dams, afforestation, couple fences etc.) In many cases the works have not started yet, because of the slope and it has caused in many cases the decrease of effectiveness of their work and the damage of the investment. In this case, the dams are filled with sediment within a year or are damaged. Overgrazing is one of the factors with a significant negative effect in raising the level of erosion as a result of natural grazing and young forests. Dense forests are not suitable for grazing (high forests of fir of streams and rivers). A sheep with its lamb consume 60 kg of dry matter per month. Charge in livestock (sheep and goats) is 87 % higher than the grazing capacity. Soil protection measures are implemented in 239 communities spreading over the whole country. The implemented measures directly reduce erosion or prevent the transport of the eroded material in the stream network.

**Key words:** erosion, watersheds, land loss, soil, environmental consequences, overgrazing

## EVIDENCE FOR ANTHROPOGENIC ENVIRONMENTAL CHANGE FROM ORGANIC GEOCHEMICAL RECORDS OF LAKE OHRID (ALBANIA, FYROM)

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### Abstract

Around 4,000 and 1,000 years ago, organic carbon and carbonate records of a sediment core from Lake Ohrid in the southwestern Balkans show distinct shifts that appear related to well-known Holocene climate fluctuations: the “4.2 ka event” and the transition from the Dark Ages (DA) to the Medieval Warm Period (MWP) at the beginning of the 10<sup>th</sup> century. The patterns observed in the proxy records may thus appear controlled by an entirely natural mechanism of ecosystem change. However, both periods are also known in archaeological and historical records for major social changes, collapse and migration as well as advances in technology. In order to investigate whether or not humans contributed to ecosystem change in the Lake Ohrid Basin, we analysed sedimentary lipid biomarkers and their isotopic composition (compound-specific carbon and hydrogen isotopes) across the observed changes in the sedimentary record. Once assigned to specific sources through isotope signature and end-member characterisation, biomarkers allow identifying changing contributions to the sedimentary organic matter from the principal organic matter pools, i.e. aquatic and terrestrial biomass as well as soils. Human interference such as deforestation and farming has the potential to tip the ecosystem out of its natural balance and, therefore, should be recognisable in biomarker profiles.

The 4.2 ka event is frequently observed in climate archives of the Northern Hemisphere. In the eastern Mediterranean and the Middle East it manifests itself as a prolonged period of severe droughts that were responsible for the collapse of some of the great empires of the Bronze Age (BA) such as the first Egyptian Empire or the Akkadian Empire. Closer to Lake Ohrid, it caused a significant decline in settlement density on the Greek mainland and the abandonment of some Aegean islands. In the Ohrid Basin, however, water never was a scarce resource. Inflow of goods and, potentially, people

from drought-affected areas is evident in the archaeological record. Over the duration of the 4.2ka event, our biomarker profiles show distinct fluctuations that we interpret as soil erosion events, based on our findings on lipid composition and isotopic signature. It is tempting to associate these events with population growth and deforestation due to the inflow of climate refugees from adjacent Aegean areas. However, this hypothesis needs to be confirmed by a focused approach that includes high-resolution work on well-dated sediments and, most importantly, is designed as close collaboration between geoscientists and archaeologists from the start.

The DA-MWP transition in Europe coincides with the rise of the medieval monastery as an institution managing land and agricultural production on an unprecedented scale and initiating the deforestation of extensive areas. Over the course of the 10<sup>th</sup> century, the monastery of St. Naum was founded at the southern shores of Lake Ohrid (905 AD), the town of Ohrid became the capital of the Bulgarian Empire and people moved from a defensive hill-top settlement towards the lake to establish what is now the town of Pogradec. Similar to the 4.2ka event, our biomarker results suggest an increase in soil organic matter supply that reflects the substantial changes in land use, triggered by a shift towards more favourable climate. In order to substantiate this conclusion we require further information on local medieval settlement history and land use change. Most important among these would be an initial date for the construction of the numerous agricultural terraces that can be found on many hill slopes around the southern shores of Lake Ohrid but appear out of use for a long time. Although intended to hold back soil and water, the terraces represent substantial earthworks the construction of which very likely contributed to some initial soil erosion.

## THE IMPACT OF WATER LEVEL AND SHORELINE CHANGES IN THE SUSTAINABLE DEVELOPMENT OF OHRID LAKE WATERSHED

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### Abstract

Lake Ohrid is the oldest lake in Europe and one of the oldest in the world. It is located in the border between Albania and Macedonia and represent a tectonic lake formed about 3 million years ago. A large number of endemic species and a unique aquatic ecosystem with worldwide importance are found in this lake. Like all natural ecosystems, it is in continue evolution due to the combined effects of natural and anthropogenic change. Indeed, the anthropogenic impacts are playing an increasingly important role in the dynamics of Lake Ohrid. The key challenges to long-term sustainability in the lake region are unplanned development, high density of tourists in a short season, water-quality deterioration and breaking of the natural fishery.

Furthermore, the drop of water level and expansion of the road Thana-Thushemisht along the western side zone have been recently additional pressures on the sustainable development. Consequently, it's needed an assessment for the impacts of the above mentioned additional pressures and a sustainability analysis of lake watershed within the Albanian territory.

Changes in water levels, materialised by a drop in the water level is recorded in October 2013, with water level decrease of 1.2 m below the lowest level recorded in 1990. Significant lake level drops would also increase the concentration of wastewaters, pesticides and chemical fertilizers which runoff from agricultural land, waste material deriving from the mining sites around the lake and a variety of industrial plants are likely to contribute to the pollution of the lake waters. All of these will have significant impacts on biodiversity for aquatic species of Ohrid Lake.

Shoreline changes – the expansion of the road Thana-Thushemisht, the road expansion along the western shore of the lake in the segment Lin-Hudenisht is made partly into shore and partly inland. In this way, a large amount of soils is moved into the littoral zone causing the destruction of habitat and reed-bed fragmentation, notably along the road segment Lin-Hudenisht. It includes a littoral length approximately of 5 km which is about 1/6 of all shoreline of Ohrid Lake in the Albanian territory. This damage has a significant impact on the lake's ecology.

In addition, along the road segment Lin-Hudenisht are constructing several new restaurants and hotels which will increase the negative trend.

In conclusion, these two additional pressures, the damage of about 1/6 of the Albanian littoral habitat and increased concentration of routine pollutants, will cause a negative impacts on biological-physical-chemical processes and as consequence, dramatic changes in species composition in the lake may be occurred.

In response to these pressures, it's suggested to reduce the fishing activity in general, fishing ban of threatened species and reducing tourism no more than 20 % of actual rate for 2 years at least. Every year, a sustainability analysis will be needed.



## WELL-ADMINISTRATION OF ALBANIAN TERRITORY THROUGH ENVIRONMENTAL GEOLOGICAL MAP SERIES

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### Abstract

The history of humanity since the day of its creation, is developed separately from the natural world of plants, animals, soil, air and water, which were created billions of years ago and the world of social institutions and artificial, created by mankind for serve and to use science, technology and political organization, which for the degree of integration continually cause tensions. From the time man believed to have power over nature, which brought no normal developments in theoretical and natural sciences, as well as contributed to the development of industry and agriculture unheard of, but these activity increased level of recent (and industry agriculture) undoubtedly resulted in the phenomenon of “environmental crisis” with the destruction of the physical conditions of life in general. Thanks to this all the way in the development of man has created its own ways and styles of life, customs, traditions and cultures that have made the difference in different countries or continents. Environmental or ecological crisis is characterized by air pollution (mostly from industrial emissions and car engines) together with rainfall, absorb pollutants from the atmosphere, have harmful effects on plants, animals, humans and all living things on earth, by contaminated water, mainly from industrial and mining waste, which mainly contain groundwater, sediments of various forms of artificial fertilizers, used in agriculture and residues of herbicides, insecticides and fungicides and where the greatest risk of pollution caused by urban waste water (especially from agents of detergents, etc.), by some human activities (cutting of trees, changing the course of rivers, etc.) often have significant negative impacts on vast territories and sometimes have global consequences (increasing desertification, erosion surfaces, changing climatic parameters) as results of concentrating population in major cities, which are related especially to infrastructure effects. And finally a very important aspect in the long road to

environmental protection is also regarding to the “eco” national product recognition technologies to reduce the amount of waste, through which is possible that reduced production of waste in minimum and transformed into secondary material resources. Two positive side are: conservation of resources and raw natural protection against environmental pollution. High pollution of natural environment should be discontinued as a phenomenon accompanying economic growth in developed countries, but also in countries that claiming to be developed, as is the case in Albania.

Based on new realities, with major concentrations and movements of population to the lowlands and valleys, as the most favorable conditions for a better life, the necessity of studying them (coastal lowlands, interior holes, river valleys, etc.) and their complexity, in order to create environments that, in relation to the community to be only beneficial, bringing goods and favorite livelihoods and current perspective for coming generations. As these territories, as well as all Albanides create interesting environments for man, not only require complex environmental-geological survey, but dictate and keeping them in constant monitoring to maintain the natural parametric values needed in relation to the parameters very vulnerable to human activity. These environments have values as landscapes, natural resources, therefore, should be used very carefully, especially in relation to sustainable decay values, not the maintenance of which cause chain reactions to the unrepairable damage. As such we can mention: river beds, underground water basins, new ground, erosional effects, etc. Necessarily the whole community and development require, first of all, sensibility, prognosis in other words, regarding the sensitivity and adaptability of lithological-formational series to any particularly affects, as groups, or in the total, taken together.

Thus, the series of maps has elaborated on the subject, Albanides, geologically, by regional map series (map of tectonic regionalisation,

geological map, litho-formational map, map of new depositions, map of the geological resources, geological-engineering map, map of river basins), and geological-environmental map series (map of geological observation sites, basic geological map, new tectonic zoning map, map of water-bearing basins, map of construction suitability, geological map for environmental protection, map of geological hazard). All above mentioned maps are based on geological formation, by potentials and properties involved in the study: georesources, water aquifers, construction suitability, environmental behavior towards pollution and geological and natural risks.

So, it comes to a presentation form that is dedicated to an important problem, necessary, more practice in regional context, around Albanides and perhaps beyond, as such relates to all complex mapping work, made so far, to build a series of maps, with the aim to reflect the latest scientific level, contemporary, unifying them under views and options, with the only purpose, that may have in well-administration and research of all Albanian territory. So, in other words, the Albanian territory, seen as a sum of geological formations with a spatial placement, in a dynamic evolution, can be controlled completely in scientific point, as composition, setting, origin, age, as potential resources, as water-bearing potential, as infrastructure and environmental potential, etc.

Of course in this presentation will not find methodical treatment of their preparation, which is also widely treated before, but the features that have Albanides by these points of view, which is treated for the first time and takes important values, not only scientific, but also applicative for the entire community and beyond, under which all make a living and socio-economic activities of their own.

It is understood that these maps were not built from the beginning, but are based on all existing maps, constructed previously: Geological Map of Albania 1:200,000 scale and explanatory text, published in 2004; Tectonic Map of Albania 1:200,000 scale and explanatory text, published in 1999; Neo-tectonic Map of Albania 1:200,000 scale and explanatory text, published in 1996; Metalogenic Map of Albania 1:200,000 scale, without explanatory text, published in 1999; Map of Mineral Resources of Albania 1:200,000 scale, published in 2011; Hydrogeological Map of Albania 1:200,000 scale, published in 1985; Geological Hazard Map of Albania 1:200,000

scale, published in 2000; Formational Geological Map of New Deposits of Albania, 2005. Only four maps: Geo-engineering map, construction capability, and geological-environmental and geological risk map, will be constructed for the first time within this recent study.

However the data for these phenomena, according to which the maps are built, are long-standing, almost contemporaneous with man, which until recently were treated separated from that geological context, the natural environment as a whole, with all its constituent elements. So, under these complex-studies, we can outline the development corridors, can determine human relations with nature, we can prevent risks and prevent the inevitable disaster. For example, according to these studies, human being is directed, where he can and must touch nature, to get its resources to the benefit of providing the goods, without prejudice to the next and future generations of his. These regional maps, give a more complete information on the properties of the upper part of lithosphere, associated with various figures and graphs, as the most appropriate tools to communicate with specialists from different fields to the general public. In this aspect, study orientates work concerning: With the use of man's land surface by physical features and characteristics, especially for expansion of urban space, the rational use of land and subsoil, the interpretation of links between geological units and units near the surface of agricultural land, the determination of the occurrence of the aquifer layers near the surface and in the depth, the determination of geological environments for collection, disposal and landfill waste and the sources of building materials, determination of geological-engineering characteristics of near surface geological units, etc.

In this context, the environment (landscape, land, resources) is treated as geological formation, with lithology, genesis and age, available for use by other studies in more detail in the service of the whole community to further increase in of goods, and in general the standard of living, enabling business strategy of sustainable development and efficient.

So, the object of the study are thicknesses of these deposits (geological formations) with all their characteristic: Geomorphological conditions (category of slopes, type of accumulation, etc.); Vertical and horizontal homogeneity of a rock body (total thickness, stratified, unstratified or lenticular development, homogeneity of lithology);

Mineralogical and petrographical composition (lack or presence of clay minerals, pyrite content, consolidated or unconsolidated clastics); Granulometric and soil mechanical characteristics (grain diameter, coefficient of permeability, compactness, porosity); Macrostructural parameters (stratification, fracturing); Tectonic conditions (seismicity, geodynamics); Surface stability (consolidated or unconsolidated surface,

threatened or no by surface movements); The presence of a mineral deposit (mineral deposits) in the subsoil of the study area or its neighborhood; Hydrogeological conditions (phreatic groundwater table, natural water content of rock strata).

**Key word:** *Albanides, Environmental-Geological Maps Series*

## GEOCHEMICAL EFFECT OF ULTRABASIC OPHIOLITIC ROCK CHEMISTRY AND ANTHROPOGENIC ACTIVITIES ON GROUNDWATER CONTAMINATION: THE CASE OF ATALANTI AREA, GREECE.

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### Abstract

A geochemical survey was undertaken in the greater area of Atalanti (Central Greece). The objectives of the study were to assess the possible effect of the ultrabasic ophiolitic rock chemistry, occurring in the area and the agricultural land use, to the concentration of environmentally important elements and chemical compounds in the groundwater. Thirteen groundwater samples were collected and analyzed by spectrophotometry, for the main anions and by flame photometry and atomic absorption spectroscopy, for the major and a number of trace elements. The interpretation of the analytical data showed that the content of the groundwater for a group of trace elements (e.g. Cr, Ni, Fe, Zn etc.) was considerably influenced by the chemical composition of the surrounding rocks, especially those of the ophiolitic series. The impact on the chemical composition of the groundwater varies, depending on the degree of serpentinization (weathering) of the ultramafic rocks. The impacts of seawater intrusion and anthropogenic activities on groundwater quality were also assessed. Samples located near the sea present elevated Cl concentrations up to 75 mg/L. In areas where the use of fertilizers and pesticides for agricultural purposes is extensive, an increase in concentration of various anions has been observed (average concentrations of 73.3 mg/L, 33.8 mg/L, and 0.2 mg/L for NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup> and PO<sub>4</sub><sup>-3</sup> respectively).

**Keywords:** groundwater geochemistry, trace element and anion concentration, ultramafic rocks, Atalanti, Greece

### Introduction

The quality of the groundwater in any agricultural-residential area, like the area of Atalanti, is considered as one of the most important concerns in environmental issues. The main factors controlling the groundwater quality are both natural (including e.g. the lithology of the area

of the aquifer, the types of interaction between water and aquifer and the quality of recharge waters (Chen et al. 2007) and the anthropogenic activities. The lithology of the area and the intense human activities are affecting the groundwater composition, by the introduction of potentially harmful, trace elements and chemical compounds. Thus, the assessment of the quality of groundwater and the maintenance of their quality is of major importance. It is indispensable to protect these resources and ensure their sustainability. The contamination of groundwater can pose long term environmental and health implications (Kabata-Pendias 2007).

Geologically, the studied area of Atalanti belongs to one of the westernmost Geotectonic Units of the internal zones of Greece, the Sub-Pelagonian unit (Aubouin 1959; Mountrakis 1985). The valley of Atalanti is comprised of Post-Alpine deposits (Fig. 1), mainly Quaternary-alluvial sediments, consisting of weathered material from the surrounding local rocks. In the surrounding rocky mountains appear different types of rocks e.g. limestone, dolomite, quartzite, flysch (see Fig. 1A), and rocks of the ophiolitic series, which are mostly ultrabasic rocks. These formations are observed to the south of the valley at higher topographic locations. Many of them were found near the village of Kirtoni. Petrological types of the ultrabasic rocks include peridotite, dunite, pyroxen-peridotite and olivinite. The degree of serpentinization varies (Aggelidis 1991; IGME 1965) from slight alteration to complete serpentinization, gabbro, gabbropegmatite. In addition, some basic rocks are also present including diabase-dolerite, pillow lava and spilite.

Many studies have proven that weathering of ultrabasic rocks, triggers the enrichment of specific elements in groundwater e.g. Co, Ni, Cr, As, Fe, Mn (Kabata-Pendias 1995; Economou- Eliopoulos et al. 2011; Kanellopoulos and Mitropoulos 2013). In the present research, an area in which mainly small scale agricultural activities take place was



**Table 1.** Concentrations of chemical and physicochemical parameters, hydrochemical type, SAR, EC, MH values and classification based on SAR-EC.

	Co	Cr	Mn	Ni	Fe	Zn	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>+2</sup>	Ca <sup>+2</sup>	PO <sub>4</sub> <sup>+3</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	T	pH	TDS	EC	Hydroc.	SAR-EC	SAR	MH
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	°C		g/lt	ms/cm	type	classif.		
AT-1	1.4	<0.2	1	1	270	18	35	5	41.3	49	0.12	35.2	16	23.6	312	18.5	7.36	0.26	0.3	Mg-HCO <sub>3</sub>	S1-C1	0.89	58
AT-2	0.8	4	<0.5	2	13	23	34	6	40.4	54	0.2	36.1	15	40	285	18.5	7.45	0.31	0.59	Mg-HCO <sub>3</sub>	S1-C1	0.85	55
AT-3	0.3	12	1	<0.6	4	15	36	5	44.7	45	0.19	23.3	3	34	300	18.9	7.17	0.35	0.67	Mg-HCO <sub>3</sub>	S1-C1	0.91	62
AT-4	0.7	23	3	<0.6	6	14	37	6	57.7	73	0.17	144	36	68	287	19.7	7.17	0.49	0.95	Mg-HCO <sub>3</sub>	S1-C1	0.79	57
AT-5	<0.2	6	5	<0.6	4	16	39	9	58.3	76.2	0.44	101	62	75.2	370	19	7.66	0.56	1.13	Mg-HCO <sub>3</sub>	S1-C2	0.82	56
AT-6	<0.2	25	5	2	6	29	31	11	55.1	70.4	0.38	113	64	63.6	293	19	7.74	0.54	1.08	Mg-HCO <sub>3</sub>	S1-C2	0.67	56
AT-7	<0.2	13	<0.5	<0.6	5	16	31	8	60.3	69.1	0.21	114	54	61.6	360	19.2	7.8	0.54	1.1	Mg-HCO <sub>3</sub>	S1-C2	0.66	59
AT-8	<0.2	2	<0.5	<0.6	3	12	20	3	41.1	42.4	0.1	7.5	8	30.8	360	20.7	7.88	0.32	0.66	Mg-HCO <sub>3</sub>	S1-C1	0.52	62
AT-9	<0.2	3	2	2	3	32	23	3	39.7	33.2	0.34	25.1	18	21.1	308	18.5	8.27	0.36	0.74	Mg-HCO <sub>3</sub>	S1-C1	0.64	66
AT-10	<0.2	3	3	5	4	15	21	4	37.2	32.6	0.22	35.2	15	50.4	262	18.5	8.22	0.36	0.73	Mg-HCO <sub>3</sub>	S1-C1	0.6	65
KL-1	<0.2	2	<0.5	15	3	<2	30	8	17.1	106	0.3	144	64	24.5	308	16	7.83	0.49	0.99	Ca-HCO <sub>3</sub>	S1-C2	0.71	21
KL-2	<0.2	2	<0.5	2	5	3	18	4	29.2	71.4	0.11	77.4	33	17.7	273	16.7	7.89	0.37	0.75	Ca-HCO <sub>3</sub>	S1-C1	0.45	40
KL-4	<0.2	2	<0.5	2	14	0.65	17	3	85.4	0.15	96.8	51	14.1	244	244	16.8	7.77	0.38	0.77	Ca-HCO <sub>3</sub>	S1-C1	0.44	41
PV.		50		20								50											

\* All samples have Cd <0.1µg/L. Pb≤1µg/L, \*\* All samples are from drills, except KL-1 and KL-2 which are from springs.

studied. The aim of this study is to assess the impact of both anthropogenic and natural factors on the geochemistry of groundwater.

## Materials and Methods

A total of 13 groundwater samples were collected from springs and boreholes mainly used for agricultural activities and water supply of local villages. Sensitive physicochemical parameters such as pH, temperature, electrical conductivity and total dissolved solids were measured in the field. All samples were vacuum filtered, acidified to a final concentration of 2 % nitric acid, stored in polyethylene bottles and preserved in a refrigerator. Water samples were analyzed in the Laboratory of Economic Geology and Geochemistry, University of Athens. The anion concentrations were measured spectrophotometrically (bicarbonate was measured by titration) while the major and trace element concentrations were measured by Flame Photometry and Atomic Absorption Spectroscopy (AAS).

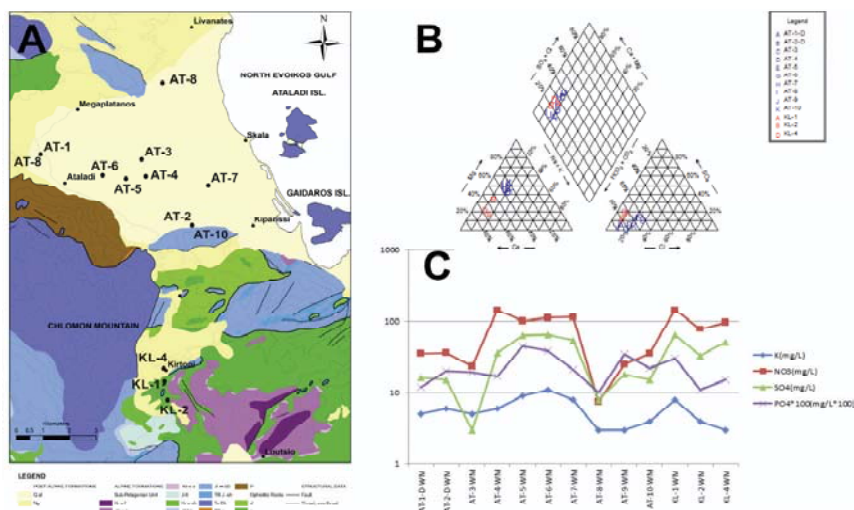
## Results and Discussion

Two distinct groups of groundwater samples are visible when results of major water parameters are plotted on the Piper diagram (Fig. 1B). Groundwater samples from Atalanti valley are of  $\text{Mg-HCO}_3$  hydrochemical type while the

samples from Kirtoni belong to the  $\text{Ca-HCO}_3$  type. This implies that the samples are collected from different aquifers, one developing within the post-alpine sediments of Atalanti valley and one developing within the weathered zone of the ultrabasic rocks of Kirtoni.

Atalanti groundwater samples also present high concentrations of Cr (up to 25  $\mu\text{g/L}$ ), Fe (up to 270  $\mu\text{g/L}$ ), Mn (up to 5  $\mu\text{g/L}$ ), Mg (up to 60  $\mu\text{g/L}$ ) and Zn (up to 32  $\mu\text{g/L}$ ). The sediments in the valley of Atalanti contain a percentage of weathered material from the ultramafic rocks. They could be characterized as serpentine soils (Kanellopoulos, 2011). While the samples from Kirtoni, which are neighboring occurrences of ultrabasic ophiolitic rocks present high concentrations of Ni (up to 15  $\mu\text{g/L}$ ). Enrichment of groundwater in these elements can be attributed to the impact of ophiolitic rocks (Robles-Camanco and Armienta 2000; Kabata-Pendias and Mukherjee 2007; Economou- Eliopoulos et al. 2011; Kanellopoulos, 2011; Namaghi et al. 2011; Kanellopoulos and Argyraki 2013; Kanellopoulos and Mitropoulos 2013). Soil also presents high concentrations of the same elements in the study area, especially Cr and Ni, even at long distances from the surface occurrences of the local ophiolitic rocks (Kanellopoulos 2011).

The highest concentrations of Cl (up to 75  $\text{mg/L}$ ) were measured in samples collected near the coast



**Figure 1.** (A) Geological map of the study area. Qal=Alluvial deposits, Ng=Neogene deposits, Kr o=f=Up. Cretaceous flysch, Kr o-k=Up. cretaceous transgressive limestone, Kr o-c=Conglomerates of the Up. Cretaceous, J-K=Lower Cretaceous limestones, Kr-o sh=Cretaceous to Kimmeridgian shales-cherts formation, J12-k=Up. Jurassic limestones, Ji-m kD=Middle and lower Jurassic limestones, TR J-sh=Middle to lower Jurassic shales-cherts formation, which also contain limestones, intercalated by ophiolites and their tuffs and serpentinites, Ts-Dk=Up.-Middle Triassic. compacted dolomites, TR-c=Conglomerate of the transgression of the Triassic system of layers, P=Permo-carboniferous layers (Graywackes, conglomerates, quartzites, violet shales, marly sandstones, green keratophytic tuffs), d=Diabase-Dolerite, p=Peridotite, dunite, pyroxenperidotite, olivinite. (B) Chemical composition of groundwater samples plotted in Piper trilinear diagram. (C) Diagram presenting the co-varying of K, NO<sub>3</sub>, SO<sub>4</sub> and PO<sub>4</sub> Cl at groundwater samples.

(Table 1) and displayed a decreasing trend towards the center of the valley. This observation provides evidence on the sea- intrusion front in the area. The co-variation of K, NO<sub>3</sub>, SO<sub>4</sub> and PO<sub>4</sub> (Fig. 1C) suggests their common source. The spatial distribution of their concentrations, points to the agricultural activities in the center of the valley of Atalanti and in lowlands of Kirtoni. Their source is probably the use of fertilizers. The serious impact from anthropogenic activities on the quality of groundwater in the valley of Atalanti has been also presented by Tsioumas et al. (2011).

In order to assess the suitability of the studied groundwater samples for human consumption, the analytical values were compared with the parametric levels imposed by the current relative legislation (Directive 98/83/EU). It is noted that the National Greek water quality legislation follows that of EU Directive 98/83/EU. More than half of the samples from both areas exceeded the parametric value for NO<sub>3</sub> (54 %) (Table 1). Specifically, the NO<sub>3</sub> content varies from 7.5 to 144 mg/L, while the parametric value is 50 mg/l. Also, the groundwater samples from the study area were evaluated for quality compliance with regulatory limits for agricultural use. They were classified in terms of salinity hazard (conductivity), sodium hazard (SAR) and magnesium hazard (MH). The SAR of groundwater samples ranges from 0.2 to 8.6. The samples are classified according to SAR categories as follows: S1-C1 (69 %) and S1-C2 (31 %). Magnesium hazard ranges from 21 to 66.4 and 77 % of the samples have MH >50, and are not recommended for irrigation (all samples from Atalanti presents MH >50).

## Conclusions

The results from the hydrogeochemical study of groundwater undertaken in the greater area of Atalanti in central Greece show that the chemical composition of the groundwater is controlled by the following three main factors: (i) the chemical composition of the local rocks (mostly ophiolitic), (ii) the introduction of sea water, for the samples located near the coast and (iii) the anthropogenic activities (mainly the extensive use of fertilizers and pesticides).

The impact on the chemical composition of the groundwater varies depending of the degree of serpentinization (weathering) of the ultramafic rocks from the ophiolitic sequence occurring in the area.

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## WHAT FUTURE FOR BIOFUELS IN ALBANIA

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### Abstract

Consumption of oil by-products continues to represent the major contribution in the total final energy consumption in Albania. The final consumption of hydrocarbons in 2011 was evaluated around 1133.2 ktoe or 59.2 % of total energy consumption. 67.7 % of oil by-products have been consumed by transport sector, which represents 37-38 % of total final energy consumption in the country. The transport sector continues to remain a permanent polluter of the environment representing the main contributor of the GHG emissions.

The EU has established a goal for 10 % renewable energy in transport by 2020. This target is set out in the EU renewable energy directive (Directive 2009/28), adopted in 2009 as part of the EU climate and energy package.

In frame of the commitments taken under the EU accession process and the Energy Community Treaty signed and ratified by Albania, the country has developed specific legislation whose sets specific targets to increase the contribution of the biofuels and other renewable combustibles in the total energy consumption in transport sector, which will not be less than 3 % of total fuels traded in the market. Starting from 2015 and after, this target will be not less than 10 %.

Biofuels are generally grouped in two large groups:

- First Generation Biofuels (biofuels from crops) produced from cereal crops (e.g. wheat, maize), oil crops (e.g. rape, palm oil) and sugar crops (e.g. sugar beet, sugar cane);
- Second Generation Biofuels (advanced sustainable biofuels) produced from crop residues, wherever there is an agricultural production, residues both from sustainably harvested and undergrowth forests, algae or other spontaneous vegetation and municipal solid waste represent other promising sources of feedstock.

Advanced Biofuels are the most attractive option for any environmentally friendly energy strategy as they are efficiently produced from different feedstock without competing with food or cash crops for fertile land and water, and reducing global GHG.

Based on the expected energy demand for oil-by products by 2020 in Albania, and assuming that the targets established in the effective legislation, about 100 ktoe are required to be met with biofuels. The enforcement of the legislation and the development of a specific National Renewable Energy Action Plan (NREAP) as stipulated by the new law on renewables require concrete commitments from the responsible authorities to take the necessary actions and measures for complying with the international commitments of Albania and the targets established by the national legislation.

The use of advanced biofuels in Albania may bring a number of potential benefits including, environment protection, energy security and economic growth, rural development and job creation.



## HEAVY METAL DISTRIBUTION IN AGRICULTURAL SOILS OF BREGU I MATIT, NW ALBANIA

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### Abstract

Agricultural soils in the Bregu i Matit area (NW Albania) have received for a long time significant inputs like irrigation with wastewater, fertilizers and pesticides. Although there was a potential risk of metal contamination of soil and plants and this risk has not yet been evaluated. This study was therefore undertaken in order to analyze the content of heavy metals cadmium, chromium, copper, nickel, lead, zinc and arsenic in irrigated and non-irrigated soils of this area in order to evaluate the soil pollution with these elements. Fifteen surface soil samples were collected from four sites (villages) in the study area and analyzed for chemical and physical properties by standard methods and for total form of heavy metals by inductively coupled plasma optical emission spectrometry (ICP-OES), after extraction with aqua regia. The level of soil pollution with heavy metals was evaluated using the enrichment factor and geo-accumulation index. Results indicate that the contents of cadmium, chromium and nickel of irrigated soils were significantly higher than non-irrigated soil, while contents of lead in three the irrigated sites, zinc and arsenic in one the irrigated site were significantly lower. Correlation analysis indicates that primary source of the first three metals was irrigation and the last three metals were originated from other anthropic sources like chemicals use, etc. Enrichment factor ( $E_f$ ) calculation shows that irrigated soils were most enriched in cadmium, chromium, copper and nickel.

The index of geo-accumulation ( $I_{geo}$ ) indicates that agricultural soils of Bregu i Matit are unpolluted to moderately polluted with cadmium, chromium, copper and zinc and moderately to strongly polluted with nickel and arsenic. The presence of heavy metals in the studied soils indicates potential risk of transfer of these elements in the food chain. Therefore, further detailed studies are necessary to investigate the mobility of heavy metals in soil.

**Keywords:** *agricultural soil, heavy metal, geo-accumulation index, pollution, Bregu i Matit*

## HEAVY METAL MOBILITY IN AGRICULTURAL SOILS OF BREGU I MATIT, NW ALBANIA

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### Abstract

Fifteen soil samples were collected at four different sites on Bregu i Matit (NW Albania) and analysed for mobile forms of heavy metals using inductively coupled plasma optical emission spectrometry (ICP-OES), after extraction with  $\text{NH}_4\text{EDTA}$  and  $\text{NH}_4\text{NO}_3$ , in order to evaluate the risk of soil pollution with these metals. The results indicated that the  $\text{NH}_4\text{EDTA}$  extractable As, Cr and Ni and  $\text{NH}_4\text{NO}_3$  extractable Cr, Cu, Ni and As increased significantly in the irrigated soils as compared to non-irrigated soil. The higher metal proportions extracted with EDTA are found for Cd 33.6%, Cu 11.34%, Pb 11% and Ni 1.37%, and for Cd 0.70% and Cu 0.28% extracted with  $\text{NH}_4\text{NO}_3$ . The order of metal extractability in EDTA was:  $\text{Cd} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Zn} > \text{As} > \text{Cr}$  indicating that Cd and Pb are associated with organic matter more than Cu and Ni, and in  $\text{NH}_4\text{NO}_3$  was:  $\text{Cd} > \text{Cu} > \text{Pb} > \text{Ni} > \text{As} > \text{Zn} > \text{Cr}$  which corresponds to the sequence of metal mobility. Only the Pb was proportional to the total content in aqua regia. The mobility of Cd, Cu, Ni, Pb and Zn is controlled by soil pH. Although there is no actual harmful pollution of soils with heavy metals, a potential risk of soil and plants pollution with Cd, Cu and Pb exists, because their mobility and bioavailability can be increased due to soil acidification.

**Keywords:** agricultural soil, ecological risk, heavy metal, mobility, Bregu i Matit

### 1. Introduction

The agricultural soils of Bregu i Matit (NW Albania) have received the agricultural inputs, including irrigation water from the polluted Mati River (Gjoka et al., 2010) over many years. Consequently, these soils are threatened by heavy metal contamination. This may have led to contamination of the food chain. In order to prevent this risk, assessing the heavy metal accumulation in soil is necessary. According to Takáč et al. (2009), the knowledge of the bioavailable forms

of heavy metals in soils is important to potential risk assessment. This is because the ecological effect of metals are related to mobile fractions rather than to total contents in the soil (Erhart et al., 2008). In this study, we analysed the mobile and potentially plant available forms of heavy metals Cd, Cr, Ni, Cu, Zn, Pb and As in order to evaluate the pollution level and potential ecological risk of these heavy metals.

### 2. Materials and methods

Soil samples (0-25 cm) were taken with soil auger from plots under various crops and with different irrigation history in four sites on the Bregu i Matit: site 1 (S1-control, Pillane village); site 2 (S2 Gajush village); site 3 (S3 Shenkoll village); and site 4 (S4, Rrile village). The results of chemical and physical properties and total metal content of the studied soils are described in detail by Kasa et al. (2014). For this study, the soil samples were analysed for mobile (at 1 M  $\text{NH}_4\text{NO}_3$  extract) and potentially plant available (at 0.025 M  $\text{NH}_4\text{EDTA}$  extract) forms of Cd, Cr, Ni, Pb, As, Cu and Zn in the labs of the Institute of Soil Science and Soil Conservation of the Justus-Liebig University Giessen (Germany). The metal concentrations in the extracts were measured with an inductively coupled plasma optical emission spectrometry (ICP-OES). Analysis of variance and least significant difference (LSD) test were used to find out statistical differences in mobile contents of heavy metals between sampling sites. Significance threshold was  $p < 0.05$ . Statistics were performed using SPSS 19. Level of soil metal pollution was determined based on comparison with threshold values by BBodSchV (1999).

### 3. Results and discussions

#### 3.1 Heavy metal mobility in the soil

The mobility of heavy metals was expressed in terms of content extractable with EDTA and  $\text{NH}_4\text{NO}_3$ . The  $\text{NH}_4\text{EDTA}$  fraction gives a good

estimate of the potentially plant available metals (Felix-Henningsen et al., 2007), and the  $\text{NH}_4\text{NO}_3$  fraction gives an indication of the immediately plant available metals (Barbooti et al. 2010). The  $\text{NH}_4\text{EDTA}$  extractable metal contents varied: Cd 0.03-0.08  $\text{mg kg}^{-1}$ , Cr 0.03-0.06  $\text{mg kg}^{-1}$ , Cu 4.08-9.81  $\text{mg kg}^{-1}$ , Ni 2.39-10.04  $\text{mg kg}^{-1}$ , Pb 0.69-2.9  $\text{mg kg}^{-1}$ , Zn 0.31-1.83  $\text{mg kg}^{-1}$ , and As 0.002-0.016  $\text{mg kg}^{-1}$ , with the higher mean values for Ni and As in the irrigated sites. But, only in some sampling points the As, Cr and Ni contents showed higher statistically significant differences. The percentages of heavy metals in this fraction varied considerably between sampling sites (Tab. 1).

The highest extractability of Cd 48%, Cu 16.4%, Pb 13.4%, Ni 2.0% and Zn 1.3% was found in S1, where the soil pH is lower. In general, the extractability of heavy metals by EDTA in the studied soils was as follows: Cd>Cu>Pb>Ni>Zn>As>Cr. This order does not corresponds to the constant of metal-EDTA complex stability (Harmsen, 1977). This suggests that Cd and Pb are respectively associated with organic matter more than Cu and Ni. The low extractability of Cr 0.02% is explained by its solubility that decreases above pH 4 (Alloway, 1995), and of As 0.05% by the fact that EDTA does not form stable complexes with arsenic (Tokunaga & Hakuta, 2002). The EDTA extractable metal contents were proportional to the total content only for Pb ( $r=0.80$ ,  $p<0.001$ ), while the non-significant correlations were found for other metals. This suggests that the  $\text{NH}_4\text{EDTA}$  (0.025 M, pH 7) is a very good extractant for Pb in the studied soils.

The amounts of metals extracted by  $\text{NH}_4\text{NO}_3$  are markedly smaller than those extracted by EDTA. This is expected after  $\text{NH}_4\text{NO}_3$  is a weaker extractant than EDTA. This metal fraction varied: Cd 0.001-0.003  $\text{mg kg}^{-1}$ , Cr 0.002-0.01  $\text{mg kg}^{-1}$ , Cu 0.12-0.235  $\text{mg kg}^{-1}$ , Ni 0.014-0.794  $\text{mg kg}^{-1}$ , Pb 0.001-0.015  $\text{mg kg}^{-1}$ , Zn 0.002-0.031  $\text{mg kg}^{-1}$ , and As 0.001 to 0.007  $\text{mg kg}^{-1}$ , with the higher mean values for Cr, Cu, Ni and As in the irrigated sites. Only in some sampling points the Cr, Cu, Ni and As contents showed higher statistically significant differences. The percentages of heavy metals in this fraction varied greatly between sampling sites (Tab. 2).

The highest extractability of Cd 2.6%, Ni 0.07%, Pb 0.09% and Zn 0.03% was found in S1. The extractability of the metals by  $\text{NH}_4\text{NO}_3$  followed the order of Cd>Cu>Pb> Ni>As>Zn>Cr. This corresponds well to the sequence of metal mobility and to metal extractability by EDTA for the first four metals. The  $\text{NH}_4\text{NO}_3$  extractable metal contents were proportional to the total content only for Pb ( $r=0.64$ ,  $p<0.01$ ). This indicates that the 1 M  $\text{NH}_4\text{NO}_3$  is a good extractant for Pb. The significant correlation between the  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{EDTA}$  metal contents are found for Ni ( $r=0.72$ ,  $p<0.005$ ) and Pb ( $r=0.57$ ,  $p<0.025$ ). The correlation analysis has shown that this fraction of Cd, Cu, Ni, Pb and Zn is controlled by pH.

### 3.2 Soil pollution assessment

The  $\text{NH}_4\text{NO}_3$  extractable metal contents are used to assess the level of pollution and potential ecological risk of heavy metals in soil (Tab. 3).

**Table 1.** The  $\text{NH}_4\text{EDTA}$  extractable metal contents as a percent of total content

Site	Cd	Cr	Cu	Ni	Pb	Zn	As
S1	48.02	0.03	16.40	2.01	13.38	1.31	0.00
S2	38.71	0.03	11.16	0.86	12.78	0.96	0.15
S3	35.82	0.02	8.86	1.20	11.22	1.05	0.02
S4	26.36	0.02	10.19	1.57	7.34	0.49	0.01
Mean metal content for all sites	33.63	0.02	11.34	1.37	11.03	0.93	0.05
Mean metal content for irrigated sites	33.63	0.02	10.07	1.21	10.45	0.83	0.06

**Table 2.**  $\text{NH}_4\text{NO}_3$  extractable metal contents as a percent of total content

Site	Cd	Cr	Cu	Ni	Pb	Zn	As
S1	2.560	0.002	0.310	0.070	0.090	0.030	0.000
S2	0.673	0.002	0.330	0.013	0.048	0.003	0.060
S3	0.682	0.002	0.238	0.017	0.048	0.005	0.037
S4	0.738	0.001	0.320	0.063	0.038	0.008	0.000
Mean metal content for all sites	0.703	0.002	0.285	0.031	0.044	0.005	0.023
Mean metal content for irrigated sites	0.698	0.002	0.296	0.031	0.045	0.005	0.032

**Table 3.** The measured and trigger/action values for  $\text{NH}_4\text{NO}_3$  heavy metals ( $\text{mg.kg}^{-1}$ )

Site	Cd	Cr	Cu	Ni	Pb	Zn	As
S1	0.003	0.002	0.168	0.130	0.015	0.031	0.000
S2	0.001	0.004	0.217	0.043	0.006	0.002	0.002
S3	0.001	0.004	0.158	0.070	0.005	0.004	0.001
S4	0.001	0.003	0.163	0.290	0.005	0.010	0.000
Trigger value		-	1	1.5	0.1	2	0.4
Action value	0.04*/0.1						

\* for soils of fields used for cultivation of bread wheat and Cd accumulating vegetables

The results show that the metal contents in all the studied soils lies under these values. This means there is no actual harmful pollution of soils with metals. Nevertheless, having a low content of heavy metals extracted by  $\text{NH}_4\text{NO}_3$  does not always mean a lower risk of metal transfer into the food chain. Narimanidze et al., (2003) reported severe accumulations of Cu, Zn and Cd in spinach and other food crops despite of a low concentration of heavy metals in the  $\text{NH}_4\text{NO}_3$  extract. In an ecotoxicological study of these soils, the knowledge of heavy metal contents in plants is important. On the other hand, the relatively high proportion of Cd, Cu and Pb in EDTA fraction, suggest a potential risk of soil pollution by these metals associated with increasing their mobility and bioavailability due to soil acidification. The  $\text{NH}_4\text{NO}_3$  fraction of Cd above 2% in non-irrigated soil and close to 1% in all the studied soils indicates a low actual ecological risk to the environment.

#### 4. Conclusions

The study indicated that  $\text{NH}_4\text{EDTA}$  extractable As, Cr and Ni and  $\text{NH}_4\text{NO}_3$  extractable Cr, Cu, Ni and As increased significantly in the irrigated soils. The EDTA shows a higher extractability of heavy metals than  $\text{NH}_4\text{NO}_3$ . The higher proportions of heavy metals extracted with EDTA are found for Cd, Cu, Pb and Ni, and for metals extracted with  $\text{NH}_4\text{NO}_3$  are found for Cd and Cu. The order of metal extractability with EDTA suggest that Cd and Pb are associated with organic matter more than Cu and Ni. The EDTA and  $\text{NH}_4\text{NO}_3$  extractable metal contents are proportional to the total content only for Pb, while the non-significant correlations are found for other metals. The mobility of Cd, Cu, Ni, Pb and Zn is controlled by soil pH. There is no actual harmful pollution of the studied soils with heavy metals, but the relatively high proportion of Cd, Cu and Pb in EDTA fraction indicates a potential risk of soil pollution.

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## ASSESSMENT OF HEAVY METAL CONTAMINATION IN SEDIMENTS OF THE KARAVASTA LAGOON, ALBANIA

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### Abstract

A study was conducted between April 2013 and December 2014 in the Karavasta Lagoon, an important ecological and economical area situated in the central part of western lowland in the Adriatic Sea, with a surface of 4600 hectares and a depth of 1.3 m. The lagoon sediments are contaminated with heavy metals through various sources such as Shkumbini and Semani river flows, intensive agricultural activities in the lagoon area and urban discharges. This study aims to evaluate the level of pollution caused by heavy metals in the sediments of Karavasta lagoon. The sediments samples from the lagoon have been collected in eight strategically selected sites during April, July 2013 and December 2014 in order to measure the impact of all potential contamination sources. The data on heavy metals (Pb, Cr, Cu, Cd) were obtained using the EPA Nr 3050 B method and the flame AAS Atomic Absorption Spectrophotometer. The results showed that the Pb, Cr, and Cu values were higher than the average values found in some of Mediterranean and Albanian lagoons. The sediment pollution assessment was undertaken using Enrichment Factor (EF). The Enrichment Factor values (EF) for Pb and Cu in

some stations showed moderate pollution, while Cr in all stations is enriched in the sediment. The Enrichment Factor (EF) among the heavy metals in the lagoon produced the following outputs: Cr > Cu > Pb. This study suggests that the sources of this contamination are the alluvial sediments coming through Shkumbini River from ultramafic areas, anthropogenic input, previous agricultural activities, contributions of the tributaries and the fish processing center.

**Key words:** *Heavy metals, sediments, assessment, Karavasta lagoon, Enrichment Factor*

## DYNAMIC OF ALBANIAN COASTAL LINE MOTION AND FACTORS RELATED (CASE: PATOK – SHENGJIN SECTOR)

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### Abstract

The coastal line motion in Albanian seaside is the most visible phenomenon and with the biggest impact in this zone. To the coastal line dynamic is closely related to the natural ecosystems, which form the coastal zone. The Adriatic Sea has an evidently coastal dynamic compared to the Ionian Sea, because and factors which define this dynamic are more complex.

The Patok – Shengjin sector composes one of the most dynamic of the Adriatic coast, for the fact that there are two of the most important rivers of Albanian hydrographic network (Mati River and Drini River), which operate in one bay.

The coastal line motion defines forms and dimensions of the new littoral formed as result of the accumulation of the sediments, also the quantity of the destroyed ecosystems as result of sea erosion.

Both phenomenons are related to complex factors, among them three are the main: geo-tectonical factors, climacteric factors and human factors. These factors have the biggest impact, as operating separately and also operating in combination with each other. The way how these factors operate in this zone, gives the environment impact, what is related directly to coastal line dynamic.

The geo-tectonic factors are related to the phenomenon like the lithology of the coastal line, quantity and the way how the sediments move along the sea shore, tectonic activity (neotectonic) ect.

The climatic factors which have direct impact on the dynamic are; quantity of the rainfalls (river flows), temperature, winds and their direction, sea waves and the increase of level sea.

The human factors are uncontrolled intervention of the human in the ecosystems which compose the coastal zone. Recently is observed a concentration of people in the coastal zone intervening in the ecosystems, so in some cases this factor become

the main one.

The used methods about the study of the coastal line motion in Patok – Shengjin sector, have been mainly the geological and topographic ones, what has made possible to give some parameters that assess the tendency rate of the coastal line movement and its environment impact on the ecosystems.

The Mati River delta is very dynamic, what has had a visible impact in the forming of the new ecosystems (Patok lagoon, also the new littoral zone nearby).

For the analyzed period in this study results: until 1985, the Mati River delta has been a fan composed of three outfalls, where the main has been the middle. During this period the delta had an accumulative regime, where the sea is withdrew 200 to 250 meters in center of the delta. After this period, starting from 1985, the position of the river outlet has changed going to the south, advancing about 500 meters, and as result is formed e new littoral (new Patok beach), with a length of about 2.1 km.

Drini River delta, had and continues to have an evidently dynamic, this is related to Drini River story, which has been subject of many changes as result of human interventions along its bed. The Drini River delta has visible impact on the other ecosystems, which are related to collaboration between the Drini River and Adriatic Sea (coastal line, beaches, dunes, wetlands, lagoons etc.).

This delta results to bee an erosive delta since 1944 until 2012. From 1944 up to 1985, the eroded surface has been about 6.1 Ha; from 1985 to 2012 the eroded surface has been 41 Ha.

As result of the collaboration between the rivers and the sea in this segment (Patok - Shengjin), the configuration of the coastal line has changed continuously.

**Keywords:** *coastal line dynamic, delta, ecosystem, erosion, accumulation*

## ASSESSING THE MOBILITY AND BIOAVAILABILITY OF HEAVY METALS IN AQUATIC ENVIRONMENTS

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### Abstract

Heavy metals released in streams, rivers and lakes may be transported as suspended, colloidal and more or less dissolved. Assessing the fractions of heavy metals will give measures of mobility and bioavailability. There are experimental methods like filtration, ultrafiltration and dialysis. These methods can be complemented by speciation through geochemical modelling with PHREEQC and MINTEQ.

This study has used filtration and dialysis in a river in Albania and in some streams in northern Sweden. The rivers Fani and Mati in northern Albania host in their catchments large amounts of waste from mining and metallurgy activities. The concerns in this connection are biotoxicity in the river itself, risk of spreading heavy metals into a large coastal aquifer (Kumanova et al. 2014) and uptake of heavy metals by the offshore farm-raised blue mussel (Joksimovic et al. 2011). By analysing unfiltered, filtered (0.2  $\mu$ m) and dialysed (10 and 1 kDa pore size), in the river water has been found that close to point sources, a notably large amount of copper is present in suspended form thus less mobile and bioavailable. Zinc and nickel were more mobile. The levels of heavy metals decreased rapidly in the point sources in downstream mirroring a rapid settling of the suspended and colloidal fractions. Sequential extraction of river sediments indicates that chromium and nickel are abundant in silicate minerals from the ophiolitic rock. This is also evident from sequential extractions from the offshore sediments of Drin and Mati rivers, in the Adriatic coast (Rivaró et al. 2007). The total elemental analysis of sediments do overestimate the risk of notably chromium and nickel pollution. The study indicates that the bioavailability of the heavy metals is low.

Arsenic is high in sediments close to point sources but the ferric oxyhydroxides provide a very efficient sink for the arsenic at oxidising conditions (Jacks et al. 2013). Provision of sedimentation dams close to the point sources would decrease the transport which is likely to occur to a larger extent only during high flow occasions. An important factor in decreasing the mobility and bioavailability is a good buffering in the river water provided by carbonate rocks and not least, the ophiolitic rocks that dominate the bedrock in the catchment.

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## Geoenvironmental Peculiarities of the Territory of Georgia.

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### Abstract

The uncontrolled relationship between the humanity and nature is a bigger threat to the existence not only for nature but also for human. The modern development of the industry, together with the positive factors gave rise to a negative tendency that is expressed in the global pollution of our Planet. The territory of Georgia is not exception. Based on the results of our study between 2000-2012, the general state of contemporary geoenvironmental protection of Georgia was strongly affected by geochemical, hydro chemical, biochemical and radiological pollution and man-made waste. Special concern is caused by mining industry. The environmental pollution index near the mining enterprises reaches catastrophic values. These are the cases of Madneuli (South-East Georgia) copper-gold mine, Chiatura (Central Georgia, Imereti district) manganese deposit and now not operational, Uravi (North Georgia, the Southern Slope of the Greater Caucasus Ridge) arsenic deposit and processing plant. At these facilities has been a steady deterioration of the geoecological conditions. As a nuclear pollution of anthropogenic origin (recorded after the Chernobyl accident), in Georgia there are natural radiation anomalies of U, Ra, Th, K etc.

These anomalies in the majority of cases are associated with granites (mainly Paleozoic) and Middle Jurassic coal rakes and are often located near settlements. The research conducted in 2012 showed that the level of contamination of anthropogenic origin has decreased. According to the results of hydrogeological and hydrochemical investigations of the rivers in Georgia, we indicated three types of their environmental systems: well-protected, poorly protected and not protected. Bacterial contamination of the river was observed in the western part of Georgia (on the Black Sea coast), where the industrial waste water flows into the sea and pollutes the coastal zone.

As a result of these studies is create 1:500,000 scale geoecological map of the territory of Georgia. Our studies have shown the necessity for continuous geoecological monitoring of the territory of Georgia.



## ASSESSMENT OF HEAVY METAL POLLUTION IN THE AREAS SURROUNDING THE ELBASANI METALLURGICAL COMPLEX IN ALBANIA AND PROPOSED MITIGATION ACTIONS

Luli K.

### Abstract

The study area is located in the surrounding zones of the Metallurgical complex of Elbasan in central Albania, affected by heavy metals more than 30 years ago.

The country is changing rapidly economically and politically getting closer to EU accession imposing the need for updating legislation. Complex urban and rural transformations, with social, economic and land use consequences pose severe threats to the environment. Various forms of soil degradation are present throughout the country, and chemical pollution is one of them.

The presence of large areas covered by ultra basic rocks is a prerequisite for natural heavy metal contamination.

The aim of this work was to evaluate the heavy metal (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Pb, S, Si, Ti and Zn) pollution in the area surrounding the Elbasani Metallurgical complex and their spatial distribution. The comparison of the soil heavy metal concentrations with the allowable internationally recognised benchmarks has been processed using a Grapher and Surfer systems able to produce thematic maps and SPSS system to perform statistical analyses.

51 GPS referenced soil samples were collected (randomly) from the agricultural topsoil (0-30 cm) in an area of about 2,000 ha and were stored

in polyethylene bags. Samples were analysed according to ISO methods. Heavy metals were determined by spectroscopy of atomic absorption treated with strong acids and distillate water.

Results show that soil pH range from alkaline to neutral (pH 6.3-7.3) and are highly polluted with Ni (2904 mg/kg), Cr (2954 mg/kg) and Cd (9.5 mg/kg) that are higher than the EU maximum permissible thresholds. Soil texture is predominantly silty clay loam, soil structure is mostly granular to sub angular blocky, soil depth is higher than 2 metres and water table could be found at 1 m depth. Environmental problems were clearly identified by severe increase in cancer and asthma cases, confirmed also by the field interviews. Attention should be given to the delineation of contaminated areas that should off limits to humans, livestock and urban/rural development.

Mitigation techniques such as bio and phytoremediation, rehabilitation of drainage system and environmental policies must be applied.

**Key words:** Heavy metal, soil pollution, Metallurgical complex of Elbasan, permissible EU limits, mitigation, remediation.

## Air pollution in Hani Elezi from emissions of CO<sub>2</sub> and SO<sub>2</sub> through Cement Factory

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### Abstract

Fresh air is essential for human life as well as for the health of all ecosystem. Air is a mixture of gases and aerosols that composes the atmosphere containing approximately 4/5 nitrogen, 1/5 oxygen and a small amount of inert gases, carbon dioxide, hydrogen, ozone, water vapors and various impurities. Air pollution affects in different ways human health and all ecosystem. Atmosphere serves as transporter of polluted substances contaminating land, air and water. Air pollution depends on types of pollutants. The main sources of pollution of the atmosphere are habitat heating, industrial activities and traffic. The most frequently pollutants are carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and micron particles of soot. Specific materials of air pollutant are also lead, cadmium, manganese, arsenic, nickel, chromium, zinc, other heavy metals and organic compounds created as a result of various activities.

In this study are presented emissions of carbon dioxide (CO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) at the Cement Factory in Hani Elezi. In this plant, till 1999, was used only mazut as fuel for cement clinker ripening.

After the process of commercialization of the Commentary Factory from the Swiss company "Sharr Beteiligungs GmbH" and subsequently privatization by the Greek company Titanic, use mazut and petroleum coke as raw material for clinker ripening process because is cheaper, but the coke content has more sulfur. In the past is known that exploitation of factory capacities and also emission of the gases were too low.

Nowadays, these reports have changed and exploitation capacities of the factory are near the 100 %. Also, by knowing that mazut and petroleum coke contains considerable amount of sulfur (2, 8 % and 4.57 % , respectively) are considered high contaminants of atmosphere. According to a calculation balance, the value of emitted gases in the atmosphere is about 373.431,77 t CO<sub>2</sub>/year and about 2903,688 t SO<sub>2</sub>/year. These results are in alert because the company "Titanik" is raising the report of containing petroleum coke in general value of fuel, as consequence of increasing levels of SO<sub>2</sub> emitted in the atmosphere.

By the result on this study, we can see that the amount of gas, micron particles of soot emitted in the atmosphere is very high. The residents of this location are threatened by various diseases as result of inhalation of dust particles through respiratory organs in organism. It is known that these particles, along their path in the atmosphere, absorb certain elements from various gases which are harmful for the human body causing the most common disease in this locality, i.e. silicosis. One of the most important challenges will be the reduction of emission of gases and dust from the cement factory in Hani Elezi.

**Key words:** *Mazut, petrol coke, clinker, cement, pollution.*

## GEOCHEMISTRY OF HEAVY METALS IN URBAN SOILS: AN ENVIRONMENTAL STUDY IN THE CITY OF TIRANA, ALBANIA

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### Abstract

This paper presents data on the geochemistry of heavy metals in the urban soils of the city of Tirana, Albania. The urban soils of Tirana were sampled at 5-10 cm depth. The content of heavy metals (Pb, Zn, Cu, Fe, Mn, Cr) in the samples was determined by atomic absorption spectrometry (AAS). Multivariate statistics and GIS techniques were applied to identify the elements influenced by the anthropogenic activity and map the spatial distribution of the heavy metals. Factor analysis identified a group of elements influenced by anthropogenic activity. In the maps of the spatial distribution of the heavy metals were observed significant anomalies, especially for Zn, Pb and Cu. The elevated contents of the heavy metals in the urban soils of Tirana are due to the industrial activity within the urban area. Another important source of pollution is the impact of the traffic. The elevated contents of heavy metals in the urban soils may imply potential health threat for the residents of the polluted areas of the city.

**Key words:** *geochemistry, heavy metals, soils, urban area, Tirana*

### 1. Introduction

The city of Tirana, the capital of Albania, was distinguished for a considerable activity of the mechanical and chemical industries especially since the 1960s. Nowadays the activity of the mechanical and chemical industries is reduced, but the traffic has increased in the last twenty years with a notable impact on the air quality. The studies have documented pollution of the urban soils with heavy metals (Purves, 1966). This study focuses on the investigation of the

spatial distribution of the heavy metals (Zn, Pb, Cu, Mn, Cr and Fe) in the urban soils of Tirana, the capital of Albania. This is the first time such an environmental geochemical study is carried out for the urban soils of Tirana. The purpose of the study was to map the spatial distribution of the heavy metals in the urban soils of Tirana, identify the polluted areas and main sources of pollution with heavy metals of the urban soils of Tirana.

### 2. Sampling and analysis

A sampling net of 500 x 500 m (Quevauviller, 2001; Mazreku and Cara 2006) was applied. The soils were sampled at 5-10 cm depth. Each of the samples is the composite of four subsamples and consists of 200-300 g. In this way were collected 289 samples (Fig. 1).

The samples were analyzed at the chemical lab of the Albanian Geological Survey. Solutions were produced by acid extraction using four acids (HNO<sub>3</sub>, HClO<sub>4</sub>, HCl and HF). The samples were analyzed by atomic absorption spectrometry (AAS).

### 3. Results and discussion

#### 3.1. Analytical results

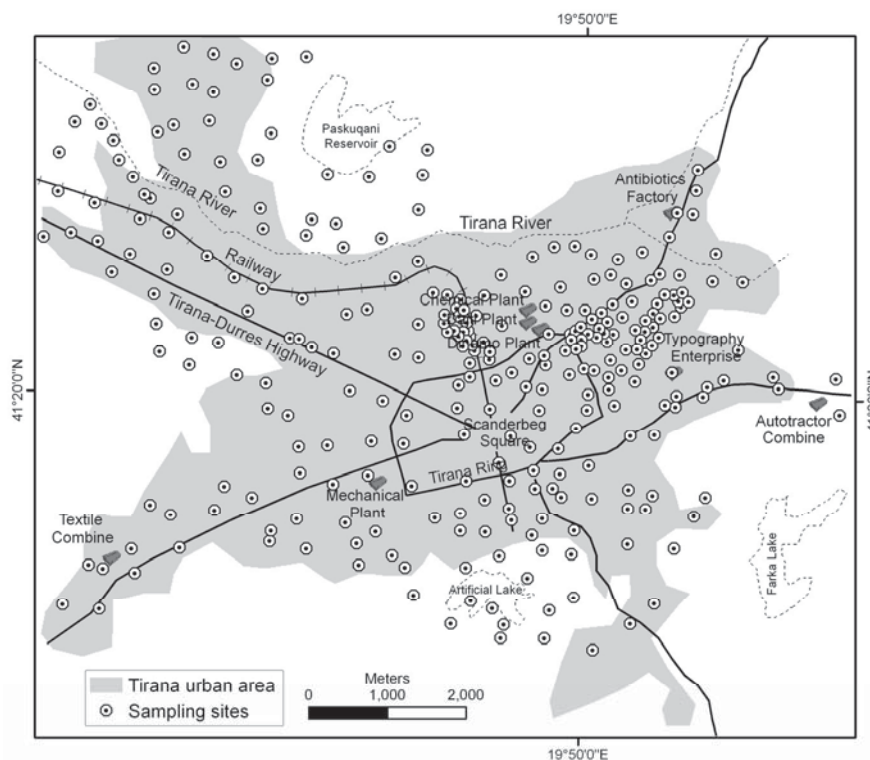
Descriptive statistics of the content of heavy metals in the analyzed urban soil samples is presented in Table 1.

#### 3.2. Factor analysis

The factor analysis requires a normal distribution of the variables (Reimann et al. 2002; Howarth, 1983). In general the distribution of the heavy metals in our dataset was log-normal. Three factors were calculated (Table 2) using the stats package

**Table 1.** Descriptive statistics of element concentration in the urban soils of Tirana, depth 5-10 cm.

	Cu ppm	Zn ppm	Pb ppm	Fe wt%	Mn ppm	Cr ppm
Mean	57.2	145.7	68.27	3.19	790.2	211.8
Median	48	107	55	3.050	725	198
SD	46.10	130.24	97.09	0.78	291.53	134.8



**Figure 1.** The location of the soil samples collected in the urban area of Tirana, Albania.

in the R environment for statistical analysis. We interpret the Factor 1 and Factor 2 to be related to anthropogenic processes (pollution in the urban soils with heavy metals due to industrial activity). Factor 3 is interpreted to represent geogenic (natural) distribution of the heavy metals in the

the maps of the spatial distribution of the heavy metals. Most polluted areas are close to the plants as it can be seen in the geochemical anomalies map of Pb and Zn.

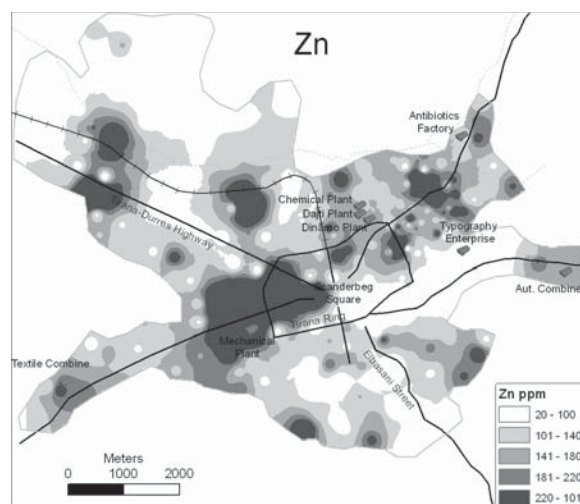
**Table 2.** Factor loadings based on log-transformed data

	Factor	Factor	Factor
Elements	1	2	3
Cu	0.977		-0.182
Zn	0.300	0.758	
Pb		0.329	-0.235
Fe	0.318	-0.124	0.366
Mn	-0.178	0.343	
Cr	-0.170		0.650
Proportional			
Variance	0.201	0.138	0.109
Cumulative			
Variance	0.201	0.339	0.448

urban soils.

### 3.3. Spatial distribution of the heavy metals in the urban soils of Tirana

Maps of the spatial distribution of the heavy metals (Figure 2) were prepared by inverse distance weighting (IDW) algorithm using the ArcGIS® software. Pollution of the urban soils of Tirana due to anthropogenic activity can be observed in



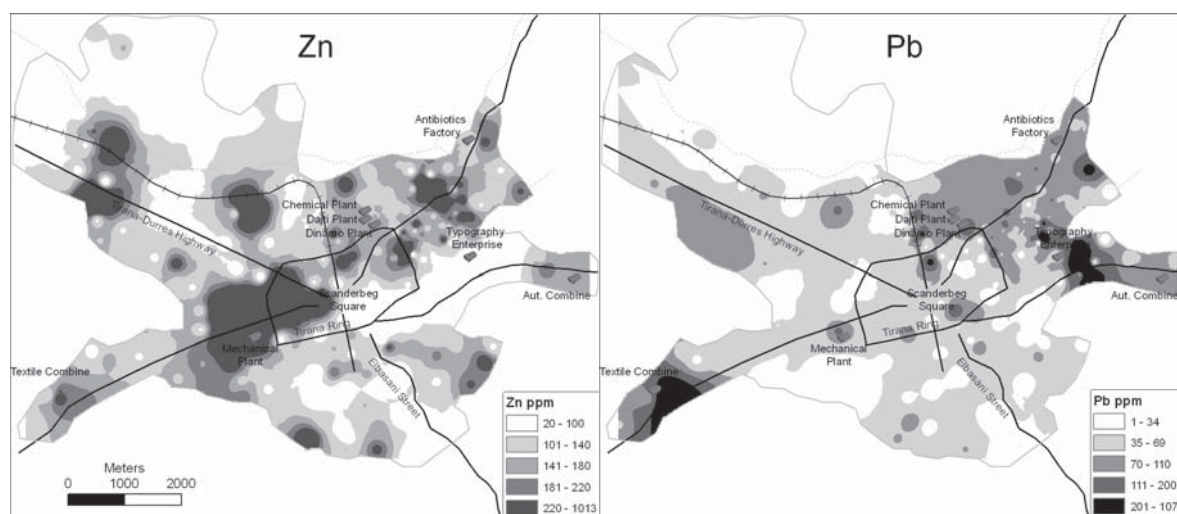
**Figure 2.** Maps of the spatial distribution of Zn, Pb, in the urban soils (5-10 cm depth) of the city of Tirana.

Lijzen et al. (2001) presented guidelines for the content of heavy metals in the urban soils that could pose risk to the public health or the ecosystem. They provide a series of values for the concentration of the heavy metals in the urban



soils grouped as Serious Risk Concentration for human ( $SRC_{human}$ ) and Serious Risk Concentration for the ecosystem ( $SRC_{eco}$ ). Based on this values the concentration of Pb exceeds the values given

and Dajti Plants, anomalies of iron in the vicinity of Tractors Combine and the Textile Combine. Despite the increase of the traffic in Tirana it is not observed a strong correlation of the road network



**Figure 4.** Maps showing areas with the predicted concentrations of Zn and Cu in the urban soils of Tirana higher than the Serious Risk Concentrations (SRC) values given by Lijzen et al. (2001) for urban soils.

by Lijzen et al. for Serious Risk Concentration for human ( $Pb > 622$  ppm) in two “hot spots” that occur close to the Typography Enterprise and Textile Combine (see Figure 3). The concentrations of Zn and Cu are also higher than these norms in several areas within the urban area of Tirana (Figure 4). These high values of Pb, Zn and Cu in the urban soils define polluted “hot spots” that merit further attention, more detailed geochemical studies and remediation activities as they may pose direct risk to the health of the residents in these areas.

#### 4. Conclusions

This study investigated the distribution of the heavy metals (Pb, Zn, Cu, Cr, Mn, Fe) in the urban soils of Tirana the capital of Albania. Using the factor analysis there were identified a group of elements that are related with the anthropogenic activity (Pb, Zn, Cu, Mn, Fe) and a group of elements that are related with geogenic processes (Fe, Cr). Through GIS techniques the maps of the spatial distribution of the heavy metals were used to visually identify the polluted areas and their relation with the industrial plants that were active in the urban area of Tirana until the end of 1980s. In this way were identified lead polluted areas close to the Typography Enterprise and the Textile Combine, Zn, Cu and to a certain extent Mn polluted areas close to the Chemical, Dinamo

with high values of heavy metals in the urban soils sampled at 5-10 cm depth. Several anomalies of Fe and Cr are interpreted to be of geological nature. Areas that exceed the Serious Risk Concentration values given by Lijzen et al. (2001) were defined. In this way were distinguished two lead polluted “hot spots” that are close to the Typography Enterprise and the Textile Combine as well as areas where Zn and Cu exceed the values of the Serious Risk Concentration. These sites are of concern and require further detailed geochemical investigation and remediation activities as high values of lead, zinc and copper may pose a threat to the health of the residents living in these areas.

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## WATER QUALITY ASSESSMENT OF VJOSA RIVER THROUGH IMPLEMENTATION OF WATER FRAME DIRECTIVE

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### Abstract

Vjosa River is one the biggest in Albania. Compilation of a management plan for the Vjosa river basin aims to build a framework for the surface waters protection.

The main instrument for fulfilling the objectives of the WFD, for each member of the EU and countries like Albania which pretends the status of candidate country, is the preparation and implementation the management plan of a river basin, as described in Article 13 of the WFD. Most important stages for the implementation of the above mentioned WFD and construction of the basin plan management instruments have been:

1. Design and installation of monitoring water quality system.
2. Pressures evaluation on groundwater and surface waters and their impact on the environment.

Determining the status of the waters in Vjosa River (under Annex V of the WFD) became river axe through monitoring river referring to the threepoints:

- Biological quality elements
- Physico- chemical quality elements
- Hydro morphological Elements

The assessment of water quality of Vjosa river has been done through analyzing the physico-chemical elements and fish population.

The placements of four telemetric stations along the river axe, from the upper stream to the lower stream, provided data for Ph, T°C, CE, DO, TDS, depth, water level, etc. Receipt and processing of these data obtained in combination with biological data, in real time, provided the opportunity to assess the water status in this axe. There are used the Standards of WFD inlack of Albanian Standards.

The first data obtained from the field surveys and laboratory analysis shown different values of electric conductivity that vary from 254-2330  $\mu\text{S}/\text{cm}$ , the values of Cl and  $\text{SO}_4$  vary respectively 12.59-561.01 mg/l and 22.50-146.06 mg/l. From the other side, the values of the nitrites vary from 9.47-39.11 mg/l. The big changes occurred in river delta or in the joining points of Vjosa river with its main tributaries as Drinos and Shushica rivers.

The proposed monitoring system included four telemetric stations placed in Three Bridges-Çarshova village, Lekli Bridge, Shkoza village and last one in Mifoli Bridge. The equipments give us periodically the values, besides the others, for DO (mg/l & %), TSS (mg/l), alkalinity (mg/l) and turbidity (NTU). The main values for total nitrogen vary from 20.25 g/l, in three Bridges in Çarshova, to 45.75 g/l in last point, in Mifoli Bridge.

There are taken in consideration the water feeds of Vjosa River as natural springs and the tributaries which discharged their waters in Vjosa River.

According to WFD for determination of water status in the Vjosa river, based on physical-chemical analyses, is identified a "good status" for these waters.

The water status is strongly related especially to drinking water supply and agricultural needs and uses.

## HYDROCARBONS POLLUTION OFF ORMER PETROLEUM REFINERY AREA IN KUÇOVA TOWN

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### Abstract

In Kuçova the petroleum refinery started its operation with lamp-oil production since 1934. After the Second World War it took technological improvements and in 1993 terminated the activity. Today there are only three chimney. The former petroleum refinery area is 25 hectares and is owned by the municipality of Kucova. Premises of the former petroleum refinery is without any industrial use. The surface of the former refinery is built on the Pliocene and Quaternary deposits. Pliocene sediments consist especially of clay and sands to sandstones belonging to Helmesi formation, which outcrops in the west side of the former refinery. The Quaternary deposits are the result of the erosion of Miocene and Pliocene deposits. Old plant is built on the Pliocene deposits (western side), while new plant premises has been placed on above the Quaternary deposits, contaminating surfaces separated by technological line refinery. Sources of surface contaminants can be separated: the technological part of the petroleum refinery; and the lagoons.

The premises of the former refinery were divided from the point of view of the potential pollution of the environment into 10 areas (hot spots) by the character of operation. The following hot spots of contamination were selected: storage tanks of crude oil (old and new refinery); oil distillation and production of oils (old and new refinery); barrels – production, filling, storage and dispatching (old and new refinery); storage tanks of crude oil, piping conveying oil (new refinery); oil distillation (new refinery); storage tanks of gasoline and crude petroleum (new refinery); coke plant– production of petroleum coke (new refinery); production of oils and their storage (new refinery); lagoons of asphalts, including municipal waste dumps (new refinery) and lagoons of goudrons (new refinery).

Alltogether, 5 objects significantly participating in the pollution of the environment have been found. In most cases, decanters, tanks for crude oil and a dump site of municipal waste in Lagoon No. 2; in addition, 5 functional oil wells have been detected (area of ex-refinery is involved in Kuçova

oilfield).

An overview of basic physical and toxicological properties was prepared for contaminants that have occurred in increased concentrations in soils or dumped wastes at the site and can therefore be theoretically involved in negative impacts of ecological loads on the environment. The substances are as follows: Total Organic Carbon (TOC); Total Petroleum Hydrocarbons (TPH).

The organic matter (TOC) is a significant factor in relation to the action of pollutants onto the sediment thanks to its negative electric charge enabling adsorption and its complex-forming activity. So TOC values depend on properties of crude oils; the rate of hydrocarbons (HC) evaporation and lithology of soil samples: moderately contaminated sandy clay (TOC = 84.4 g/kg soil); contaminated gravel (TOC = 53.5 g/kg soil); contaminated sandy clay (TOC = 27.4 g/kg soil); uncontaminated clay (TOC = 28,8 g/kg soil); slightly contaminated clay (TOC = 34,8 g/kg soil).

Total Petroleum hydrocarbons (TPH) of soil samples is as follows: waste (TPH = 61900-337000 mg/kg); storage tanks of crude oil (old refinery, TPH = 31 000 mg/kg); oil distillation and production (old refinery, TPH ≤ 50-3500 mg/kg); storage tanks for crude oil (new refinery, TPH ≤ 50-138000 mg/kg); oil distillation (new refinery, TPH = 4100 mg/kg); storage tanks of gasoline and crude petroleum (new refinery, TPH ≤ 50-8400 mg/kg); coke plant (new refinery, TPH ≤ 50-1400 mg/kg); oil production (new refinery, TPH ≤ 50-61000 mg/kg); lagoons of asphalts (new refinery TPH ≤ 50-5900 mg/kg); lagoons of goudrons (new refinery TPH ≤ 50-610); section the Pliocene (gravels – claystones, TPH ≤ 50).

The content of hydrocarbons in the former refinery sectors is higher than European standards for industrial areas (TPH= 1000 mgr/kg). Only two sectors are not contaminated by hydrocarbons, lagoons of goudrons and Pliocene section in western area of the former petroleum refinery.

**Key words:** *Old petroleum refinery, total petroleum hydrocarbons, pollution, storage tanks, lagoons*



## THE FATE OF HEAVY METALS IN THE METALLURGICAL AREA OF ELBASAN

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### Abstract

Contamination of heavy metals is one of the major threats to water and soil as well as human health. Phytoremediation has been used to remediate metal-contaminated sites. This study evaluated the phytoextraction potential of nickel hyperaccumulator *Alyssum murale* that comes from Albanian serpentine soils to grow on contaminated sites in Industrial areas of Elbasan. So are conducted two experiments; in- situ in the soil included in the area of the metallurgical plant where 4 seedlings of *A. murale* (seeds come serpentine site of Pojska) were planted in 1 m<sup>2</sup> and the second one in 1kg pots with 1/2 kg mineral residue from metallurgical plant and 1/2 kg organic fertilizer. The heavy metals content in soil and plant tissues have been analyzed and the biomass has been measured. Nickel phytoextraction yields also were calculated. The concentration of Ni in soils in the area of the metallurgical plant varied from 395 to 593 mg Ni/kg, Zn from 49 to 81 mg/kg, Co from 62 to 105 mg/kg, Cr from 207 to 367 mg/kg respectively.

In the other hand, the concentration of Ni in mineral residue from metallurgical plant varied from 395 to 12870 mg Ni/kg, Zn from 64 to 13835 mg/kg, Co from 62 to 480 mg/kg, Cr from 134 to 10649 mg/kg respectively. The concentration of Ni in plant shoots of *Alyssum murale* from the area of the metallurgical plant varied from varied from 482 to 1824 mg/kg, while Ni from mineral residue varied from 76 to 3150 mg/kg. In the soils in the area of the metallurgical plant Ni yields varied from 155.6 mg/m<sup>2</sup> to 364.8 mg/m<sup>2</sup> while that in mineral residue was 10.64 mg Ni/kg soil. In the two soils we observed the Ni hyperaccumulation ability of *A. murale*. The results showed that Ni plays an important role in *A. murale* growth and this plant has ability to accumulate Ni even in contaminated soils.

**Key words:** *Alyssum murale*, nickel hyperaccumulator, serpentine, growth indicators, biomass

## DEVELOPMENT OF THE GEOPHYSICAL DATA BASE FOR THE BLACK SEA REGION AS PART OF THE 7TH FRAMEWORK PROGRAMME PROJECT “UPGRADE BLACK SEA SCIENTIFIC NETWORK”

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### Abstract

The presented paper reveals results achieved by a team from the University of Mining and Geology “St. Ivan Rilski”, Sofia, during its work according to “Upgrade Black Sea Scientific Network”, project part of the Seventh Framework Programme.

**Key words:** *Black Sea, database, geophysical data*

“Upgrade Black Sea Scientific Network” (UBSS) is a project part of the Seventh Framework Programme. The objective of this project is to develop a monitoring system (creation, storage, analysis, visualization and spread of information) for the Black Sea basin. This information is environmental, biological, physical, geological, geophysical, hydrodynamic, etc. The accomplishment of the project’s main task is achieved by creating a database (DB). The database is similar to the electronic records, to electronic data repository. Moreover, within this database a number of operations can be performed, for example: adding, modifying, searching and spreading of information, exchange of information between partners and the interested users. The centres that perform this activity are the national centres that are integrated into the SeaDataNet infrastructure which coordinates marine research in Europe.

The database which is laid in the base of the UBSS project is developed in several stages. During the first stage, a collection of information is carried out. These are the so-called metadata, which are prepared and presented by each participant in the project. Based on the metadata can be judged on the following: what, where, when and with what devices and equipment the data are measured; who

owns this information and under what conditions it is obtained.

The second stage includes the development of a corporate database. The information collected by the partners is extremely fragmented, as the means and the methods applied by the individual partners are different. The data are unified according to indicators and a quality check of the information is also performed. Different programs are applied for standardization of data, including the program MICADO, which allows processing and analysing of large datasets. The use of the general dictionaries of SeaDataNet allows to standardize and unify data and also to interpret the records with the help of computers. Information on the data collected by the project partners is presented in a special catalogue of the European service for metadata.

The general data directory is a central point in the infrastructure of the project. It enables users to know the availability and the geographical location of the data. Furthermore, this directory is the link between the database and the users as it provides a direct on-line access to data. Within the scope of this project is standardized, above all, information reflecting the ecological status of the Black Sea.

The research team developing the project UBSS, consists of 51 partners (European) organizations, 43 of which are located in the countries of the Black Sea region. Bulgarian side includes the following 7 research institutes: the Institute of Oceanology, BAS; the Technical University, Varna; the Institute of Fisheries, Varna; the Black Sea NGO, Varna; the University of Mining and Geology, Sofia; the Central Laboratory of General Ecology, BAS; the National Institute Meteorology and Hydrology, BAS. Project coordinator is MARIS (Mariene Informatie Servise) - Netherlands.

The University of Mining and Geology, Sofia - Department of Applied Geophysics,



**Figure 1.** Overview map of the Bulgarian Black Sea coastline and location of Route 1 along which are measured three geophysical fields (gravitational, geomagnetic, radiometric).

provides information on geophysical (magnetic, gravitational, electrical, geothermal, and radiometric) fields in the Black Sea area and along its coastline. Currently in UMG functions the so-called “DATA CENTRE”. The activity of this centre is up to 2016. The data centre includes 726 SDI files and the corresponding ODV files as follows: Temperature of Geological Units - 108; Geothermal Gradient - 206; Rock Thermal Conductivity - 122; Heat Flow - 206. These data are taken from published sources and relate mainly to the western part of the Black Sea.

In June 2013, according to the tasks defined in the project, a team from the Department of Applied Geophysics, UMG “St. Ivan Rilski” - participants in the contract, carried out complex geophysical surveys along two routes following the Bulgarian Black Sea coast from Rezovo (border with Turkey) up to Durankulak (border with Romania) (Fig. 1).

Along Route 1 are measured three geophysical fields (gravitational, geomagnetic, radiometric)

from Rezovo to Durankulak (Fig. 3). The number of regular points measured along the route is 105, providing an average distance between points of 1.5-2.0 km. The points are located close to the main road following the Bulgarian coastline.

Along Route 2 is measured a detailed gravimetric network of 97 points (Fig. 2). It is starting at Varna and is reaching Durankulak. The average distance between points is about 0.25 km. The gravitational field  $g$  is measured. Route 2 deviates at some places and does not fully overlap with the main Route 1.

The geophysical equipment used for performing the measurements along the routes includes GSM-19 v7.0 Overhauser total field magnetometer; GSM-19T proton precession magnetometer; gravimeters GNU-K2; radiometers SRP-68.

The position of the measuring points is defined with the GPS receiver GPSMAP 60CSX which is providing an accuracy for the coordinates of about 1-2 meters.

The measurements of the three geophysical fields along both routes are performed and processed according to the well-known standard methodology. The Reference point in respect to which are calculated the anomalous values of the total geomagnetic field vector  $F$  and the Bouguer anomaly is located in the town of Tsarevo. This Reference point coincides with the located in Tsarevo Absolute Gravity Point from the national network. Moreover, three other measuring points along Route 1 coincide with the Absolute Gravity Points located in Byala, Balchik, and Durankulak.

The Bouguer anomalies are calculated according to the well-known standard formula:

$$\Delta_{\text{bouguer}} = g_{\text{measured}} + (0.3086 - 0.041h)s - g_0 \quad (1)$$

The chosen layer density is lower than the standard density  $\sigma = 2.67 \text{ g/cm}^3$ . The reason for this is the fact that the “Bouguer plate” in this case is situated in the range of 100 to 250 meters above sea level and the Reference point has above sea height of 100 m. This near-surface layer is characterized by an average density  $\sigma_{av}$  of about 2.30 to 2.35  $\text{g/cm}^3$ .

The evaluation of the rocks density along the routes is made taking into account data from published sources and according to measurements of the density of different rock samples performed in



**Figure 2.** Overview map of the North Black Sea coastline of Bulgaria and location of Route 2 along which are measured the values of the gravity field with a step of 0.250 km between the points.

the Laboratory of Petrophysics at the Department of Applied Geophysics. The final summarized esteem for the density value, which is applied for calculating the Bouguer anomalies is  $\sigma = 2.35 \text{ g/cm}^3$ .

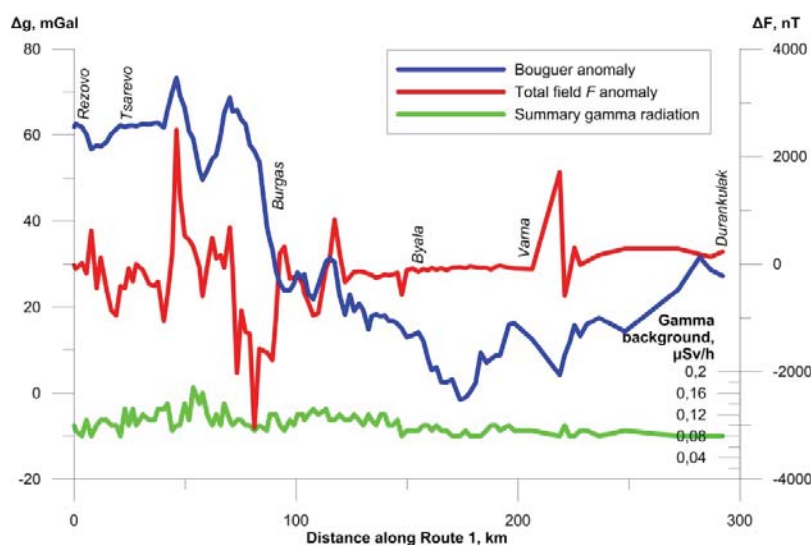
The processing of the geomagnetic measurements is based on data for the variation of the geomagnetic components recorded in the Panagurishte magnetic observatory.

The distribution of the three geophysical fields

measured along Route 1 is illustrated in Figure 3.

The measured and processed data are entered in the designed for the project “DATA CENTRE” in UMG “St. Ivan Rilski”. The database loaded on this “DATA CENTRE” is in the permanent connection to the European database (BLACK SEA SCENE DATA).

In 2012 complex geophysical studies were performed in the Black Sea, covering the shelf area in the territorial waters of Romania and



**Figure 3.** Bouguer anomaly, anomalous geomagnetic field  $\Delta F$  and background gamma radiation for Route 1 located along the Bulgarian Black Sea coastline (from Rezovo to Durankulak).



Bulgaria. They were carried out according to the

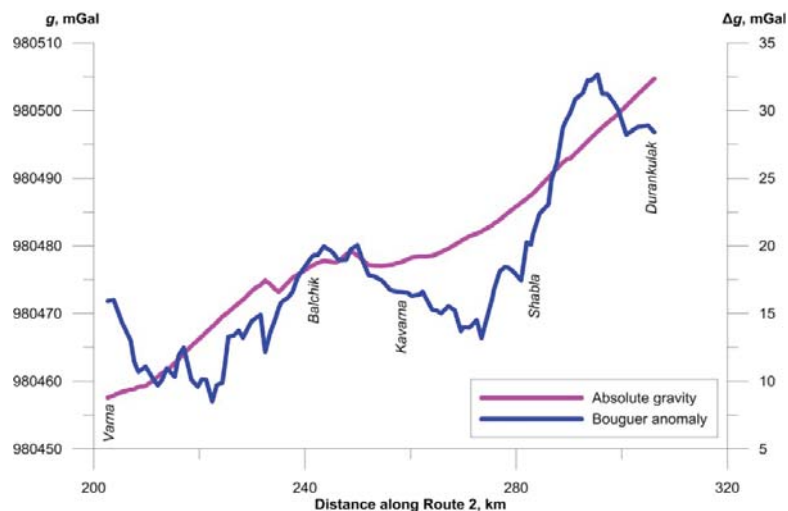


Figure 4. Absolute gravity values and Bouguer anomaly along Route 2 (from Varna to Durankulak).

project MARINEGEOHAZARD. The complex of measurements during the two expeditions of the specialized Romanian research vessel “Mare Nigrum” included continuous precise measurement of the gravitational and magnetic field. The obtained data can be used for correlation between measurements on land and at sea.

In the context of the UBSS project these measurements and their interpretation together with data from ground-based measurements provide not only a new qualitative step forward regarding the regional study of the geophysical fields, but also a possibility for unification of data from studies diverging in their size, in the used equipment, and in the applied methodology.

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## ROLE OF GEOCHEMISTRY IN MINING ENVIRONMENTAL ISSUES

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### Abstract

The concepts and technology in mining industry have changed a lot during last decades.

New and very advanced technologies are being implemented nowadays resulting in significant increase in production. On other side, the concepts of “Mine Closure Procedure” “Mine Site Rehabilitation” or “Mine Waste management” which basically are environmental issues. It is already known, that after the last major environmental catastrophes, the toxic waste dam-burst in Doñana, Spain, in 1980, and Baia Mare gold mine cyanide disaster, in Romania, in 2000 and AjkaAluminium in Hungary, in 2010, the European Union has undertaken serious action to prevent any environmental damage or pollution from mining industry. Nowadays, all member states and candidate countries should implement EU Directives dealing with mine waste management, mine rehabilitation etc.

Implementation of such new concepts requires serious environmental studies not only to give a long term solution of environmental issues but to find the best and most feasible approach being that such activities are expensive and increase the cost of the mine, sometimes this studies can decide whether a deposit is feasible or not.

Generally speaking, environmental problems at mine sites are the followings

- Waste, composition, chemical elements contained and their behavior in the surrounding environment
- Air pollution,
- Adverse impact on land use and biodiversity,
- Water pollution and availability,
- Hazardous materials,
- Noise and vibration,
- Energy use,
- Visual impacts

According to EU Directives each mine should carry out the classification of their mine waste facility

and based on the classification requirements mine waste facility or can be category A or NOT A.

Mines categorized as “Category A”, have to prepare a waste management plan and following all steps foreseen in this plan. This is a further financial burden for mining companies, therefore the classification should be done in a very meticulous and due diligent way.

Accuracy of a classification depends totally on available data.

As it can be seen from above, among other information required, the geochemical information is very important.

Therefore it is time to introduce and include in our studies the concept of “Environmental Geochemistry”

The environmental geochemistry is the application of chemical principles to predicting the fate of organic and inorganic pollutants at the Earth's surface and in the atmosphere.

This means that along with mining project, a professional environmental assessment report should be carried out taking into consideration the environmental geochemistry concept.

In practical terms, active mines operating or mines which are under designing procedure environmental assessment studies should plan interalias the following issues:

- Characterisation of waste rock and tailings.
- Static and kinetic laboratory and field testing, development and coordination.
- Conceptual and detailed waste landform planning and management.
- Integration of long and short-term mine planning with waste geochemistry management.
- Analytical and numerical waste geochemical modeling.
- Site-specific waste geochemistry management training, and
- Research and development of best practice assessment, monitoring and management techniques

Obviously geochemical data should be available

for environmental studies and a close cooperation between geochemists and environmental specialist is required.

Available data means that such data should be stored in accessible data base, geochemical maps should be already drawn and archives should be available to whoever requires data for a specified deposits.

Best results can be achieved by verifying the available data facing with fields collected data.

Being aware living in a high-techworld, as good and modern approach is using Remote Sensing technique.

Remote sensing is one of a suite of tools available to land managers that provides up-to-date, detailed information about land condition. Remote sensing uses instruments mounted on satellites or in planes to produce images or 'scenes' of the Earth's surface.

Remotely sensed images can be used in many applications, for example:

- mineral exploration
- monitoring ocean currents
- land use planning
- monitoring the condition of forest and agricultural areas.

The uniqueness of satellite remote sensing lies in its ability to show large land areas and to detect features at electromagnetic wave lengths which

are not visible to the human eye.

Data from satellite images can show larger areas than aerial survey data and, as a satellite regularly passes over the same plot of land capturing new data each time, changes in the land use and condition can be routinely monitored.

The information from remotely sensed images can be used in a number of ways for a number of purposes. It is usually combined with information from other data sources and on-the-ground observations, called 'ground truth', to get a more complete picture of what is happening and to check suspected features or changes.

The availability of this data has streamlined the process of researching a site, as it is now much quicker to gather the basic facts and history for a site for a geotechnical or geo-environmental engineer.

Archived remote sensing data can be used to monitor how areas have changed through time. Monitoring information can then be combined with landform information to help predict which areas are at risk from salinity in the future, allowing remedial action to be taken where it is needed most.

Thu, the implementation of such methods and techniques in our country will be a good step not only to assist and improve the situation in mining industry but to approach our country with other development countries as well.

## STOCHASTIC MODEL FOR LANDSLIDE RISK ASSESSMENT

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### Abstract

Modelling and assessing quantitatively the vulnerability for landslide is a complex task. The discrete nature of landslide occurrence and the dynamic movement of element at risk make it more complex than the other hazard. The aim of present study is to develop a stochastic methodology for assess the risk of landslides. The study focuses on north hill slopes of Iran. As shallow landslides can be triggered by extreme rainfall amounts, so in this research was proposed a stochastic model to forecast landslides based on the precipitation data. Also according to the lithological units' characteristics and geomorphologic properties, a map unit was developed which shows layers with similar litho-geomorphic characteristics.

Then, a probabilistic correlation was linked rainfall data and the map units in a 1 km<sup>2</sup> cell. Integrating stochastic geometry and Monte-Carlo iterations was applied for landslide vulnerability degree. The obtained results indicate that landslide risk varies greatly at different times of the day. This variation mainly was due to the dynamics of rainfall. Results indicated a good efficiency of the model, although seems the main factor of landslide occurrence in recent years refers to human activity and land use alterations.

**Keywords:** *Landslide, Stochastic Model, Monte-Carlo, Iran*



## DEVELOPMENT OF LILW REPOSITORY IN SLOVENIA

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### Abstract

Slovenia has a relatively small nuclear program with limited amounts of radioactive waste and spent fuel production. But in accordance with the international and national standards they are developing all necessary facilities for disposal of this waste. In the last few years, the work is focused on development of low and intermediate radioactive waste (LILW) repository for which in 2010 the site was adopted with a governmental decree on the National Spatial Plan for LILW repository at Vrbina site in Krško municipality.

During the last decade different investigations and planning activities have been performed in order to construct the repository. Extensive geological, hydrogeological, geotechnical and geo-chemical field investigations have been carried out in three phases supporting the preparation of safety analyses for repository and its design.

The most important activity at the starting phase was siting and site characterization for the repository. In the first step, characterization of two most promising sites took place, but after the siting was completed, the characterization of the selected site at Vrbina, Krško continued in two successive phases among which the last one is still running.

Characterization is devoted to the determination of geological structure on the site, the hydrogeological model (groundwater level in two different aquifers, groundwater water flow direction, piezometric water levels, etc.), geomechanical model (differentiation of "homogenous" zones with similar mechanical characteristics, determination of physical, deformation and strength parameters for each of the units) with prediction of behaviour under different loading conditions (construction, earthquake, etc.) and geochemical model, together with sorption and other chemical parameters important for the safety analysis. At the same time, the zero state capture on radionuclides, heavy metals and other human contamination have been taken.

In former steps, the wider area has been investigated, while the, last running step is devoted to the characterization of the hosting soil in immediate vicinity of the silo repository. The findings so far show that the silo underground repository is feasible but not easy to construct and much care should be taken for sufficient support at all phases of construction, to minimise disturbing of the hosting rock.

In parallel, with the aim to decide on the optimal technical design of repository from nuclear and radiation point of view, Special Safety Analyses have been performed for three repository types at Vrbina location, close to the NPP Krško:

- for a surface vault – type repository, constructed on artificial embankment (variant E),
- for a near-surface silos – type repository (variant B), and
- for an underground repository (variant D).

The safety assessment of the three repository types consisted of dose assessment for workers within repository through its operating and closing phase: for the normal evolution of events and for abnormal events, as well as for the post closure repository phase: for the design scenarios and for some alternative scenarios.

The assessment has been performed in accordance with the IAEA recommendations and Slovenian National Regulatory Acts. With the first step, potential events have been identified and in accordance with the repository type characteristics and scenarios have been developed. These scenarios have further been analysed from the nuclear safety point of view: each of scenarios identified as important, either due to the high occurrence to be expected or due to the expected strong consequences, has been modelled and calculated. The resulting effective equivalent doses to a member of the critical group have been compared to the international dose constraints. This way, 6 scenarios for normal events within the period of repository operating and closing phase have been treated and 12 scenarios for the

abnormal events. For the post closure repository period, we have identified two design scenarios for each of the three repository types and a number of alternative scenarios: 7 for the surface repository, 3 for the silo and 4 for the underground type of repository.

The doses to a member of the critical group have been calculated for each of the mentioned scenarios. Results proved that very low doses for all design scenarios through the operating and closing repository period were to be expected. The doses from abnormal events were some higher. The highest dose to the worker has shown for container fall-and-crash scenario within the surface and silos repository and for the fire scenario within silo and underground repository type. In both cases, the doses were well below the dose constraint prescribed by Slovenian regulation.

Dose calculations for the post closure period gave very low doses to the members of the critical group for all three repository types. For the surface repository, the calculated dose was one order of magnitude below the dose constraint, while for the other two types, these values were 5 orders of magnitude lower. The calculations for alternative scenarios gave some higher doses, especially for the case of all - barrier - demolition scenario (after 300 and 10.000 years). This scenario is highly unlikely to occur; it was taken as the limit scenario. In this case, the calculated dose was one order of magnitude higher than dose constraint for normal operation, but was well below the ICRP recommendations.

## IRON - NICKEL LATERITES – A POTENTIAL MINERAL RESOURCE FOR ALBANIA

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### Abstract

The tendency of the development of the present world mining industry is the increase of the demand for mineral commodities. In this context, beside chromite and copper ores, the Fe – Ni and Ni-silicate ores of lateritic type represent one of the most important potential mineral resources for Albania. These laterites are related to the eastern ophiolitic belt of Mirdita zone and are formed by the chemical weathering of the ultramafic rocks. In general, the laterites are stratigraphically well defined, overlying ultramafic rocks and underlying the Cretaceous carbonatic rocks. This generalized fact was used as a field guideline on the prospecting – exploration for lateritic ore deposits in Albania.

The outcrops of the lateritic horizon extend for several tens kilometers, from Kruma-Kukesi area, in northeast, to Librazhdi-Pogradeci, in centre, and Bilishti area, in southeast. There are several known Fe-Ni and Ni-silicate lateritic ore deposits and occurrences all over the eastern part of Albania. Only at Kruma – Kukesi area, the outcrop of the lateritic horizon, consisting mainly of Ni-silicate mineralization, delineates a promising area of ca. 120 km<sup>2</sup>.

Based upon their geological features and mineralogical composition, three main promising sectors have been distinguished, separated by each other by the Shkoder-Peja, Elbasani-Diber and Prespe-Tepelene transversal faults: 1) Has-Kukes-Lure; 2) Librazhdi-Pogradeci and 3) Bilishti.

*Sector Has-Kukes-Lure* occurs between two transversal faults Shkoder-Peja and Elbasan-Diber. The mineralization of this sector consists of the full lateritic section with Ni-silicate at the bottom and Fe-Ni ore at the top.

Only some separated objects have been prospected and explored in Kukesi and most of the area is a greenfield. The explored ore deposits are Trull –Surroi, Mamezi and Nome. The calculated ore reserves explored so far are 52.8 million tonnes Ni-

silicate with 0.92-1.395 wt.% Ni, 0.05 % Co and 25 wt.% Fe and 27.4 million tonnes iron – nickel ore with 0.80 wt.% Ni, 0.06% Co and 35- 43.3 wt.% Fe. The estimated probable lateritic ore reserves for Hasi-Kukesi-Lura area are enormous.

*Sector Librazhdi-Pogradeci* lies at the Central Albania, between the transversal faults Elbasan-Diber and Prespe-Tepelene. The laterites of this sector differ from the ones of the two other sectors from their origine and time of formation. The ore horizon consists only of iron-nickel ore type. Ni – silicate is absent because before the overlying by limestones in Upper Cretaceous, there was a marine transgression that caused the mixing of both the ore types. The ore deposits of this sector are totally explored before the year 1990 and they are ready to be developed and exploited. The total calculated ore reserves are 103.8 million tonnes and so far only 17.8 million tonnes of them have been exploited.

*Sector Bilishti* lies south of the transversal fault Prespe- Tepelene and the laterite mineralization is represented by Bitincka ore deposit, several occurrences and Kapshtica ore deposit. Ca. 58.3 million tonnes Ni-silicate ore with 1.32 wt.% Ni and 14.3 wt.% Fe, and 52.5 tonnes Fe-Ni ore with 1.12 wt.% Ni and 43.6 wt.% Fe, have been explored so far in Bitincka ore deposit. Kapshtica ore deposit is only partly explored close to its outcrops.

The laterite Ni-silicate and Fe-Ni mineralizations of Albania are one of the most important mineral commodities in Europe and among the Western Balcan countries where these mineralizations occur. The potential resources of Fe-Ni and Ni-silicate ore are estimated to be enormous, higher than 1 billion tons. This is a good basis for the attraction of the investors interested on the development of the related mining and metallurgical industry for exploitation and smelting of the Fe-Ni and Ni-silicate lateritic ore.

## STUDIES, EXPLANATION AND ECONOMIC EFFICIENCY FOR INDUSTRIAL MINERALS AND ROCKS IN ALBANIA

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### Abstract

The industrial minerals and rocks are of sedimentary, magmatic and metamorphic origin.

These resources are used by humans since the origin of human society. Our country is rich important and various industrial minerals and rocks.

**Keywords:** *industrial minerals and rocks, resources, magmatic and metamorphic.*

### Introduction

#### a. The industrial minerals and rocks with the sedimentary origin.

Below will be shown some analytic data about industrial minerals and rocks in Albania. Phosphorite. Were discovered 11 deposits, were calculated up to 54 million tonnes reserves and are excavated up to 200,000 tones.

##### 1. Limestone

The carbonate rocks occupy a surface about 7300 km<sup>2</sup>, were discovered and are in exploitation more than 300 objects and deposits and were calculated more 1 milliard m<sup>3</sup> industrial and geological reserves.

##### 2. Dolomites

In the dolomites from Kruja and Ionian zones were discovered and studied 7 objects and deposits, were calculated more than 189 million tons geological reserves, are excavated more than 450 000 tones dolomite mineral.

##### 3. Tripoli (are with biochemical – sedimentary origin)

Were studied and discovered 2 deposits and were calculated more than 3.3 million tonnes geological reserves.

##### 4. Rock salt

In our country were discovered 5 deposits, with more 590 million geological reserves and are excavated more than 16 million tonnes.

##### 5. Gibbsite and anhydrite

In our country, the biggest distribution have the regions of Peshkopi, Dumre, Kavaja and Vlora when were studied and discovered 25 objects and deposits, with more than 100 million tonnes geological reserves, are excavated 700 000 tones.

##### 6. Claystone

In our country were studied and evidenced more 60 clay stone deposits, were calculated up to 300 million tonnes and until now are excavated 7 million tonnes. Placers (digging)

In our country they are located in deposits of different ages within different geological and tectonic zones and regions. In Korabi zone, the placers are encountered in of Ordovician deposits and it is assumed that there are also present of in the Werfenian deposits. (Luma serie). In the Neogene deposits, in the inner depressions as Devoll, Moker, Rreshen, Burrel, there is evidence of placers. In the lowland near the Adriatic Sea, which is situated up north continuation of the Kruja and Ionic zone and partly up Sazani zone, are some deposits and outcrops placers within the Middle Miocene and Pliocene deposits. The most of the outcrops and deposits of placers are situated in the coastal zone of the Adriatic Sea from Talja – Rile in north, to Narta in south, located in Quaternary deposits. As well, in the Quaternary terraces are observed placers as in Çerrave, Qukes, etc.

##### 7. River aggregate

The geological studies for the valuation of the river aggregates are performed in all the Albanian rivers, more detailed studies being done in their lower flows and near of the urban centres like Shkodra, Tirana, Durrresi, Elabani, Vlora, etc. In our country were studied the river aggregates in more 50 deposits and objects and were calculate more than 300 million tons of aggregates on the river beds.



## **9. The Kaolin**

In Albania the kaolin is related to the ophiolites of the western belt, which are geographically placed in the regions of Puka, Shkodra, Lezha and Mirdita. Until now, in these regions is known a large number of evidences, objects and deposits kaolin. In whole, the belt of the kaolin distribution occupies a large territory with a surface about 100 km<sup>2</sup>, a length of 40 km and a width of about 2-5 km. In the geographical and geological aspect, from north to south, in this belt are separated 7 regions with kaolin. Most of them are formed as result of the weathering of magmatic rocks as gabbros, troctolites, plagiogranites etc. In our country are known in some regions as Gomsiqe (Dedaj – Levrushk), Qerret, Korthpula, Vome (Vigu) and Kashnjeti.

## **b. Industrial minerals and rocks with magmatic origin**

### **1. Albitophyres**

Here are included volcanic alkaline feldspar rocks with high content of alkaline feldspar as are dacites, rhyolites, trahytes and the glass kinds of them. Are known the Guri i Zi (Shkoder).

### **2. Asbestos**

The asbestos mineralizations in our country have a relatively a large distribution. This mineralization is situated mainly in ultrabasic rocks near of the contacts with the gabbros, plagiogranites, volcanites and volcano sedimentary rocks, in the tectonic zones. The asbestos deposits are found in Tropoja, Puka and Korça regions. Are known the asbestos bearing belts of Gegaj – Buçaj – Tropoje – Fierz and Qafe Milice – Qafe Prush – Vlahen – Golaj. In the Puka region is known the mineralization of the Korthpule-Kaftalle-Qerret – Puke. In the Librazhd – Pogradec – Korçe regions there are a lot of outcrops in s: Kosharishte – Qarrishte – Qafe Thane, Zmblak – Plase – Dishnice – Drenove – Boboshtice – Mali Kuq.

### **3. Barite**

The barite outcrops are known in the granitic massif of Levrushk. They were intensively studied and have a practice value, doing the calculation of the reserves and technologic testing an application for the exploitation.

## **4. Basalts**

In our country the basalts are widespread. They mainly encountered are in Mirdita zone and with intense development in the in the central part (especially in Puke – Mirdite). These types of rocks have a porphyritic texture, with phenocrystals of plagioclase and rare of augite. The most representative deposits are in: Rubik, Kroi i Ftohte, Ura e Cekajve, Malth Guri i Shpatit t, Llange etc.

## **5. Magnesite**

The magnesite mineralization is evidenced for the first time 60 years and today studies and valuations are still made in some places as Gomsiqe (the only in Albania), Levrushku (Bulqize, Shebenik (Katjel), Devoll massifs and terraces of Devolli river, in Gramshi region.

## **6. Olivinites**

Olivinites are a mineral matter with content of olivine mineral up to 98%. It is a fresh ultrabasic rock, monomineral, completely crystallized. Olivine composed mineral matter with using complex values. These are used widely in metallurgical industry for the production of the bearing sands fire matters.

Olivinites were studied and valued in some zones as Kalimash, Çabrat – Dege, Qafe – Luzhe, Kepenek, Zogaj, Vlahen, Demaliaj, Zherke, Almarine, Thekna, Shkalle, Iballe, Spaç, Krrabe – Tmug, Qerret, Grep - Sane, Mirake, Ura e Graboves, Mali i Sogores etc.

## **7. Volcanic glass**

The volcanic glasses are volcanic rocks with helpful values as materials and non metallic matter, with widely usage in economy, especially in construction field. In our country were made valuations for the magmatic glass in Puka – Mirdita area, Lumbardhi, Qaf Bari, Lumeziu, Litite. Were performed studies and generalizations for all volcanic glasses of Mirdita zone (Qafë Mali-Qafë Bari-Munellë, Gurth, Letitën, Shebe-Rrënjollë, Kaçinar) and researches in this region in objects: Porav, Përbibaj, Munellë, Guri i Korbit-Qafë Bari Jugor, Qafë List, Sukë Pele-Gurth, Kodër Spaç, Beqiraj, Shebe, etc.

## **8. Talc**

The talc mineralizations are evidenced for first time in the geological research and mapping works realized in some regions as: Burrel (Frankth, German), Puka, Korça, Tropoja, Kukes,

Peshkopi and other regions. The most important are Zemblaku in Korça and Puka, while the other objects are with smaller dimensions and as results they have limited reserves.

### **c. Industrial minerals and rocks with the metamorphic origin**

#### **1. Decorative stone**

In Albania, the use of decorative stones is known since the prehistoric period until now. Marbles are known in the Muhurri, Kovashica, Gjerasi, the platy limestone which are used not only in Albania but also in Europe.

The most known deposits of decorative stones and marbles are: Muhurri, Kovashica, Rasfiku, Treshi, Kosova, Dervishani, Jergucati, Shkalla, Ura Vajgurore, Zhitomi etc. Between the decorative stone and marbles are individualized especially calcitic marbles, dolomitic marbles, marble limestone, dolomitic limestone, conglomeratic limestone, brecciated marble, granites, quartz diorites, gabbros and troctolites, olivinites, dunites, etc. The decorative stones have diverse colours, from white, grey, dark or red. Between the known outcrops and deposits of decorative stones are: Muhurri, Gjerasi, Kovashicës, Zogajti, Ostrenit, Kolesjanit, Qafë Shtamë, Darsit, Malit të Thatë, Dërstilës, Bilisht, Polenë, Vithkuq (Korçe), Munellë, Lis (Mat), Tepe (Shkodër),

Spiten-Manati-Tresh (Lezhë), Prosek (Mirditë), Qafë Priskës, Zall Dajti, Milotit, Laçit, Gjormit, Sarandë, Himarë, Borshi, Zhitomi, Kosovës së Madhe, Rapshe, Kalimashi, Lugu Zi, Shkallë Cerruje, Lure, Qafë Kumbulle, Qelzës, Tërbun, Shkopet, Bulshar, Kurbnesh, Kaçinar, Vig, Dragostunje, Fierze, etc.

#### **2. Quartz**

In the present the quartz is very necessary in some economic branches and sectors. The main usage of the quartzites and sandstones is in the production of the refractory matters, in constructions, chemical and metallurgical industry or in the manufacture of abrasives. In Albania country were studied in Kernaja, quartz, Shishtavec and Kallabaku, quartzites, quartz sands and sandstones in Tirana and Korça, etc.

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## ACHIEVEMENTS IN STUDIES OF THE PLATINUM GROUP ELEMENTS IN ALBANIA AND BREGU I BIBES DEPOSIT IN TROPOJA OPHIOLITIC MASSIF

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### Abstract

Platinum has been reported for the first time in Albania (especially in Valbona Valley) in 1907 by German explorer in 1907. In 1933, in the Jesuit Museum of Shkodra a platinum nugget has been displayed. Later on the exploration and exploitation flourished, starting with the presence of Italians and culminating with the period from 1970 to 1990 when most of research and exploration were carried out. The research continued until 2005.

The results of these studies are reflected in many geological reports and various scientific studies. Our work aims to present some data and conclusions based on these previous studies.

### Some dates about the platinum mineralization in Albania.

In the Albanian ophiolitic complex, the platinum mineralization is mainly related to the ultramafic section and partly to the lower level of gabbros. Based on geological and metallogenic data, the mineral paragenesis, elements and forms of occurrences of the Platinum Group Elements (P.G.E.) and their mineralization can be grouped in following ore types:

**The first type** of the P.G.E. mineralization is present in most of mantle chromitites. This mineralization is rich in Os, Ru, Ir, which is observed randomly in ophiolites. In Tropoja, the mineralization shows a clear positive Ru. The sum of the P.G.E. doesn't extend 90 ppb. The main minerals which content P.G.E. are sulphides as laurite and alloys of Os, Ru, and Ir.

**Second type** of the P.G.E., contains mainly Palladium (Pd up to 720 ppb and ratio Pt/Pd close to 0.3). Until now, in the Tropoja ultramafic massif 3 chromites deposit with this P.G.E. content are found. (Çabrat – 1, Çabrat – 4 and Qafa e Milices). They are located in the northern part of the Tropoja massif (base of the transition zone), where the aluminum values are higher

(12 wt% < Al<sub>2</sub>O<sub>3</sub> < 26 wt.%) than those of the first type (8 wt.% < Al<sub>2</sub>O<sub>3</sub> < 14 Wt%). The spectrum of this mineralization has a positive trend but with a positive Ru anomaly. There are SMB, mainly millerite and pentlandite, with Pd content (0.33 wt.%), Pt (0.19 wt.%), Rh (0.24 wt.%), Os (0.21 wt.%) of one Pd. These sulphides are similar to the palladium-bearing mineralization of Bulqiza massif because of the pentlandite predominance compared over others sulphides, the absence of P.G.E., the Pt/Pd ~0.3, the enrichment in Au (200 ppb) and the high content of aluminium in the surrounding rocks.

**The third type** of the mineralization is the platiniferous one (Pd up to 500 ppb, Pt/Pd up to 25) and is located in the mantle chromite, in the southern sector of the Tropoja massif: Leniq, Maja e Sukes, Kami 6 (transition zone). The P.G.E. spectrum has a positive trend from Os to Pt, then a negative trend. It is similar to the spectra of the fourth type of cumulates (Bregu i Bibes), but the Pt contents are lower and the mineralogy is different. Only sulphides of Ir, Pt, and Os were found.

**The fourth type** of mineralization is totally platinifer. It is located within the cumulates of Stoberda region, at the boundary between dunite and pyroxenite, but with discontinuity in the platinum content. The spectrum has a positive trend, with an very strong anomaly in platinum, contrasting to the low content of Pd and Au. In the Bregu i Bibes deposit, there is a positive correlation between Cr<sub>2</sub>O<sub>3</sub> and Pt-Pd content. An interesting aspect is the development of the Ni-Cu sulphide mineralization preferentially at the ultramafic-mafic transition zone. The Ni-Cu sulphide mineralizations, are mainly located within the dunite or plagioclase, dunite, which belong to the lower part of the cumulative sequence or to the most upper part of the mantle section. These mineralizations are observed in Qafa e Dardhe, Kurdary, Patine, Cerruje, Kraste, Hotolisht, Rune, etc. The presence of these mineralizations at the base of the magmatic chambers, confirmed by the change of mineralogical, geochemical and petrological features, is an important

characteristic of various massifs in Albania. The detailed petrologic-metallogenic study of the magmatic chambers can be subject for future work. The presence of Ni-Cu mineralizations in the chromite concentrations within cumulates as well as the chromite in the upper mantle part of both ophiolitic belts of Albania, are challenging. In all cases, the P.G.E., mainly palladium, are present in chromitites, for example in Vrith, Livadhas, Fang, the western side of Shkopet, Cerruje, Kraste, Rrasa Martinit, Qafe-Lame, Kunji i Gjate, Kalimash, Vlahen of the eastern belt. It is important to emphasize that there are many types of sulphides and arsenides which are observed in the both ophiolitic belts. These are represented, Ni sulphides and arsenides, Cu-Ni, Ni-Cu, Co-Cu-Ni sulphides and Cu-Co-Ni sulphides and arsenides. These specific mineralizations occur as disseminated grains, veins and lenses in serpentinites and tectonized zones of the mantle sequence near the podiforme chromite bodies, or

in cumulate dunite, in the lower part of the layered gabbros. This phase of mineralization is related to the hydrothermal fluids produced by the ultrabasic rocks during the serpentinization.

**Key words:** *Platinum mineralization, ophiolitic complex, Platinum Group Elements*

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## RECENT EXPLORATION AND PRODUCTION SUCCESSES IN ALBANIA AND THE HOPE OF A NEW FRONTIER IN THE PERIADRIATIC REGION

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### Abstract

The appraisal of a new discovery by Shell and the sustained increasing oil production by Bankers Petroleum in Albania, has led to an increase in the investor's interest in the entire Periadriatic region. Hence, an understanding of the basin evolution and hydrocarbon plays in Albania may shed some light on what might become new frontiers in Croatia and Greece.

The geological structures in Albania form part of a foreland fold and thrust belt system that includes Mesozoic-Eocene carbonate sequences of the Ionian Basin. The later is incorporated into three major Tertiary thrust sheets verging towards Apulia foreland in the southwest and overlain by foreland basin deposits, part of which form the Durresi Basin. The oil and gas fields are all concentrated onshore in the western Albania in these two basins. This presentation discusses some important features that control tectonic history as a prerequisite for assessing the petroleum systems as well as the type and location of accumulations and plays.

A new geodynamic model based on structural and kinematic observations is presented here that predicts that anticlockwise rotation of the Apulia

foreland along with its uplifted promontory in the southwest of Albania provided a buffer stop for the incoming 'train' of the Ionian basin thrusts during the Oligocene to Pliocene. A regional shear couple was formed between the hinterland and the buffer stop which was accommodated by strain partitioning along the strike. The Ionian basin thrusts were uplifted and exhumed in the south as they buttressed towards the promontory, while propagating freely in the north towards the foreland and overlain by Durresi foredeep basin during the Miocene-Pliocene.

Such a geologic framework formed the natural setting for the formation of two petroleum systems, one in either of Ionian and Durresi basins. In the Ionian Basin, all source rocks have good to excellent potential for liquid hydrocarbon generation and are of types II and I. The highest maturation occurred in the Triassic and Jurassic source rocks of the Ionian basin buried beneath the southern part of the Durresi Basin in central Albania. The beginning of oil generation from the source rocks is related to this Miocene and Pliocene burial. Oil accumulated in two types of reservoirs. The first type of accumulations relate to deep-water carbonates of Late Cretaceous-Eocene age. The reservoirs are fractured with predominantly vuggy porosity. The second type of accumulations relate to molasse deposits of the

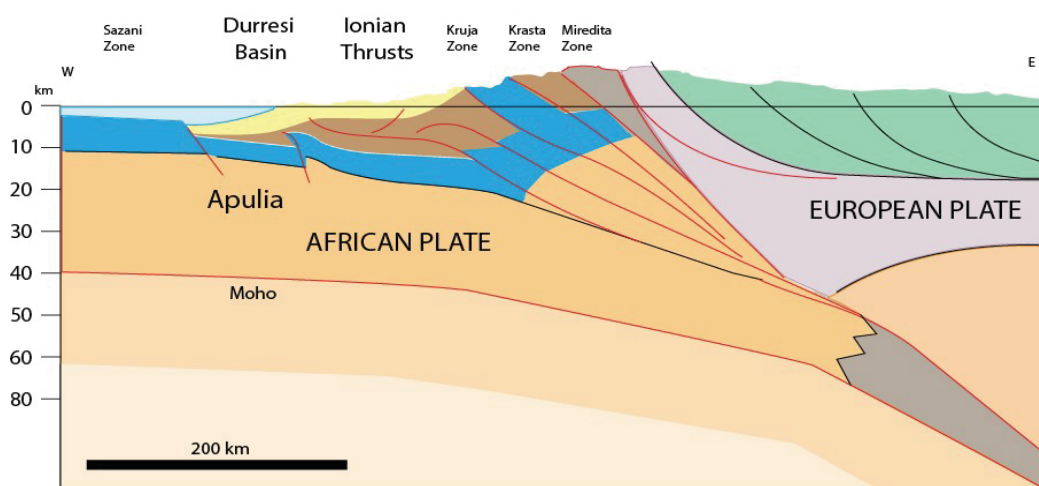


Figure1. Albanian foreland fold and thrust belt system.

foreland basin. The oil is located in stratigraphic traps formed during the Late Miocene. In the Durresi Basin, the source rocks consists of Tortonian turbidity sequences and Pliocene shales. A large volume of gas was generated by bacterial action. The reservoir is provided by the same Tortonian-Pliocene turbidity sequences and shales.

There are three main types of traps and possible complimentary plays, all located onshore Albania: (i) a carbonate oil and gas play that comprises Upper Cretaceous-Eocene deep-water carbonate reservoirs of the Ionian basin in fault controlled anticlines sealed by Oligocene flysch and charged from the Mesozoic source rocks; (ii) an oil clastic play that comprises Tortonian-Messinian reservoirs of the Durresi basin in Tortonian-Messinian sand pinch-outs and sand lenses sealed by intraformational Tortonian-Messinian shales charged by Mesozoic deep water carbonate rocks of the Ionian basin, and; (iii) a gas clastic play that comprises Tortonian-Messinian reservoirs in the Durresi basin in Tortonian-Messinian sand pinch-outs and sand lenses sealed by intraformational Tortonian-Messinian shales charged by the terrigenous source rocks of the foreland basin.

The hitherto investigation of the petroleum systems in Albania suggests that future complimentary oil and gas plays may still occur within the Ionian basin. Some gas plays may still be found in the Durresi basin. For both these plays, the HC charge is known, and the key risk lies mainly in the trap configuration and to a lesser degree, on the timing of generation, migration and accumulation.

## BEST PRACTICE IN PETROLEUM PROJECT EVALUATION

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### Abstract

A petroleum project represents the link between the petroleum accumulation and the investment decision-making process. A top-down process for the evaluation of the petroleum projects will be presented that comprises the following key elements:

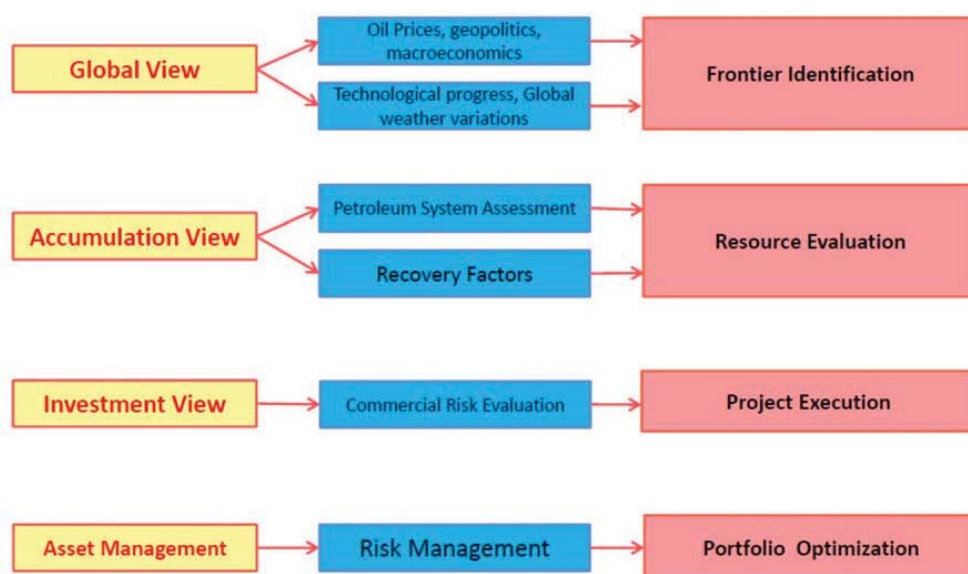
1. *Global view.* Unlocking new frontiers requires first and foremost an analysis of oil prices, geopolitics, and macroeconomics. This is coupled with knowledge and application of technological advances as well as the role the global weather plays in unlocking new frontiers.
2. *Accumulation view.* An assessment of petroleum systems and recovery factors is essential in obtaining ideas and evaluating potential opportunities. The significance of the sedimentary basins and some key indicators of hydrocarbon occurrence will be discussed here.

3. *Investment view.* A traffic light approach will be presented here that supports managing portfolios at various stages of exploration and development using the concept of increasing chance of commerciality as the key enabler.

4. *Integrated asset management.* Portfolio optimization and management requires a proper understanding of the value of the subsurface information, as well as having the right attitude towards risks and uncertainties.

These elements are used consciously or subconsciously by any successful petroleum explorer or producer and form a best practice in the oil industry. My aim is to put them together within a simple framework that could help to streamline the process of petroleum resource assessment, project definition, and investment decision.

## The G A I A framework



## ENERGY RESOURCES – COAL AS POTENTIAL DEPOSITS FOR THE DEVELOPMENT OF OUR COUNTRY

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### Abstract

The Republic of Kosovo is very rich in geological resources: metallic and industrial minerals, construction materials and energetic minerals (coal) that are a very important factor for the economic development of the country.

The genesis of coal deposit is one of the geotectonic evolution products of Kosovo basin. The coal genesis of Kosovo basin has not been studied in detail by the previous geological researchers.

Within the geotectonic evolution in Kosovo basin, five main stages can be distinguished on the coal genesis:

- In the first stage, during Miocene, the subsidence of the basin starts and the first stage of sedimentation happens;
- In the second stage, Lower Pontian, the deposition of the footwall of coal seam and related equivalents are done. During this time, the relatively shallow bottom is sunk with approximately the same rate followed by deposition of various sediments among which the clastic sediments (sand, gravel, clay, marls, etc.) dominate. At the end of this stage, in most part of the basin, the conditions that enabled the formation of coal seam, predominate;
- In the third stage, the old segment of Pontian -Pliocene epoch is the time of formation of the coal seam and its equivalents;
- Coal is created in the conditions of hot subtropical climate, with profusion of vegetation in bogs. Depth of clashes was small, in most cases up to a meter and rarely up to several meters. The rate of deposition of plant mass at relatively long time intervals has been according to the rate of the sinking of basin, which has conditioned the creation of the coal seam with high thickness that in some places reaches up to over than 100 m;
- In the outskirts of the bogs, time after time, the deposition of the intercalations of the plant mass and clastic sediments of rock

mechanical alteration, occurred. This process has conditioned the stratification of the coal seams and the barren intercalations.

In the initial phase of the third period, these frequent intercalations of coal and barren material occur all over the Kosova coal basin.

This way, the present transition between coal seam and its footwall is originated.

Later on, the isolated small bogs changed in a big marsh. The palynological analysis shows that the big marsh was for a long term relatively stable and the quantity of plant material over these areas, has been continued and abundant:

- Marshy zone (reeds);
- Marshy zone of forest vegetation, with marshes of coniferous forests that are typical for more moisture conditions and relatively high level of the water table (0.8-1.5 m);
- Marshes zone with bushes and
- The dried marshes zone with palmas.

Depositions of the above mentioned materials, with heterogeneous plant origin, have created the humite and xylite components in the coal seam. Humites are created by low plants -bushes, while xylites by higher woody plants.

Except the above mentioned plants, there was present microflora, represented by microscopic algae with SiO<sub>2</sub> skeleton in the common life of marshes.

During the fourth period, the sedimentation of hanging wall (gray clay, more rarely sandstones and sandstones) happened because the quick formation of marshes and bogs due to the rapid growth of the water table and the impact of the other factors.

As a consequence of disturbances in Kosovo plateau and of the elevations with other lakes, the water discharged from Kosovo lake through palaeo- flows of Iber and Lepenc rivers. In the fifth period, the current geomorphology of the basin of Kosovo has been consolidated.



## THE GEOLOGICAL SETTING AND EXPLORATIONS IN VLORA-SAZAN REGION

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### Abstract

Vlora-Sazan region is a well studied area from the geological point of view, where the contribution of regional seismic line and new processing ones have been of great importance. The object of this article is to give analyses of geological setting, tectonic mechanism and hydrocarbon prospect. Based on new geological and seismic data, a new interpretation is accomplished to evaluate the possible carbonate structure. The paper is a brief summary of a regional study in which many problems about stratigraphy, geodynamic, hydrocarbon potential and the exploration discovering ways are in details treated. Vlora region represents the most complicated zone from the tectonic point of view. In its south (Llogara Pass), the tectonic Çika zone is confronted in an intensive collision with Apulia-Sazan folded part. In Vlora Sazan region, the deposits of carbonate, flysch and molasses formations take place from Upper Triassic to Pliocene. This area is consisted of the possible hydrocarbon objects. From the oil exploration point of view, the prospect is concentrated in the top part of Vlora structure, which is not proved by the well, yet. In Vlora Sazan region, the deposits of carbonate, flysch and molasses formations take place from Upper Triassic to Pliocene. According to the genetic context they will be described in two great tectonic units:

- Sazan Zvernec zone;
- Ionian zone.

In Vlora-Sazan region from this study results that is effectively increased the interest to continue the exploration methods in oil gas bearing fields discovering. It is for the fact that, now, it is not difficult to recognize the zones of a great interest for study and exploration. Firstly, it will be included the zones that need more seismic lines and deep processing, such as:

- The zone in Zvernec, in the depth 3000-3500 m, which is predominated by clay and discussed to represent an anticline deep structure;
- The zone in Vlora region, in the time 1.5 - 1.6 s (lines 129/94, 126/94 ecc.), which is discussed to be contained as an individual slice of so-called shallow Vlora;
- The zone in the south of Vlora structure, where another structure begin beneath Tragjas overthrust anticline, as a continuation of the known Vlora structure;
- The deep Vlora structure, which we expect to be a fundamental one, in the time from 2.6 s. down to 3.5 s.

## OPPORTUNITIES AND CHALLENGES FOR THE DEVELOPMENT OF THE ALBANIAN NATURAL GAS SECTOR

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### Abstract

With 30 % less CO<sub>2</sub> emissions than oil and 45 % less than coal per unit of energy delivered, natural gas is the cleanest form of fossil energy. Technological development is making its delivery more and more competitive and for this reason natural gas is taking an increasing share in the world energy balance. European Union keeps environmental protection policy high in its agenda while it is also implementing a liberalisation reform of the electricity and natural gas sector and giving priority to its security of energy supply. Ensuring gas supplies from the Caspian and Middle East regions via the Southern Corridor is very important for the European natural gas sector.

Albania on its side, during the last two decades has experienced high levels of economic development which have been associated with an important increase in energy demand. This has transformed the country from a net exporter to a net importer of energy, particularly in the electrical power sector. Albania remains committed to its integration in the European Union. As a Contracting Party of the Energy Community Treaty, Albania is progressing in the implementation of the *Acqui Communautaire* in the energy sector.

Albania has a rich history in the oil and natural gas sectors, the last one including more than 3 BCM of cumulative production, however the exhausting of the discovered gas reserves in place during nineteen nineties has lead to the cease of the activity in this sector and closure of important economic activities.

Approval of the final investment decision in Baku on 17 December 2013 for the development of the Shah Deniz II gas field and all related chain for the transportation of natural gas up to the European markets is an important decision in the right direction.

Due to such developments including also a positive development of recently announced discovery of Shpiragu, Albania and the whole western Balkan countries, are about to experience remarkable changes, which would have otherwise been very difficult to be achieved. Trans Adriatic Pipeline project (TAP) which is a constituent part the Southern Corridor that goes across Greece and Albania and lands to Italy, offers Albania and the region an excellent opportunity to develop their natural gas, energy and economic sectors.

The article aims to provide a summary of such developments with a particular focus on the opportunities and challenges for the development of the natural gas sector in Albania:

- Once gas become available, Albania can very easily develop a gas demand at a level of nearly 300,000,000 NCM/year to grow up to 1 BCM in middle term. Such local demand needs to be harmonised with regional developments;
- The legal, regulatory framework and agreements in place allow for the developments or the natural gas sector in Albania and implementation of the Energy Community Gas Ring, Ionian Adriatic Pipeline (IAP) being the next most important project to follow. Development of the underground storage in Dumrea salt dome can contribute in the balancing of the regional market;
- Development of gas transmission and distribution infrastructure for the main anchor loads and harmonisation with the perspective development of the residential sector;
- Attracting investments, defining a market model and developing competition.

## THE ACCURACY OF GEOLOGICAL ORE RESERVES DISCOVERED IN THE SULPHIDE COPPER DEPOSITS OF QAFE MALI – SPAC OF CENTRAL MIRDITA ORE BELT, ALBANIA

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### Abstract

For a long of time, among mining and geologist engineers a very important problem regarding to the accuracy of the geological reserves discovered by the Albanian Geological Survey has been subject of discussion and debate. Of course, projections and mining works for exploitation of a deposit will be of a high cost, which would be increased even more if ore reserves would not be verified by geological and exploration works. Not only that, but the mine planning for the extraction of these unverified ore reserves, would bring severe economic consequences for the mining companies. The intensive development of exploration and mining activity for more than 40 years in the copper mines of Albania, created a more accurate image for discovered ore bodies, their shape and size, layering elements, etc. These facts, enabled the opportunity to give a more accurate opinion regarding to the accuracy of the geological reserves discovered by geological works. Presently, in the conditions of market economy, foreign or domestic companies, interested in obtaining a mining permit, naturally raise the question: *how*

*accurate are the geological reserves reported by Albanian Geological Survey through related geological reports and other geological materials belonging to different ore deposits?* A correct and argumented answer, would constitute the core of the problem with a strong impact, to attract or not an investor for the opening of a new mine. Based on our experience of the past 10 years, where we dealt with intensively accuracy of copper reserves in Albania, we want to present and publish for the first time in this paper, very interesting data regarding to accuracy of the geological ore reserves, discovered over the years, based on the archival records, not only of the Albanian Geological Service, but also of previous partial or fully exploited mines. We believe that this paper will not only guide the various investors who want to exploit different copper ore objects or deposits in Albania, but at the same time, it would be a serious support for the institution of the Albanian Geological Survey, giving it correct arguments for the authenticity of mineral resources discovered by it.

**Key words:** *Geological and exploration works, geological reserves, extractable reserves, mining works, exploitation works, investor*

## KAOLIN OF ALBANIA, PRODUCT OF WEATHERING CRUST OF GABBROS OF THE OPHIOLITES

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### Abstract

The kaolinitic weathering crust is well developed in the terrains of Albania. It originates by the chemical weathering of the underlying rocks consisting of gabbros and troctolites, belonging to the ophiolites of Mirdita unit. There are several kaolin deposits and occurrences of different sizes and interests, whose outcrops extent like a chain along entire the northwestern edge of Mirdita ophiolite. Among them, Korthpula, Dedaj, Vig-Tanushaj, Qeleza, Kashnjeti and Qerreti are the biggest kaolin deposit known so far in Albania. Their explored parts are of different size, up to 1.5 km long, 800 m wide and 20-30 m thick.

Based on the available data on geology, mineralogy and chemistry of these deposits, three kaolin types have been distinguished: 1) white kaolin, 2) yellow kaolin and 3) light grey-green kaolin.

The thickness of the weathering crust of gabbroic rocks partly to intensely altered, together with the industrial kaolin, varies from 10-20 m, to 30 m, 40 m up to 50 m. The highest thickness belongs to the sectors covered by the formations of Neogene-Quaternary and in this case the kaolin crust is well preserved. The thickness of the overburden varies from 5-10 m in the area Vig-Kashnjeti to 20-25 m in Korthpula and Qerreti. The thickness of the industrial kaolin within this weathering crust varies 5-10 m to 15-20 m.

The vertical section consists of three kaolin types from the bottom to top: the lowest one, with nonindustrial kaolin; the middle part, with industrial kaolin and the upper part, with kaolin

contaminated by overburden and ground waters. Locally, these kaolin types show transitions and/or intercalations between them.

The primary rocks, that are moderately to intensely altered, are part of gabbroic mafic intrusions. They consist of gabbros, leucocratic gabbros, mesocratic gabbros, microgabbros, gabbro-norites, troctolites, gabbro-pegmatites, their veins and pegmatites. Although they are gabbroic rocks, they show differences in their petrography and chemistry from a sector to the other ones. This highly affects the mineralogy and chemistry of the originated kaolin crust in the known deposits and occurrences.

The mineralogy and lithology of kaolin change in individual deposits and occurrences, this due to the lithology of the primary gabbros and the intensity and kaolinization grade of the weathering process. The chemistry of kaolin is:  $\text{Al}_2\text{O}_3$  (28-32 wt.%),  $\text{Fe}_2\text{O}_3$  (1.5-4.5 wt.%) and  $\text{SiO}_2$  (42-46 wt.%).

All the kaolin deposits are “in situ” deposits, originated by the chemical weathering of the mesocratic-leucocratic gabbro-troctolites and anorthozites.

The calculated kaolin reserves of Albania are 7.5 million tonnes, proven ones, and 15 million tonnes, estimated ones.



## SULPHIDE MINERALIZATION IN GABBRO AND PLAGIOGRANITES IN OPHIOLITES OF ALBANIDES

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### Abstract

Copper sulphide mineralization in plagiogranite and gabbro series represents an important typical metallogenic feature of the Albanian ophiolites. Albanides. These mineralizations are known as “quartz – sulphide mineralizations”.

The most significant concentrations are related to the levels of gabbro-plagiogranite rocks of this complex. They are represented by several important deposits as: Kurbneshti, Thirra, Gdheshti, Golaj, Nikoliqi, Kcira, Tuci lindor, Tureci, etc. A number of mineralized outcrops are recognized as well. The prospected and accounted reserves of this type of mineralization constitute about 20 % of the total industrial copper reserves discovered in Albania.

**Key words:** *Ophiolites of Albania, copper sulphide mineralization, gabbro, plagiogranites*

### 1. Location of gabbro and plagiogranite rocks in ophiolites section of Albania

The gabbro-plagiogranite sequence is placed in upper part of the ophiolite sequence and below the series of volcanogenic rocks and sheeted dykes. The mineralogical composition of gabbro-plagiogranite consists of plagioclase of anortite type (An<sub>50-80</sub>), amphibole and pyroxene in amphibole gabbro, quartz in plagiogranite, quartz-diorite and quartz-gabbro. The chemical features are characterized by a high content of SiO<sub>2</sub>, a higher content of CaO, a relatively low content of Fe and Mg and a very low content of K. These feature alongside the low content of Ti clearly distinguishes these rocks from their analogues of stratiform massifs. The gabbroid-plagiogranitic rock sequence occupies an area of 650 km<sup>2</sup> and is widely spread in the northern-eastern ophiolites, where forms the gabbroid massifs of Kaptena, Bulshar-Kurbneshti, Gjegan-Gojani and the plagiogranitic massifs of Shemria, Oroshi, Tuci, etc., and partly spread in the western ophiolites, where forms the massifs of Kçira, Qelza and Kashnjeti.

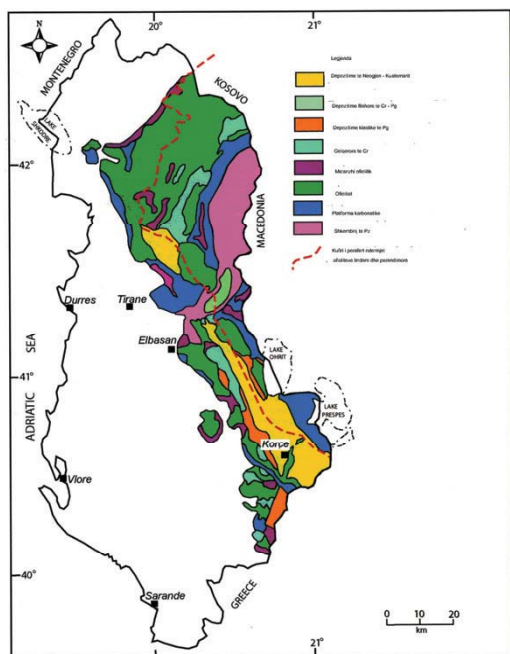


Figure 1. Map of the ophiolites spreading in Albania.

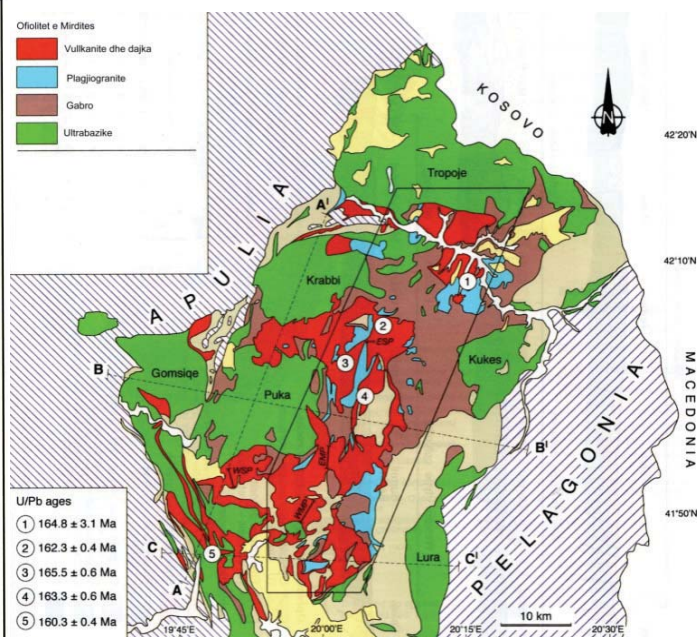


Figure 2. Geological Map of ophiolites in North Mirdita.

## 2. Spatial position of quartz-sulphide mineralization

The spatial position of quartz-sulphide mineralization is almost determined. Important concentrations are located in the levels of gabbroic massifs built by gabbro-norites associated with norites and gabbro-pyroxenites.

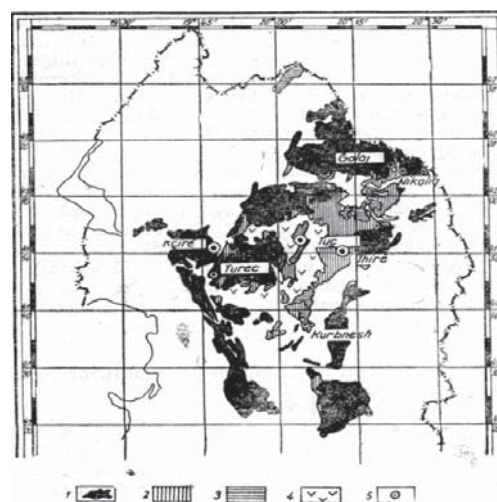
In the western ophiolite belt, the mineralization is concentrated in the lower levels of the gabbroic massifs section as in the case of Turec and Kçira deposits, in Kashnjeti and Puke-Qelza region. Quartz-sulphides mineralization consists of vein and lens bodies and it is accompanied by chlorite and quartz chlorite rocks, etc. These rocks represent secondary oriole of hydrothermal changes in gabbroic and plagiogranite rocks. In plagiogranite, quartz - sulphide mineralization has limited spreading, although there are cases where it forms larger concentrations in the form of deposits such as Tuçi lindor, Perlat and Shëmri. Typical mineralogical co-association is of quartz - pyrite - pyrrhotite - chalcopryrite 4 vv - sphalerite type, depending on rocky environment where the mineralization is located. For plagiogranite mineralization, the typical mineralogical co-association is quartz – pyrite - cahalcopryrite vv hematite .

## 3. The features of the main deposits of quartz-sulphide mineralization prospected in Mirdita Ophiolite

### Kurbneshe Deposit

The most important concentrations of mineralization are located in the lower part of the gabbro section.

Sulphide mineralization is represented by a large number of ore bodies wrapped by hydrothermal



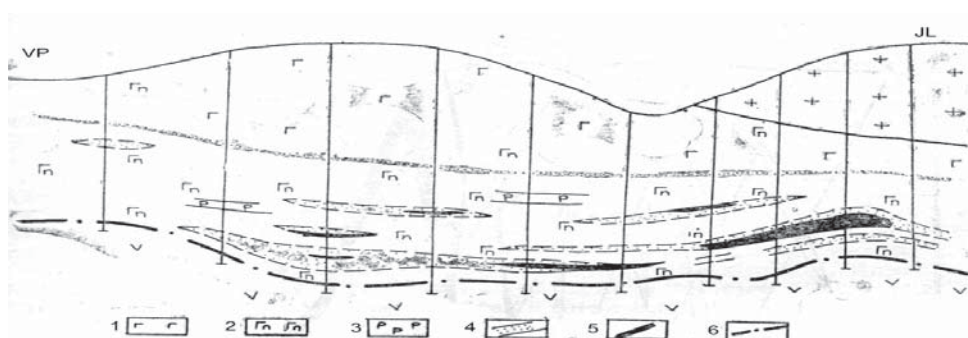
**Figure 3.** Extension of main deposits of sulphide mineralization in gabbro and plagiogranite.

areas with relatively limited thickness. Mineral bodies are presented in the form of lenses and veins, with the occasional bounce and dilutions, and rarely isometric. The mineralogical co-association is typical of pyrrhotite - pyrite - chalcopryrite mineralization. Mineralized zones and mineral bodies within them form a 220 m thick belt.

Mineralized zones and mineral bodies are concordant with surrounding gabbro structure.

### Golaj Deposit

This deposit is located at the contact between gabbro and ultrabasic rocks. The deposit is divided in two bodies (1 and 1a) and some mineralized lenses of limited size. The mineral body consists of co-association of pyrrhotine, pyrites and chalcopryrite and less from magnetite and hematite. Gangue minerals are quartz, serpentine, chlorite and calcite. General reserves of this deposit are 1,507,340 tonnes with 1.15-5 wt.% Cu. In some analyzed samples has Au up to 0.13 ppm and Pt



**Figure 4.** Cross section of Kurbneshe deposit; 1. gabbro; 2. gabbro-norite; 3. pyroxene; 4. mineral body; 5. mineralized zone

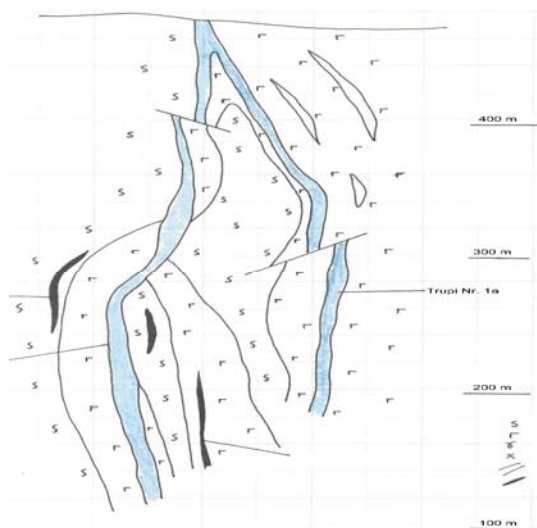


Figure 5. Golaj deposit, cross section, scale 1: 2,000.

up to 0.01 ppm.

### Nikoliq deposit

This deposit consists of three mineral bodies named 11, 12 and 12a. Mineral body 11 consists of quartz and chlorite with pyrite-pyrrhotite and chalcopyrite. Mineral Body 12 is localized within pyroxene gabbro and gabbro-norite and consists of quartz - chlorite with less chalcopyrite, pyrite and pyrrhotite. Mineral body 12a is intercepted within quartz gabbro and it is composed by quartz-chlorite with less chalcopyrite and pyrite. Mineral body 11 has 383 659 tone with 2.09 wt.% Cu. Mineral body 12 has 250 138 tone of 2.68 wt.% Cu. Mineral body 12a has 20 893 tone with 2 wt.% Cu.

### 4. The perspective of further exploration of sulphide mineralization in gabbro and

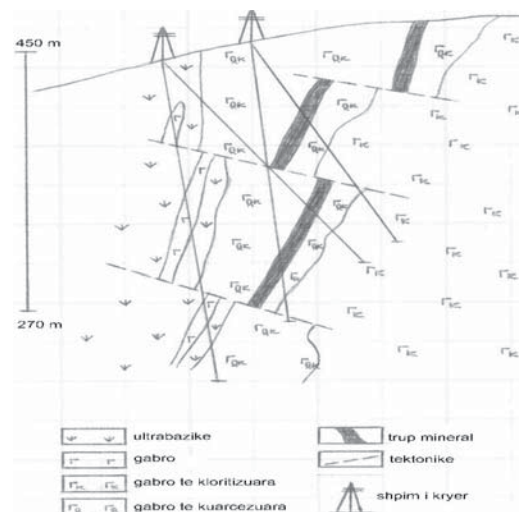


Figure 6. Mirun deposit, cross section, scale 1: 2,000.

### plagiogranite of Albanide ophiolites

Based on the lawfulness and features that were discussed above, the deepest and middle parts of gabbro display the most perspective environment for quartz - sulphide copper mineralization. Spatial position of sulphide mineralization is somehow determined: the most important concentrations of sulphide mineralization are located in the section levels composed of gabbro-norite associated with norite and gabbro-pyroxenes.

The outcrop of gabbro and plagiogranite rocks of eastern ophiolites and gabbro-peridotites rocks of western ophiolites represent the main copper-bearing belt of quartz-sulfure mineralized veins. Amongst the two ores belts, the Eastern one has the greatest mineral-bearing potential, which is conditioned by the large development of gabbro-plagiogranite sequence with metalogenic features

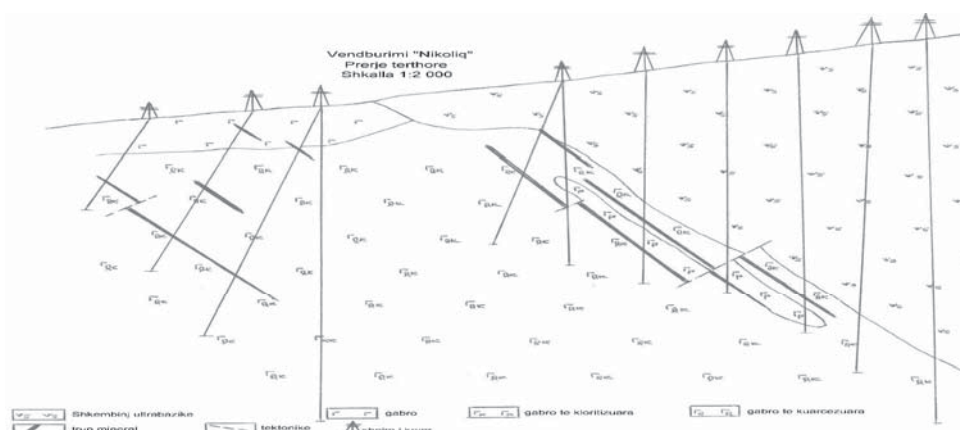
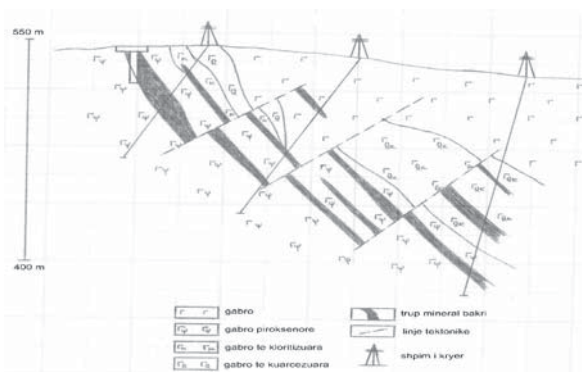


Figure 7. Nikoliq deposit





**Figure 8.** Krume deposit, cross section, scale 1: 2,000.

for Cu and Co. Within ores belts there are outstanding main ore areas belonging to the lower – middle levels of the gabbro massifs, represented by gabbro-norite, norite and gabbro-pyroxenite of eastern ophiolites (regions of Kurbnesh-Bulshar and Thirre-Gdhesht-Golaj-Nikoliq-Krume in gabbro massive of Kaptena) and western ophiolites in the region of Qelez-Kçire-Kashnjet.

The first perspective regions remain the spreading in layering and depth of Kurbnesh, Thirre, Golaj, Nikoliq, Tuci Lindor deposit. The lesser importance is the assessment of the mineralized outcrops where complex geological data testify to the possibility of the presence of quartz-sulphides industrial bodies.

## Conclusions

Sulphur mineralization in gabbro and plagiogranite of Albanides ophiolites are characterized by diverse mineral co-associations conditioned by genetic connection with their bearing-rocks. It is localized mainly in the basic rock types that constitute the middle and middle-lower part of the plagiogranite and gabbro massifs section. Gabbro and plagiogranitic rocks of Albanian ophiolites have a sufficient mineral-bearing potential for sulphide mineralization, so we can find in them important mineral concentrations of this type.

The main mineral-forming minerals are quartz - sulphides where predominate pyrrhotina, chalcopyrite, pyrite and quartz. These minerals meet in different quantitative ratios between them as in separate mineral bodies, and within the same mineral body. Main mineral textures are characterized by vein, banded, reticular and druze textures.



**Figure 9.** Qarri deposit, cross section, scale 1: 2,000

Mineral bodies have sharp contacts with the surrounding rocks. The hydrothermal metasomatic zones in general are thick, ranging from a few centimetres to several meters. In the pinch-out parts of mineral bodies, zones of hydrothermal changes expressed by chlorite or quartz – a chlorite rock formed on gabbro expenses, are clearly expressed and reflects sign for mineralized zones layering and dipping continuity.

Surface gabbro outcrops in the context of the Albanian ophiolites, labeled as special massifs, belong to the same gabbro level within the ophiolites section, as in geological-petrography terms and also in the metalogical context.

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## SPATIAL AND TEMPORAL RELATIONS BETWEEN EPITHERMAL AND PORPHYRY STYLE MINERALIZATION IN THE LECE MAGMATIC COMPLEX, SERBIA

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### Abstract

The Oligocene Lece Magmatic Complex (LMC) of southern Serbia (32-28 Ma; Schefer et al. 2011) comprises andesitic volcanic and volcanoclastic rocks including lava flows, pyroclastic breccias, crystalline and lapilli tuffs. It hosts epithermal Pb-Zn-Au-Ag occurrences (Banjska reka, Brajšor, Ždraljevića kuće, Sijarinska banja and Bakrenjača) together with the Lece Pb-Zn-Au-Ag mine (2.88 Mt grading at 1.55 wt.% Pb, 3.43 wt.% Zn, 3.78 g/t Au and 16.16 g/t Ag). The Lece sub-volcanic diorite intrusions host porphyry mineralization at Degrmen as well as the Tulare dioritic porphyry cluster (33.0 to 31.8 Ma; Tosdal 2012) with the Kiseljak as the most prominent Cu-Au deposit (300 Mt grading 0.27 wt.% Cu and 0.26 g/t Au). Although seven mineralized domains are distinguished within LMC, a comprehensive understanding of its magmatism, particularly the relationship between its chemistry and timing on one hand and the Cu-Au-Ag-Pb-Zn mineralization on the other, has not been well developed. The LMC unconformably covers and intrudes the amphibolite-grade metamorphic basement of the Serbo-Macedonian Massif (SMM) which comprises biotite and quartz-feldspar gneisses, two-mica schists, and marbles. To the west, it is flanked by a Cretaceous marine flysch sequence of calcareous shales, marls, sandstones and conglomerates of the Vardar Suture Zone. The Oligocene LMC magmatism was channelled along dextral strike-slip faults that resulted in a transpressive crustal shortening and collision of the Serbo-Macedonian Massif as part of European plate and Jadar-Kopaonik composite nappe of the deformed Adriatic plate margin as a promontory of the African plate during the Alpine orogeny.

The three ring structures, interpreted to be caldera margins are Gajtan, Džavolja varoš and Tulare (Pešut 1976) although there may be a significantly larger number of smaller volcanic vents (Serafimovski 2000). Two characteristic types of mineralization in LMC overall are: i) structurally controlled quartz breccia zones permeated by Pb-Zn-Cu-Ag-Au epithermal-style veins that generally trend northwest and east and are hosted in andesitic volcanic rocks, and ii) porphyry style, Cu-Au mineralization within diorite stocks intruded into the SMM gneiss and schist and comagmatic volcanic and volcanoclastics. The epithermal Pb-Zn-Au-Ag mineralization of the northern LMC shows north-westerly and easterly trends and is more distal from the Vardar Suture Zone relative to the coeval porphyry mineralization. In the southern LMC, the epithermal quartz-carbonate veins are dominantly east-west trending. A significant portion of the LMC is propylitically altered with chlorite-epidote as the dominant assemblage. The outcropping porphyry mineralization is potassically altered with magnetite-quartz-biotite assemblage and transitions distally to a sericite-pyrite-quartz assemblage. Prominent silicified breccia zones laterally transition to quartz-clay alteration within epithermal aureoles.

## CALORIMETRY AND PHYSICAL-MECHANICAL CHARACTERISTICS OF MALIQIS PEAT

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### Abstract

Coal is and will remain for a long time one of the main raw materials for the production of natural energy Worldwide, about 40 % of electricity is generated by burning coal and also, they constitute about 65-70 % of the known reserves of fossil energy. The global market consumes about 4-5 billion tone of coal per year, where about two thirds of is used to produce electricity.

Albania is a country having modest coal reserves. Over time, there are produced up to 2 million tone of coal per year, 40 % of which was burned to produce thermoenergy and the rest of it was used for municipal and industrial consumption. Until now our country has not affected its peat reserves.

Practically, Albania generates almost all its energy from hydroresources which are primarily concentrated in the north of the country. These are the arguments that assess that Albanian energy system is virtually non balanced and things depend on climatic conditions.

The peat deposit in Maliq is a quaternary continental sedimentary deposit. The spread surface of the peat layer is 43 km<sup>2</sup> with an average thickness of about 5-6 m. In 60 % of the surface, the peat does not have a cover, the rest is covered by clay packs of a 0-2 m thickness.

Maliqi peat are characterized by a high content of moisture and ash. Sulphur content is relatively low while the calorific power of the raw material is about 3200 kJ/kg.

The application of technologies for de-watering of the Maliqi's peat from 80 % to 30-35 % made them an interesting matter for combustion and energy production.

During 2008 were conducted 31 shallow depth drilling with an average of 11 ml. each, from which we took and analyzed 120 samples of the drilling column with a weight of about 740 kg. Calorimetric analysis in natural moisture gave interesting possibility of industrialization of Maliq peat. In the about 5-7 wt.% moisture, peat power input ranges from 1600 to 3700 kcal/kg, with an average of 2590 kcal/kg, ash content varies from 35 to 58 wt.% with an average of 45.4 wt.%, while sulfur content varies from 0.73 to 1.25 wt.% with an average of 1.01 wt.%.

**Key Words:** Peat, Maliqi, caloric power, ash, sulfur and energy

## ELECTRICAL PROSPECTING IN SEARCH FOR POLYMETALLIC MINERALIZATION IN ZHEGOVC AREA, KOSOVO

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### Abstract

This paper focuses on improvement of effectiveness of Induced Polarization and Resistivity methods through IP/Resistivity “Real Section” technique and employment of powerful instrumentation in search for polymetallic mineralization in Zhegovc area, Kosovo.

The obtained results presented below, indicate a very interesting IP and Resistivity anomaly at depth below 100 m from surface in a recognition survey line, which will be subject to borehole verification and further IP/Resistivity “Real Section” survey lines on strike.

**Key words:** *Polymetallic mineralization, induced polarization, apparent resistivity, IP/Resistivity “Real Section”*

### Introduction

Electrical Prospecting with Induced Polarization and Resistivity methods has been recently applied in search for polymetallic mineralization in Vardar zone in Kosovo with two novelties. One of them is the IP/Resistivity “Real Section” technique, developed in Albania in late seventies and widely applied in Canada and other parts of the world after 1991. The second novelty is the recent implementation of a powerful IP/Resistivity instrumentation in these surveys, comprised of transmitter VIP-10000 and receiver ELREC Pro. Both of these novelties have markedly improved the effectiveness of mineral exploration through increase of investigation depth and better determination of target’s attitude and resolution. The obtained results presented below, indicate a very interesting IP and Resistivity anomaly at depth below 100 m from surface, which will be subject to a verification borehole soon.

### Materials and Methods

The Zhegovc area is located in Gadime – Plitkovic zone, Lipjan commune, about 22 km southeast

of Prishtina. Geologically, it takes part in the Vardar zone, well known as a host of Trepca giant polymetallic deposit. The geology of survey area (see Fig.1) consists of the following formations: Zhegovc metamorphic series, Jurassic sediments (ophiolitic mélange with limestone olistoliths, serpentinite, diabase) sediments of Cretaceous Vardar zone (sandstone, marl, aleurite, carbonaceous marl), Oligocene formations (mostly trachyte), Pliocene sediments (clays, sands, gravels), as well as Quaternary sediments (gravel, sand, silt and lignite layers). The area of survey is covered by topsoil and vegetation but the smelter slags encountered around witness for an early historic exploitation of the polymetallic mineral occurrences in this territory.

The known polymetallic ore deposits in Kosovo are numerous and their depths vary from near surface to over 300 m. The conventional electrical arrays such as Dipole – Dipole and Pole Dipole do not provide good results at depths below 200 m in this environment without losing the resolution. For this reason, a modification of gradient array with multiple spacing called IP/Resistivity “Real Section” (Langore, Alikaj and Gjovreku, 1989; Roth 1997; Alikaj and Gordon 2000) has been implemented in electrical prospecting in Kosovo since 2004 (Frangu 2006). Proprietary software for terrain correction and electrical current lines scattered in section are also employed. To make these corrections, a mathematical approach of current flow distribution between current electrodes and its distortions due to terrain variations are merged into a special algorithm. As proved in similar surveys in Albania, this software markedly improves the accuracy and resolution of target interpretation. Due to presence of some low resistivity formations in Vardar zone, like clays, chloritic-sericitic slates and schists, serpentinitized ultramafics and presence of massive polymetallic sulphide bodies at medium depth, the conventional IP/Resistivity transmitters of medium power (up to 3 kW) often fail to reach depth of investigation below 200 m.

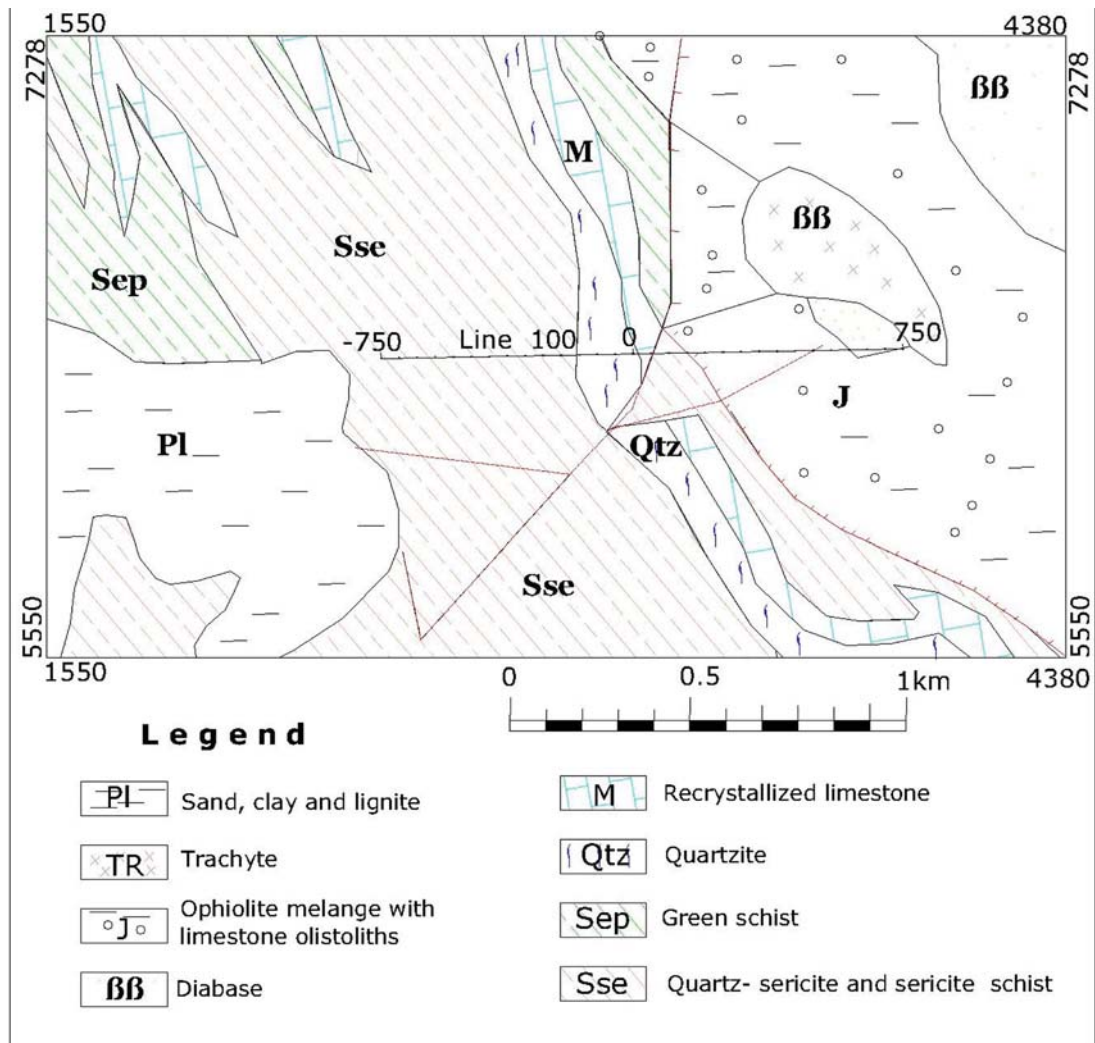


Figure 1. Geological map of Zhegovc area with IP/Resistivity survey line.

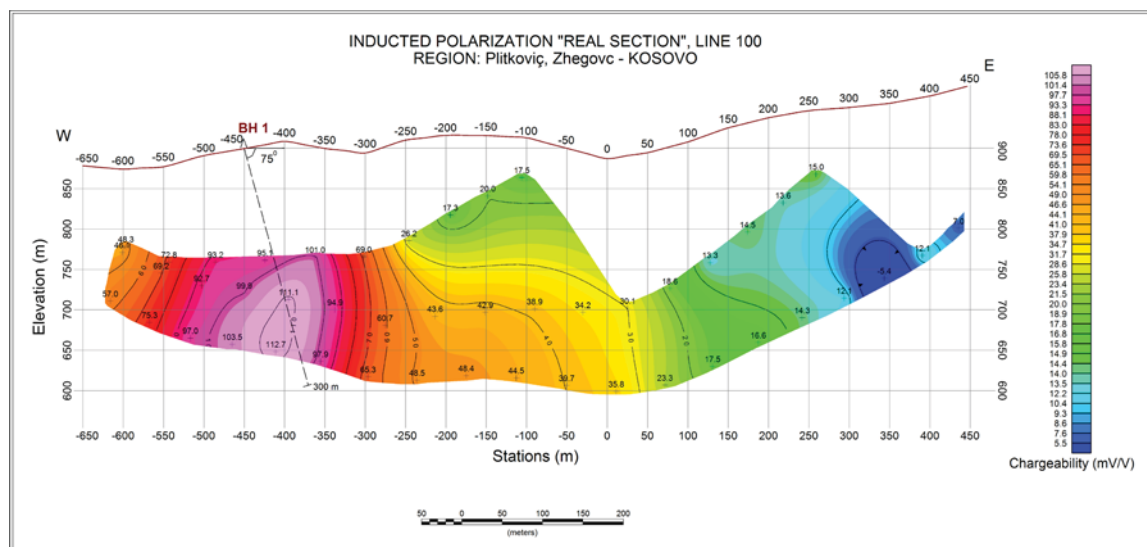


Figure 2. IP "Real Section" of survey line.



This is more emphasized in cases of rather old anomaly is located amidst Zhegovc metamorphic

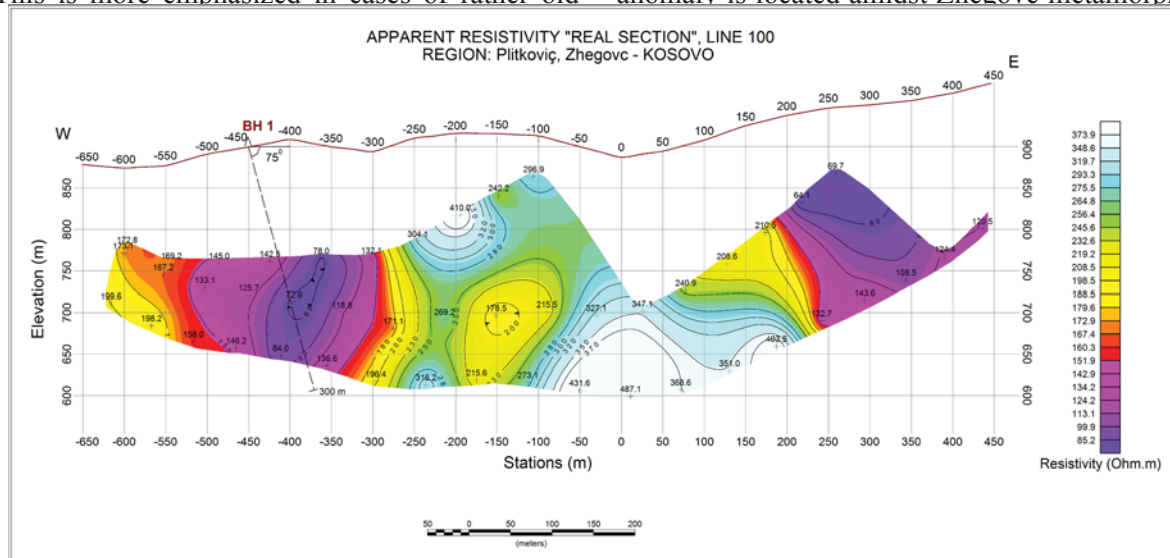


Figure 3. Apparent Resistivity "Real Section" of survey line

technology receivers, which are more affected by electrical noise of different origins. For this reason, recently, the company RAF Geophysics based in Kosovo, acquired new IP/Resistivity instrumentation for deep exploration, consisted of transmitter VIP-10000(max 10 kW, 20 A, 3,200 V) and receiver ELREC Pro, produced by IRIS Instruments, France. This instrumentation has markedly improved the quality of chargeability and resistivity measurements, even for long spacing arrays ( $AB = 2 - 3$  km), increasing the depth of investigation and reliability of the data. Repeated measurements prove a small error (less than 5 %) in these measurements.

### Results and Discussion

Onerecognition survey line was conducted in Plitkovic area, Gadime commune, Kosovo with IP/Resistivity "Real Section" technique (Fig.1). The measurements were carried out with gradient array of various spacing which provided various depth of exploration, from 100 m to 300 m (Alikaj et al. 2013). In figure 2 is presented the IP "Real Section" obtained in survey line. The chargeability values in this section vary between 10 mV/V to the east and 112 mV/V in the center of an anomaly, obtained to the west, on station -400. This anomaly is outlined by contour 70 mV/V and reaches its peak at depth 200 m. It has a good corroboration with apparent resistivity parameter presented in the Resistivity "Real Section" in Fig.3. The resistivity drops from 250 Ohm.m in the surrounding background to 72.8 Ohm.m in the center of chargeability anomaly. Geologically, this

rocks, consisted of sericitic, quartz – sericitic and chloritic slates. The presence of polymetallic deposit is known within these rocks in Vardar belt. Due to corroboration between chargeability and resistivity anomalies, the chances are high this anomalous zone to be related with presence of massive polymetallic sulphide without outcrop. For this purpose, a borehole (BH-1) is proposed for its verification on station -450, with bearing  $90^\circ$  and length 300 m.

In addition to this IP/Resistivity anomaly, another one, less prominent but with good corroboration between chargeability and resistivity parameters, is observed between stations -50 and -200. The apparent resistivity anomaly is better outlined, compare to IP anomaly. This might be due to superposition effect caused by both, the presence of massive sulphide and the scattered sulphide halo. After verification of the first anomaly, another borehole will be projected to verify the center of the second anomaly, primarily the core of apparent resistivity anomaly at depth of about 200 m from surface. In case of positive result of borehole BH-1, several other lines of IP/Resistivity "Real Section" survey will be carried out on both sides of the first line, spaced 100 m apart.

### Conclusions

The IP/Resistivity "Real Section" recognition survey performed with a powerful instrumentation has been effective in outlining two interesting IP/Resistivity anomalies at depths below 100 m. A borehole is projected to be carried in this

anomaly at depth 300 m for verification. In case of positive results, two other recommendations are immediately to be followed:

1. Several other survey lines with IP/Resistivity "Real Sections" should be performed on both sides of the central line spaced 100 m apart.
2. A second borehole should be drilled in the second IP/Resistivity anomaly already obtained in the first line, around station -150.

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## GEOLOGICAL FRAMEWORK AND OIL-BEARING OF AMANTIA AND RAMICA AREA

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### Abstract

It is located in the southern part of the Ionian zone, in the southern continuation of the thrust chain of Selenizza, Gorisht Kocul and Amonica (Fig. 1). The spilling point between Amonica and Amantia clearly appears based on the seismic lines. From lithological point of view, this structure is built of Paleocene-Eocene limestone as well as of Upper Cretaceous limestone. The Lower, Middle and Upper Oligocene deposits have a total thickness of 250 m. After that, the Chatian-Aquitian deposits are covered by the Burdigalian transgressive system tract. This event has a large surface starting from Velça-1 well up to Ballsh oilfield.

Concerning the Oligocene flysch, it is in full disharmony with the top of limestone because of tectonic compression creating figures type like blind thrusts. We can see the disharmony within the limestone section in the boundary between the Paleocene-Eocene and Upper Cretaceous. This phenomenon is expressed clearly in the seismic section 187/83.

The high pressure exercised from the structure of Griba as well as the big difference between the Tragjasi and Çika structures create possibilities for normal and thrust faults. A big influence in the framework of this region has the separation of Çika from Tragjasi, expressed in the big difference of the thickness of the Burdigalian of Çika structure compared with that of Tragjasi (4000 m in the Çika structure and 2800 m in the structure of Tragjasi).

In this region there are three wells drilled from which two are deep, Amantia-1 and Velça-1. From the data of these wells, the Burdigalian unconformity is clear, which continues from north to south but not on the Ramica structure where it lies successively.

This geological situation imposes to think that this structure of Amantia is shallower compared to Ramica structure. The bottom of Velça is of Middle Oligocene age. Knowing that the total

thickness of Oligocene is about 250 m, then this well is expected to encounter the top of limestone about 3100 m. Such a value is even for Amantia-1, thus 3100 m.

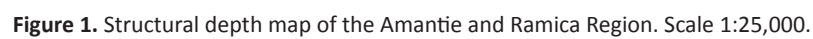
The structure map has been constructed based on these two values (3100 m in Amantia and Velça) as well as on the rare data of the seismic lines which are assumed to be shallower than the value 3100 m in the wells Amantia-1 and Velça-1 (see the structure map, Fig. 1).

Concerning Ramica structure, the structural map and the seismic lines clearly indicate the course of a seismic horizon. It is present in several seismic lines, especially in the seismic line number 254/89. The continuity and the distribution of the thickness of this horizon must be around the tectonic boundary between Tragjasi structure and Çika structure. An important problem is the age and the lithology of this horizon. It does not have any direct or concrete relation with any well, but it appears very clear and can be mapped easier with seismic lines.

Concerning the reservoir, it is expected that the fracture porosity to be predominant because of the presence of the faults oriented NW-SE and micro faults oriented NE-SW.

Accepting this disharmony between the Paleocene-Eocene limestone with the Upper Cretaceous limestone increases the presence of the fracture increasing the distribution of the fracture porosity. For the similarity with the Gorisht-Kocul Oilfield, where there are caverns and cavities because of acid presence, the same thing is expected in the reservoir of Amantia.

Since the seismic sections are not of a good quality, which does not impose a solid construction of the structure map, we have tried to build a structure map based in all data, such as the mapping geology, similarity with all the structures of the same chain (such as Gorisht-Kocul, Amonica, Amantia). The factors that influence the geology of this region are: mapping and structural geology, the thickness of deposits in this area and the unconformities. The





last one is the most important because put face to face two thicknesses of Burdigalian, the thickness on the top of Amantia structure (which is thinner) and the other on the top of Ramica structure (which are much thicker than that we mentioned above).

This kind of analyze makes us to be more optimistic with the zone of Amantia (north). Related with this area, it is accepted that the isolines in the area between Amantia and the Velça are shallower than the area in the South.

The trap is an important and indispensable element. The main role in the both structures is played by the the Lower, Middle and Upper Oligocene shales (*Globigerina ciperoensis* zone).

Concerning the oil and gas migration, the problem is considered resolved because these structures are in the same chain of structures such Cakran, Gorishti and Amonica.

The water mineralization of the formation is high

based on the data of Amantia-1 indicating that there is not any contact with the fresh water.

For this region, the quality of the material in the whole is not good concerning the seismic lines. The structure map is based more on the surface geology and that of depth and it is not clear the transition from the block of Amantia to the block of Ramica. Qualitatively, it is traced there where the thickness of the Burdigalian is changing drastically, where in the South there is not any unconformity, angular or stratigraphic one.

In addition, the increase of the quality of the seismic lines should be possible by reprocessing of the existing ones or to reshoot again but not with traditional methods.

In case that we cannot resolve the problem with the above mentioned methods, we can probably resolve the problem by drilling of wells.

## GEOLOGICAL STUDY ON THE DUMRE OIL EXPLORATION BLOCK

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### General knowledge

The Dumre block is an integral part of the external Albanides and from paleogeographical point of view is thought to represent a pull-apart basin.

It thrusts partly as a result of a convergence of the right lateral. This caused the convergence between Kruja Platform-Berat block against the Southern Adriatic Platform.

The structure of the Dumre block is covered by a large mass of evaporates formed by many thrusts caused by out of sequence. The object of our study is represented by a limestone section where which is expected to be a good reservoir mainly in the Upper Cretaceous and Paleocene and Eocene deposits.

### Potential generation of hydrocarbons

In the Mesozoic carbonate section, the source rocks display a high content of TOC. The kerogen is of type I and II. By using the temperature gradient of 1.6 °C/100 m, the depth of oil entering the window is greater than 5000 m. To use the temperature gradient 1.35 °C/100 m, the depth of the oil window is over 7000 m. It is entirely possible that older levels of source rocks have entered the oil window and are probably deeper, producing thermogene gas. For these reasons, the Dumre prospect may be filled with all sorts of hydrocarbons.

### Assessment of the prospects

Geological and seismic data have shown the existence of the Dumre prospects (Fig.-1). Prospects represent a regular anticline structure with a tectonic fault in the west. This is the result of a convergent movement right between Krujë-Berat block against the Southern Adriatic block. The regional presence of parallel faults with the stratification could encourage similar phenomena in Dumre structure. This phenomenon can cause regular structural closure (four way dip closure) even larger.

### Recommendations

We recommend the drilling of two wells, in the Dumre block, Dumre-9 and Dumre-10 (Fig. 1).

The purpose of the drilling of this well in Dumre Block is to test the hydrocarbon potential of the Upper Cretaceous and Paleocene-Eocene limestone section (Fig. 1). The total depth is projected to be within the carbonate sequence. The top of limestone is estimated to be 6500 m (relative level).

### Introduction

Regional geological data and the new data obtained in Dumre block were analyzed to achieve the goal of this study and can be summarized as follows:

- To drill two wells (Dumre-9 and Dumre-10) in order to determine the hydrocarbon content of carbonate section in the northern and southern part of the Dumre block. (Shalësi and Dragoti prospects);
- The best mapping of carbonate prospect of Dumre-10 and 9;
- A qualitative assessment of reservoir properties in the wells Dumre-9 and 10.

### Determination of prospects of Dumre block

The Dumre structure is thought to be the result of a pull-apart basin, as part of a strike-slip fault started in Triassic. During the compression (Upper Cretaceous and later), the same “strike-slip” fault is thought to be active, but in the opposite direction.

### Tectonic evolution

Based on a new interpretation of the data across the Albanide, their tectonic evolution and tectonic style are different from the one that was described earlier.

They may be better interpreted as a convergent

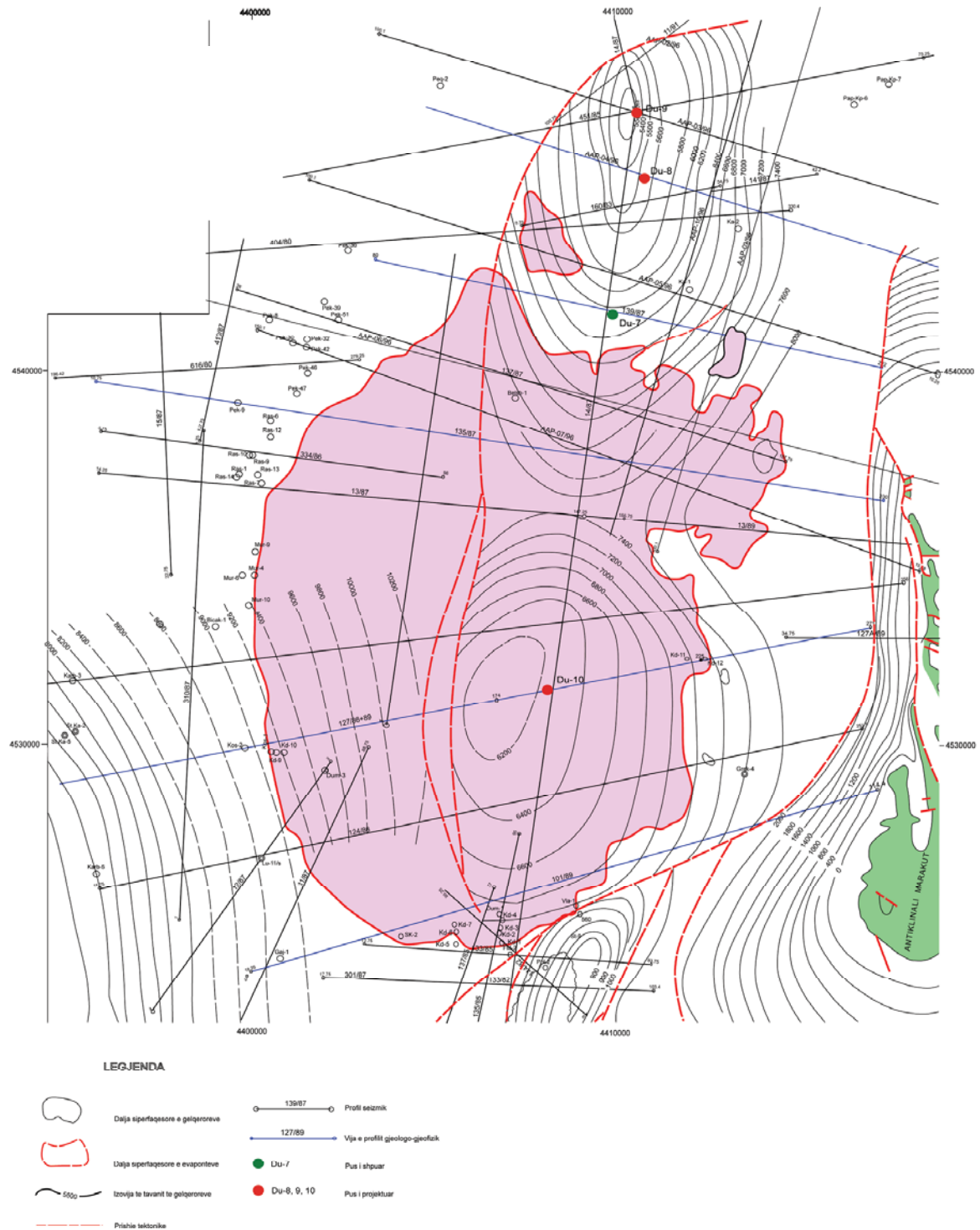


Figure 1. Structural depth map of the Dumre Region. Scale 1:50,000. Year 2014.

strike-slip belt than a simple thrust and fold belt. It is thought that the largest strike-slip fault was a strike-slip between the tectonic plates, associated with the high of Mirdita Ocean (Shkodër-Pejë segment).

During Upper Triassic and Cretaceous this fault acted as a left divergent strike-slip fault.

During the Upper Cretaceous and later on, this fault (Shkodër-Elbasan-Corfu) acted as a convergent fault, right strike-slip.

In these conditions, the tectonic regime changed the environment of pull-apart basin of the Dumre in its northern and southern part (Shalësi and Dragoti structures).

The extensional regime that dominates the basin-forming faults with NE direction can cause the exposure of the evaporates on the bottom of the basin, as noted above.

Along the Upper Cretaceous, Paleocene and Eocene deposits, the building-basin faults form the shallow carbonate platform which supplies the basin with allodapic and detritic material. In addition, some levels of mega-breccia are expected.

This is based not only conceptually, but with some facts: section of Lower Oligocene, near the intersection of restraining bend with releasing bend.

Based on some stratigraphic and azimuthal unconformities, expressed very well in Kruja region and Dumre basin, it is expected to have at least the same number of breccia levels as the number of surfaces erosional breccia caused by tectonic activity and the differential rising of the blocks.

The largest horizontal overthrust of the Albanides happened during the Burdigalian.

In both bends (releasing and restraining bends), it is thought that evaporate body exposed thrusting respectively to the northern side - on the Dumre structure and to the southern side - on the Verbas structure.

In Elbasan valley we can see very clear the normal faults expressed very well on both sides of releasing bend, the northern and southern side, as well as the thrust on the restraining bends, the eastern and western side.

This tectonic phenomenon in extension and in compression helps a lot in increasing of the porosity of fractures and karst.

## Structural style and trapping conditions

As noted in previous studies (geological and geophysical) in a structural style, some levels of detachment have a regional distribution. They include:

- The Triassic evaporite;
- Upper Cretaceous shale;
- Posidonia shale of Toarcian;
- Oligocene Flysch.

Based on outcrops and wells data, the Triassic evaporates, Upper Cretaceous shales and Oligocene Flysch are levels that dominate the structural style of the Dumre block (for both Shalësi and Dragoti prospects) (Fig. 1).

The Toarcian shists are the best level for detachment faults. They are expressed very clear in the wells and seismic profiles of Kruja and Berat region. Given the fact that we mentioned above, it is expected that some stratification parallel faults are present in the limestone section of Dumre (Shalësi and Dragot structures included).

## Assessment of Dumre reservoir

The reservoir in the Dumre prospects (Shalësi and Dragot) includes lithological section of the upper Cretaceous, and Eocene-Paleocene. It is believed that oil is accumulated in vugs, caverns, fractures, tectonic breccia and sedimentary grains and paleokarst formation from water and acids.

Considering the many discussions and concepts about the above characteristics, it would be better to have some discussions on this subject. The presence of cavities is based only on the Albanian experience. There are many wells, in some of them we have seen the partial loss of mud and in some others, a complete loss. In addition, current oil production is up to two times higher than expected, based on the evaluation of the porosity of fractures. Another factor that has influenced the creation of cavities or funnels has been the presence of sulphuric acid, which has caused the dissolution of  $\text{CaCO}_3$ . There are several springs of hot water in the Dumre block, which are associated with deep faults.



## THE COMBUSTIBLE MATERIALS IN ALBANIA (COALS, PEAT, BITUMINOUS SANDS)

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### Abstract

From energy resources, except oil and gas, on our country are explored coals, peat, pyrobitumen (bituminous gravel).

### Coals resource

Coals are used in our country since the First World War. The first mines were in Krraba, Mborje Drenova and Memaliaj. Their exploitation until 1991 has been done in order to fulfil the needs for electricity production in TECE (Tiranë, Elbasan, Maliq, Korçë, Vlore and Shkoder), for steam production for municipal use and partly for export. In neighbouring countries, Greece, Macedonia, Kosovo and Montenegro, the electricity is produced with coal in TEC. Coal reserves in are about 770.4 million tones (Gjoni V. etj.2009, Leka Gj.etj. 2012). From geological resources during the years 1950–1992 it was possible to found over 40 coal deposits (Bakllabashi J. Gjoni V. Vaso P etj 2005), spread mainly in: Tirana basins where were discovered around 86 % of total reserves (Dimo LL, Imami S. etj.1980); Memaliaj 4 % (Ylli M, Kuçi Xh, etj 1978); Moravë-Gorë-Mokër, Pogradeci, Devolli, Kolonja 10 % of reserves and less in other zones. Generally, our coals are of lignite type, with analitical calorific power of cylinder, which moves within the limits of 2000-5600 kcal / kg ( on the avarage 3,200 to 3,300 kcal / kg). In Albania, the coal is related with the molassic deposits of lowland placed over the internal and external zones. The Carboniferous formation are formed during the late development of Albanides and their migration in time and space has moved from the internal zones to the external ones, creating basins with age and own features. Separated in three basins carboniferous (Dimo LL. Pashko P. Vaso P, etj 1989):

- Oligocene – Lower Miocene
- Tortonianian (Miocene)
- Pliocene-Quaternary.

### Peats

In Albania, the peat deposits are encountered in Maliq (Korçe), Orikum (Vlorë) and Çukë (Sarandë). The peat is used for household and communal purposes, for the generation of electricity, for the production of active coke, water purification, substances of plant cultivation, for soil fertilization or plants, for medicine, for insulation etc. Some peats areas mainly with autochthonous origin of paralic character are signaled in the Adriatic coastal marshlands edge, starting from Shkodra to Vlora and in the fields of Korca and Vurgu as: the source of peat former marshland in Maliq, peat appearances in Terbuf, Vrakë, Seman, Vjosë, Butrint and Balldre (Lezhë). Generally, the peat marshy zones have great extension.Until today only, in the site of the former marshland Maliq, in the field of Korce, were found peats deposit with considerable extension. With further research and studies it can be found considerable peat reserves, in the former lands of lowland marshy of Adriatic Depression, as are Kakariqi, Tërbufi etc, and the addition of reserves in the former and the Marshland of Maliq (Karanxhi M, Kallajxhi P 1974).

### Pyrobitumen (bituminous gravel)

The first evidence for bitumen date back in 1700. At the beginning of the last century there was lot of evidence of exploitation that were done for natural Bitumen resources by foreign companies. At the beginning from the Turkish Empire, later from English societies, French and later Italian ones before and during World War II. First Mine organized as such, dates back around 1830 and is established by a British company. Biggest development took after World War II.

Meets together with natural bitumen in mineral source of Selenicë, about 7.5 million tons. Has carbon content (C) free 70-92% and calorific power of 3500-7500 kcal/kg, content varies 38-45% ash, with calorific power of 4200 - 4800 kcal/kg. Bituminous gravel is used as fuel together with imported coke for metallurgy of Elbasan.

**Key words:** coal, peat, bituminous sand, bitumen, pyrobitumen, bituminous gravel

## THE CAREER CONSULTING CENTERS – A PROMOTION POSSIBILITY FOR GEOSCIENCES. STUDY CASE: COLOMBO CENTER ALBANIA

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### Introduction

Educational Career Consulting Center is a counselor service provider which engages diverse community of scholars in developing successful strategies for career planning and helps future leaders for a variety of industries through leadership development, mentoring and multicultural awareness.

It guides students in exploring studies and career options that look interesting and intriguing - before determining which career they want to pursue. It begins with self-assessment, to understand better yourself - your strengths and weaknesses; it is a life-long process, but starting at the right moment will be immensely valuable in facilitating the assessment of career options and goals.

‘Colombo Center Albania’ is an educational non-profit organization, operating in educational field of Albanian market. It is relatively a new organization, created and leaded by the fact of informing the Albanian society, students and their families, about the new opportunities of studying, working and experiencing new international life abroad; providing the highest quality of academic courses and consultancy services, in order to fill up the education needs, not only in basic education but also in preparation for University and Post university studies.

‘Colombo Center Albania’ helps adapting them to the new educational institutions, culture, language, environment, study programs, society and way of leaving.

The aim of this paper is to check the important role of the career centers in guiding students towards professional studies including geosciences and to indicate some ways how to do this.

### Strategies of orientation to the professional international education

Our activity is focused in two base services:

1-Marketing and consultancy service for the students aiming to study abroad;

2-Academic preparation service offered as one to one tailor made courses, for the students interesting to increase their level of knowledge, in different natural and social science and language programs.

In reaching our first goal we have created an international network of the language schools, institutions and universities with which we collaborate.

We are working intensively to expand our international collaboration network not only in Europe but also in other continents, in order to inform and guide our students to the different, diverse, plenty study and job opportunities offered today also for Albanian students.

In order to maintain high quality service, exploring new opportunities and update our students with new study environments, we attend regularly international educational fairs. We have participated at the International Consultant for Education and Fairs, ICEF Berlin 2012 and ICEF Berlin 2013.

We have created close relation with the high public and private schools in Tirana and other cities of Albania, by visiting the students at their schools together with our international partners, informing them about the new study opportunities, each academic year.

### Starting with marketing strategy

It is true to accept that Albania is a very small country with a number of population close to 3,000,000 habitants where about 20,000-30,000 students finish every year the high school. Although the students study the career counseling subject within the high school program in Albania, it is impossible for them to be fully informed about the ways how to realize their desire and their proper skills related to their professional future.

Their study choices are conditioned by many factors like: high school average votes, the lack of information related to their career counseling, family financial standard, labor market demand. By our experiences, only a limited number of students is oriented to geosciences. A Career Program should be used as a vehicle to highlight the potential of promising new geoscience faculty within their home institutions and ensure that best practices in education are broadly implemented Huntoon et al. (2005).

Referring to Huntoon et al. (2005), the geosciences are relevant, intriguing and integrative. The geosciences provide concrete examples of the application of concepts and skills from all of the STEM (science, technology education and mathematics) disciplines.

This is why; we have developed very strong links with high quality international educational providers, who we can trust to undertake our marketing and promotion campaigns in the country.

The Albanian students actually studying in Germany are the best 'ambassadors' and witnesses of our high standard as consultant service provider organization and key missioner links between student' families and international Institutions in long-term collaboration, a key fact that has increased our reputation in Albanian educational market.

### Consultancy service strategy

Our consultant strategy it is focused in intensively informing the student, scanning his academic background profile, understanding his motivation and reasons to be part of the prospective international students and their entire study project

for the future.

Establishing a long-term collaboration, including application process preparation, integration to the new international school environment and society and at later phase, integration into higher educational system of the guest country, is another strong point of care and consecration highly evaluated from their parents.

We suggest to the students a suitable field of studies according to their academic skills and to the demand of the international labor market.

Our goal of consultancy is to guide the students how to step on the secure road professionally and reach their sustainable future.

Our consultant experience with Albanian students has been involved with the demands of studying mainly in Germany.

The economic power leader of Europe has opened the gates of the higher education also for the best international students highly demanded in the international professional labor market. Its advantages of having free higher education study programs for international students, working opportunities during and after their studies, competitive multicultural education environment and combination of theoretic methods by the practice and scientific research have been very attractive for the Albanian students who look for better higher education opportunities.

An increasing interest for studying in Germany was observed especially for the middle level of society, who sees the studies in Germany as the best qualitative and economic beneficial, sealing their professional life preparation into the public German universities. The percentage of the students studying in Germany against the total number of the students who study abroad was

## Number of the students per year

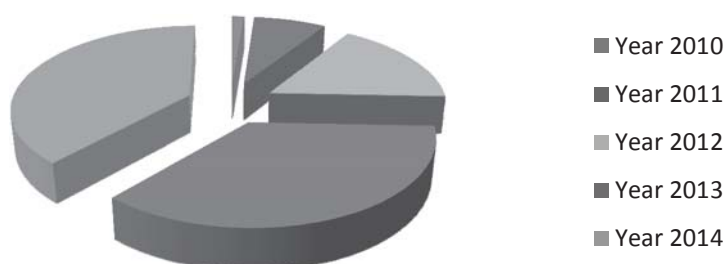


Figure 1. Number of the students per year

yearly increased as it appears in the pie chart (Fig. 1): 1.25 % in 2010, 7.5 % in 2011, 16.25% in 2012, 35% in 2013, 37.5 % in 2014.

The students have mostly chosen to study medicine,

engineering and there is no interests at the other engineering field of studies although the engineering spectrum derivate it is really huge in Germany.

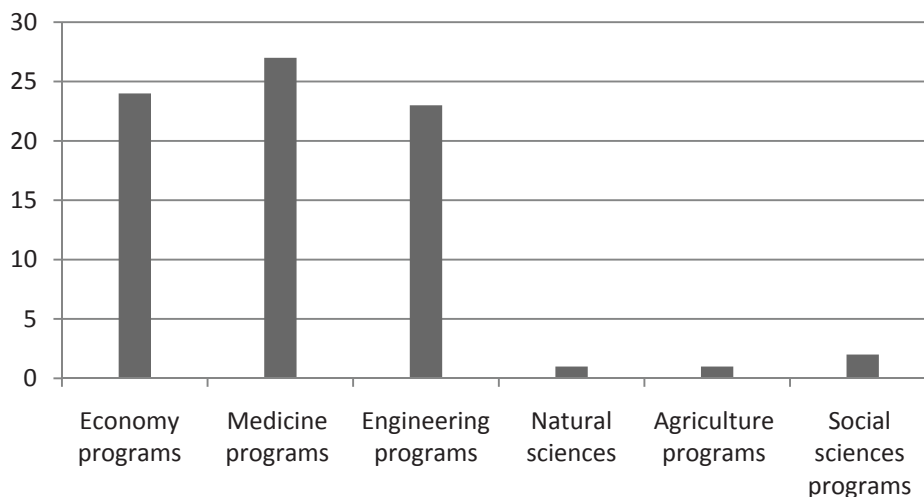


Figure 2. Number of students per program

engineering and economy and very rarely social sciences.

Such a strong tendency to attend professional study programs was expected considering that the applicants are students that attended natural science program at high school.

The most frequented is medicine program followed by economy and engineering ones (Fig. 2).

With the orientation to the engineering field of studies our students' interests have been mainly concentrated at the computer engineering, construction engineering, architecture engineering, and electronic engineering following by physical engineering, mechanical and renovation energy recourses engineering. Low demand it is noticed for the geophysical, economic and electrical

Of course the number of the engineering specialization in Germany it is huge, and further Post university studies in very specific engineering field of Geosciences can be possible also for Albanian students, although at the first sight the interest in this field of studies seem to be not in high demand figures.

In manner to have an increase of applications in geosciences we have to collaborate and build new social structures. According to Marlino et al. (2004), this requires:

- New types of partnerships across academia, government agencies, and the private sector;
- Multidisciplinary collaborations between geoscientists, information technology specialists, and educators;

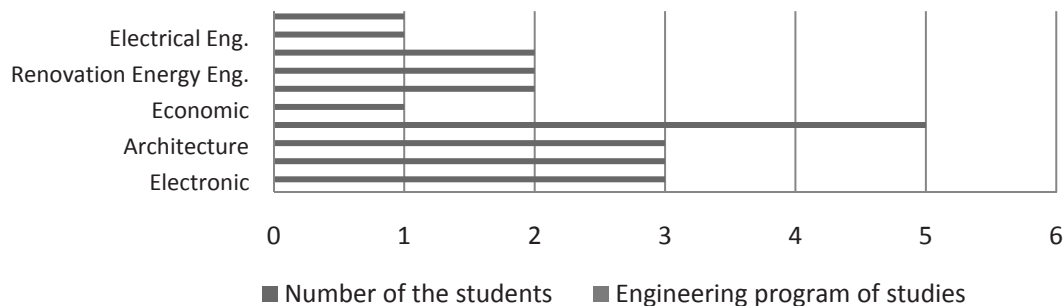


Figure 3. Distribution of the students number according to the special Engineering field of studies



- Mentoring, scaffolding, and collaboration across age groups;
- Increased transparency across geopolitical boundaries so that global concerns and solutions can be applied to local communities.

In addition, an analyze of the ratio of the students interesting in a very special field of engineering compared to the total number of the students interesting at the engineering field it is presented below:

The fact analyzed above shows a part of interest only referring to the limited number of the students, who applied to study abroad at the Engineering field, through our organization and it is based also at their favorite study program selection. It is obvious, that talking about e bigger group of the students, the figures will be different, mainly when we are talking and considering also demands of the market for the professionals at the special field, also the study orientation will be focused according to this needs.

## Conclusions

As positive experience related to the important role of the career centers in guiding students towards professional studies such as geosciences are, and referring to different ways of how to do this we can mention:

1-The market demand for engineering professionals and especially geoscientist professionals in nowadays it is very high not only in Albania but in all other countries. It means, there is a lot of benefits and potential to be considered in the global professional environment.

2-A possible marketing seminar research analyze

of the market labour demand in the home country, will clarify our prospective students to be well selective and obtain smart professional solution, leading to fit best into the market needs based on their scientific background data. Improvement of the very well selected key marketing strategy should guide the geosciences professional future of the potential students facing their academic background, the actual and future global professional market needs and the new developments of the geosciences environment.

3-Nevertheless, outcomes such as designing and implementing of the new investments study orientation politics should be applied, in order to increase Albanian students' interest in investing in that industry, actually showing not an efficient investment. It will contribute to building a healthy foundation for the further development of Geosciences professional.

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## MODELING IN GIS OF DATA FOR CALCULATION OF STOCK RESERVES IN THE MINE OF BULQIZA

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### Abstract

One of the reasons for the exploitation of chromite ore in Bulqiza mine is related to the presence of a relatively considerable amount of mineral in the mining waste dumps. These dumps are created during a 66 years exploitation of this mine mainly with the open spaces (the sublevel) mining method. Several geological and mining factors such as the frequent faulting of the orebody, its dip angles varying from higher than 65° to less than 30-40° and thickness with considerable fluctuations (5-15 m), the lack of ore selection in the loading stations and demand for low amount of barren rock in the ore material sent to the selection or enrichment plants, have caused a part of chromite ore to go to the mining waste stockpiles and consider it as technological loss. An increase in demand for chrome ore in the 2007-2012 period led to an increase by 7 times of its price compared to the previous years.

This increase in price made the exploitation of the chromite ore present in the waste stocks highly profitable. In these conditions there was the need to calculate the waste stockpile volume and the related ore amount that might be obtained by their exploitation. This paper shows the calculation of the volume of these stockpiles by GIS modeling method based on the available data on the relief of the stockpile area before the waste stockage, the surface of the present stockpiles and the use of tools like ArcGIS 9.3 for their computerized construction. To help the exploitation planning in accordance with the terrain features and to reduce its environmental impact in the area, the three dimensional model of the stockpiles and their spatial relations with the mine surface area, is also built. This model is shown only for one stockpile but it can be applied for all the waste stockpiles present in the mine surface area.

**Key words:** Mining waste stockpiles, selection, map of terrain surface, map of stockpile surface, technological loss, TIN

## MORPHOMETRIC FEATURES OF THE CHROMITE OREBODIES OF THE SOUTHERN PART OF BULQIZA ULTRAMAFIC MASSIF

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### Abstract

The ultramafic massif of Bulqiza is the most important chromite-bearing massif in Albania and it belongs to the eastern ophiolite belt of Albanides. The mantle sequence consists substantially of harzburgites and less of dunites and they occupy the most part of the massif outcrop in its eastern and southeastern part. The cumulate section is less developed in western and southwestern part. The magmatic section from the bottom to top is as follows: harzburgites with dunite intercalations and lenses of different size and frequency, transitional dunites and less cumulate wehrlites, pyroxenites and gabbroic rocks. The ultramafic massif of Bulqiza has southeastern-northwestern general extension and consists of folded structures with southwestern dipping. The intense folding and faulting is typical for this massif.

The most important known chromite deposits in this massif are: Bulqiza, Batra, Thekna, Shkalla, etc. Two main mineralization types can be distinguished: podiform and stratiform ones. The podiform chromite ore bodies occur at different levels of the mantle sequence, from the deepest harzburgites with clinopyroxene and Al-rich refractory chromite mineralization to the middle harzburgites-dunites with Cr-rich metallurgical mineralization up to upper level of the tectonic sequence with Cr-rich mineralization less important. The stratiform chromite mineralization lies within the transitory dunite sequence and it consists of banded and disseminated ore bodies of lower ore grade.

The ore deposit Bulqiza-Batra is the biggest one known so far in the Bulqiza ultramafic massif. The tabular orebody is highly affected by folding and faulting. Its morphology is represented by several flanks linked between them by syncline and anticline flexures. In the other deposits, tabular and lensey chromite orebodies of smaller size, predominate. The pipe-like chromite ore bodies are also present in several ore deposits of the mantle section. Until to the middle of the years '80 of the last century, Shkalla was the only known pipe-like chromite ore deposit in Albania. Later, the geological information collected by the intensive and extensive prospecting-exploration and developing mining operations carried out in this massif, enabled the founding of other new pipe-like chromite orebodies. Generally, they occur within the mantle section (tectonite harzburgites) and they have high oregrade ( $>45$  wt.%  $\text{Cr}_2\text{O}_3$ ), average thickness 1.5-5 m or higher, extension from 300 m to more than 1 km and southwestern dipping. They occur mainly outside the folded structure of Batra ore deposit, in its west and east, such as the ore deposits Lugu i Qershise, Lucana, Perroi i Lopes, at its western flank, and one blind orebody and the one of Liqeni i Sopeve, at its eastern flank, and outside the folded structure of Bulqiza ore deposit such as Almarina chromite ore body. Pipe-like chromite ore bodies are found also within the folded and faulted structures of Batra and Thekna chromite deposits.

## **OCCURRENCES OF HYDROTHERMAL MINERALIZATIONS IN THE AREA TROJAK - VARRI I SEJMENTIT - STANET E PRESHIT - BURIMET E IZVIRIT – Qafa e ROSNIKUT**

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### **Abstract**

This work focuses on the hydrothermal mineralizations from Trojaj-Varri i Sejmenit-Stanet e Preshit-Burimet e Izvirit-Qafa e Rosnikut considered the most important and of great potential in the area of eastern Dibra. They include all the mineralizations and ores of hydrothermal origin, known by geological, mineralogical and metallogenic investigations undertaken in the area. These hydrothermal mineralizations and ore from the area of eastern Dibra, mainly in the Kercisht – Rrafshi i Korabit are not accepted to belong to the same primary source. The iron mineralizations from Avdanica and some polymetallic mineralizations might be related to granites; in the case when the arsenic predominates among the other elements, they may be related to thrusting and the sulphur mineralizations, strontium and thermal water springs may be favored and supplied by gypsum domes.

Some of the main known ore will be described in this work.

### **Ore showing “Trojak”**

The deposits consists of red radiolarian platy limestones with scarce pelagic bivalves overlain by white crystallized biomicritic limestones containing small crinoids and diagenetic calcite. The limestones are altered and brecciated due to the frequent cracks. In the upper sections, the arsenic mineralization occur within these cracks in the form of thin rims without filling them. The realgar –orpiment can be macroscopically observed. The data obtained from exploration activities carried out in 1988 by Hoxha & Alliu and a Canadian Junior Mining Company show that the mineralization becomes more important and is related to the Jurassic-Upper Cretaceous (Cenomanian) flysch, mainly to carbonatic rocks, although the complicated geology due to the lying of mineralization close to the overthrust

of Palaeozoic formations. There is an oxidation zone along a stream, generally typical for other showings of this type, dominated by reddish, yellow and grey colors. We consider that the mineralization might be related to the circulation of telethermal solutions through the overthrust planes; in this case, the overthrust of Palaeozoic on the Jurassic - Cretaceous flysch and that of Paleocene-Eocene flysch represent interest for further exploration.

### **Ore showing “Varri i Sejmenit”**

Here the mineralization occurs in a complicated tectonic situation, folded by gypsum diapirism that brought from the depth fragments of rocks belonging to different geologic ages: evaporites, Jurassic-Upper Cretaceous (Cenomanian) flysch, serpentinites and serpentinitized peridotites, massive limestones, graphite sericitic argillaceous marly schists with quartz grains and veins and Eocene – Oligocene flysch. The arsenic mineralization occurs in the rocks of different ages, mainly in the Jurassic-Upper Cretaceous (Cenomanian) limestones in the form of irregular rims, disseminations, spots, veins and consists of realgar and orpiment. Within the gypsum there are biomicritic limestones, siliceous slates, carbonatic slates, rocks highly changed in quartz, feldspar, sericite – chlorite as well as amphibole gabbros with coarse crystals. It is of interest the fact that along this interval there are gossans and realgar – orpiment disseminations that indicate the distribution of the sulphur mineralization. Blood-colored prismatic crystals and yellow needle radial crystals can be observed on freshly-exposed surface. The mineralization follows the bedding planes of limestones. The elementary association is the one typical for the telethermal mineralizations: Sb = 0.02 – 0.15 %; Pb = 0.002 %; Sn = 0.0003 – 0.0004 %; Ga = 0.0005 %; Ag = 0.00002 %; Mo = 0.00015 %.

The exploration activities show an ore zone



more than 350 m long with As up to 4 – 5 % and Au up to 7.5 ppm. These two elements are present in different values along entire ore zone. The mineralization lies mainly in the Jurassic – Cretaceous flysch representing the main screen of the telethermal solution. This flysch called the “old flysch” overthrusts the Eocene – Oligocene flysch.

### **Ore showing “Stanet e Preshit”**

The outcrop of this ore showing is a weak gossan with yellow, reddish – brown and white colors. It lies on the overthrust of  $T_{1-2}$  formations on the flysch of  $Pg_{2-3}$ . There are also other opinions concerning these facts. The ore zone consists of highly tectonized and changed rocks due to the salt diapirism and hydrothermal activity. Generally, all the rock types are affected by quartzization and carbonatization. The mineralization consists of realgar and orpiment in the form of disseminations, rims and veins within the fissures of rocks. The marcasite is also present in the form of disseminations and less as aggregates and veins. The successive works (Kodra etj. 1986; Hoxha & Kolgjini, 1988) show that this ore showing should not be considered only like a As showing, but a more complex one. So, the high values of some elements as: Au 5.6 – 11.59 ppm, Sb to 0.06 %, Sn to 0.006 % (to 0.21 %), Mo to 0.0006 %, are of interest. It can not be excluded the presence of Be and Ba, that are not assayed and Hg detected in the soil samples. All this elementary association shows the presence of low temperature hydrothermal mineralizations of practical interest, with the prominence of As like a potential indicator of mineralizations of this type. It should be also mentioned that the successive mining activities (Hoxha e Kolgjini, 1990) encountered in depth mineralized zone represented by realgar, orpiment, pyrite and scarce fine chalcopyrite disseminations. The assays show these values????:

As to 10.17 %, Au to 1.04 gr/ton,  $Fe_2O_3$  to 18 %,  $MnO$  0.5 %, etc. The successive works (Alliu & Hoxha, 1988) show promising data on Au up to 2.62 ppm in the samples collected in the outcrop of the mineralized zone.

### **Ore showing “Burimet e Izvirit”**

This showing lies at the exposure of the overthrust plane of the Ordovician deposits on the Triassic and on the Jurassic – Cretaceous formations. The

mineralized zone consists of: a- limestones with malachite, azurite, crystals of galenite where the spectral analysis is 1 % Pb, 0.01 % Sb and 0.025 % Cu; b- quartzitised limestones with malachite and pyrite crystals and the spectral analysis shows the presence of Cu, Zn, As and Pb; c- quartz with massive pyrite and chalcopyrite disseminations, with Fe 20 %, Cu 0.05 %, Zn 0.17 %, As 0.04 %, Pb 0.013 % (Kodra etj. 1986). The presence of several elements, especially As and Pb, shows that the overthrust plane is a path for the circulation of hydrotherms. The radiometric investigations, (Nasi etj. 1980), indicate the anomalies up to 28 gamma and up to 0.015% U and emanation anomaly up to 66 eman. It is also mentioned that the radioactive minerals are associated with other minerals of hydrothermal origin such as sulphures of As, malachite, etc. In some surface workings, the zone of arsenic mineralization is 2 m thick and 20 m long. Realgar and orpiment occur in the forms of rims, disseminations and veins within the voids of the rocks. As is higher than 5 % and the chemical assays show: Cu = 0.03 – 0.29 %, Zn = 0.02 – 0.03 %, Fe = 2.7 – 4.46 %, Mn = 0.28 – 0.42 %, Au = 0.61 – 1.4 ppm. In the adit nr.1, the spectral analysis show: Pb = 1 %; Cu = 0.3 %; As = 0.5 %; Sb = 0.05 %; Mn = 0.23 %; Mo = 0.005 %; V = 0.025 %; Fe = 2 %. The chemical analysis show: Cu = 0.4 %, Pb = 0.77 %; Fe = 3 %; Mn = 2 %. There are also zones with Cu 0.45 %, Au 0.7 – 0.82-1 ppm, As up to 3.7 %. In the adit nr.8 at Izviri, at the interval 226 – 227 m, the realgar and orpiment mineralization are present as well.

### **Ore showing “Qafa e Rosnikut”**

The works carried out later, (Kodra et al. 1986), consider this showing as very promising but only for arsenic. The mineralization lies in a tectonic zone that is the plane of the overthrust of Kollovozi subzone on Malsia e Korabit one, some 40 – 50 m wide. The lithology consists of highly altered ultramafic rocks that change into schists (altered peridotites, chloritized and carbonatized serpentinites up to intensely changed rocks). The arsenic mineralization occurs in the form of rims and disseminations following the fissures in serpentinites and veins and nests. The chemical analysis show high As values and the presence of other elements, such as Cu to 2 %, Au, Sb, Pb, Ag, Cd, Co, W, Mo, etc,. The most recent works in this showing (Hoxha & Kolgjini, 1997), based on the data from the samples collected in trenches and

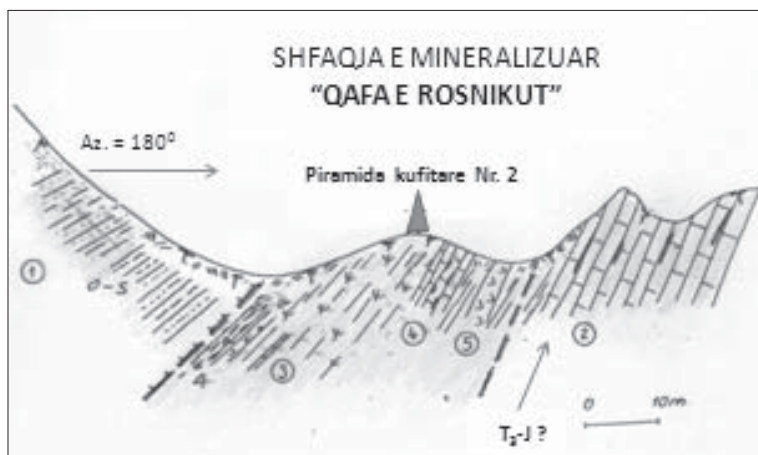


Figure 1. Ore showing "Qafa e Rosnikut" or "Piramide Nr. 2".

1. Quartz – sericitic sandy schists of O-S;
2. Platy to massive limestones with grey cherty intercalations.
3. Ultramafic rocks. Serpentinized peridotites, chloritized and carbonatized serpentinites, serpentinite schists, intensely chloritized and carbonatized rocks, carbonatic schists with rims and disseminations of realgar – orpiment.
4. Platy limestones with cherts. Uartzized carbonates with As sulphures, etc.
5. Agglomeratic

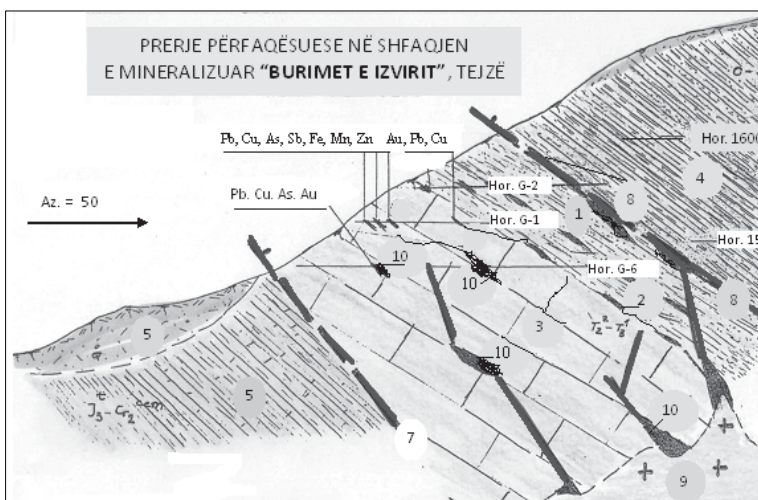


Figure 2. Representative section at ore showing "Burimet e Izvirit", Tejzë.

1. Clayey – cherty – sandy – quartzous schists.
2. Clayey – phyllitic schists with veins of sulphur mineralization.
3. Thick layered to massive marbled limestones.
4. Clayey – phyllitic – sericitic sc carbonatic flysch.
6. Quaternary slope deposits.
7. Overthrust.
8. Granosienites of Bjeshka e Preshit, thought to be in depth.
10. Known and expected sulphur mineralizations. (According to Kodra 1986, Hoxha & Kolgjini 2001).

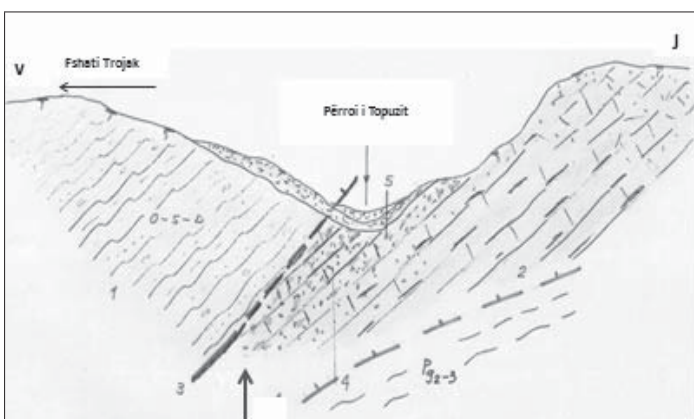


Figure 3. Geological section at ore showing "Trojak"

1. Unseparated palaeozoic formations.
2. Red radiolarian limestones, recrystallized biomicritic limestones, etc.
3. Fault.
4. Mineralized zone with As sulphures, etc.
5. Exploration shallow well with As sulphures, etc.

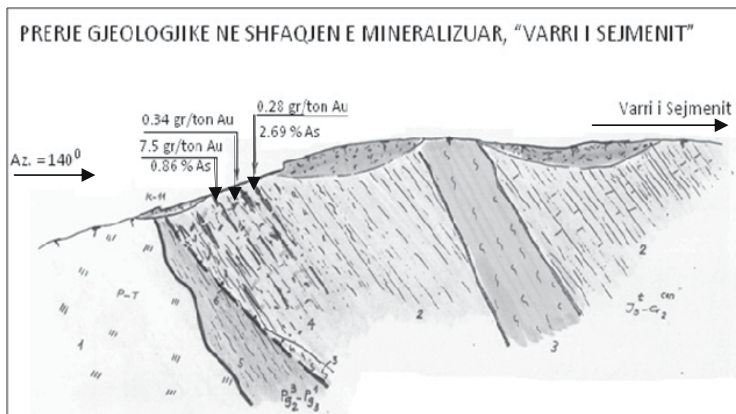


Figure 4. Geological section at ore deposit "Varri i Sejmenit".

1. Evaporites/
2. Dark clayey – carbonatic and phyllitic flysch.
3. Serpentinites and intensely serpentinized peridotites.
4. Arsenic – bearing sulphur mineralizations.
5. Eocene folded deposits of Eocenit;
6. Supposed overthrust.

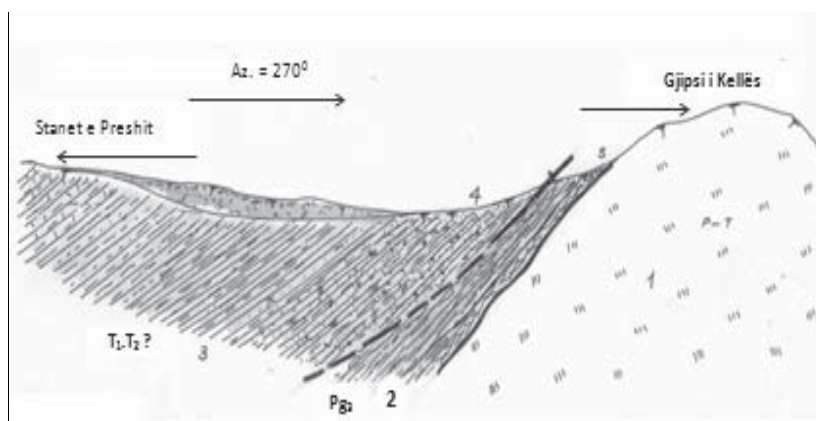


Figure 5. Geological section at ore showing "Stanet e Preshit".

Explanation:

1. Evaporites.
2. Eocene flysch.
3. Clayey-chlorite-sericitic, clayey-sericite, marly-quartz, cherty microcrystalline, carbonatic schists.
4. Mineralized zone.
5. Rocks of the contact with gypsum, with brown color, intensely altered.
6. Overburden.

wells, show high values of several elements: Cu up to 2.26 %, Au up to 7.65 gr/ton, Ag to 0.3 gr/ton, S to 5% and the presence of Sb, Pb, Zn, Co, etc. This elementary association explains the nature of the stream sediment anomalies (Alliu, 1986) and the showing of "Piramida nr.2" represents the small outcrop, even though "masked", of this

mineralization. These outcrops belong to low temperature hydrothermal mineralization that has favourable geological conditions to be developed in depth. In this case, for its geographical position, the showing "Piramida nr.2" serves like a sure guideline for the prospection of the mineralization westwards (Rrafshi i Korabit).

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## HERCYNIAN AND ALPINE STRUCTURE OF THE SOUTHERN VEPORICUM DOMAIN (WESTERN CARPATHIANS) AND ITS COINCIDENCE WITH METALLOGENIC ANOMALIES: A COMPLEX GEOLOGICAL, GEOPHYSICAL AND GEOCHEMICAL APPROACH

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### Abstract

Southern Veporicum tectonic subunit represents a geologically very complicated region lying in the tectonic position beneath the Alpine sheet of the Gemericum superunit. Its geological structure is particularly composed of Hercynian metamorphic, granitoid rocks and younger Palaeozoic (Slatviná and Rimava Fms.) to Triassic cover sediments (Foederata Fm.), overlaid by the Gemericum superunit in the tectonic position. This region has been intensively studied tens of years, due to Hercynian and Alpine history of the rock formations, but many times with controversial results of the P-T conditions of the Alpine metamorphic reworking. This territory was a subject of very intensive exploration in the past because numbers of metal and non-metal occurrences have been revealed here (Au, W, Mo, Cu, Sb, talc, magnesite, graphite, and quartz). During our complex investigations within the area approx. 1200 km<sup>2</sup>, a complex of geological, geophysical and geochemical methods have been carried out in order to reveal more precisely geological structure from the surface to deeper parts, and defined influence of this structure on the widely present mineralization. Geological mapping, in spite of a strong Alpine reworking, has revealed fragments of primary Hercynian tectonic relationships. Alpine shear zones were detected on the surface and in subsurface positions using geophysical methods (gravity, magnetics, induced polarization and resistivity ones). These were performed on regional profiles, most of them were situated in granitoids and are without signs of mineralization. Lower Palaeozoic metamorphic rock sequences consist of two rock sequences: 1) ortho- and paragneisses with amphibolites, hornblende rich paragneisses with different, but higher degree of Lower Carboniferous granitisation and 2) micaschists and metasandstones with lower degree of granitisation or without it. Both sequences presented here are metamorphosed during Hercynian stages in different degree

and they had a different crustal position during Devonian/Lower Carboniferous granitisation period. Granitoid rocks of Mesohercynian stage are represented by huge masses of trondhemitic, granodioritic to granitic compositions. Geometry of such intrusions indicates mechanism of laccolitic sheets, with schliered granitoids of trondhemitic to granodioritic compositions placed at the bottom part and granodioritic to granitic compositions, usually with porphyric facies, on the roof. Permian postcollisional granitoids and granite-porphyries form only small intrusive bodies in the meta-sandstones with lower degree of Hercynian granitisation. A positive magnetic anomaly accompanied by negative gravity one in the eastern part of the territory represents the Upper Cretaceous hidden granite body connected with W-Mo mineralisation. Alpine shear zones (mostly NE – SW trending sinistral narrow zones) put together different Hercynian crustal blocks (crystalline basement) with/without Upper Paleozoic-Triassic cover. This process was accompanied by Alpine recrystallization and mylonitisation. Alpine shear zones are the place of intensive replacement of Hercynian mineral associations by newer - Alpine, usually lower temperature mineral associations. This recrystallization is connected with the migrations of ore-forming fluids. Presence of the Hercynian lithology with disseminated ore minerals like metaultramafic rocks, amphibolites, micaschists (mostly containing magnetite), with intercalations of black quartzites (with pyrrhotite) are usually easily detected by ground magnetic and aeromagnetic methods. They form linear magnetic anomaly, which is caused by incorporation of Hercynian micaschist into Alpine shear zone. The most pronounced Alpine shear zone in the SW part of the Southern Veporicum area, accompanied by Hercynian micaschists (with inventory of serpentinites, metabasalts and black quartzites) lying in the depth, are clearly source of Alpine remobilised metals (mainly Sb, Ag, Cu, Bi and As). It is manifested by the coincidence of metallogenic and geophysical anomalies in the narrow zone, more than 20 km long.



## GEOTECTONIC POSITION OF THE COPPER-BEARING GEOLOGICAL FORMATION OF GJEGJANI, KUKESI AREA, NORTHEASTERN ALBANIA

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### Abstract

The Gjegjani copper deposit in Kukesi area, northeastern Albania, constitutes a unique copper deposit in our country. Geological reserves of 5.8 million tons of Cu with a grade of 3.71% Cu have been calculated. For many years (1960-1990), the Gjegjani deposit was the main copper resource in Albania. In order to increase the reserves and find other ore bodies, a large amount of prospection-exploration works and thematic studies were carried out in the area. However, these works have not given important results. In relation to the structural make-up of the Gjegjani formation there have been two main lines of thought: (1) The structure of the Gjegjani formation (and the copper deposit) has a normal southeastern continuity, the roof of the Gjegjani formation is constituted by the Upper Triassic-Lower Jurassic limestones and the floor, by the ultrabasic rocks. The age of Gjegjani formation was considered to be Lower-Middle Triassic (Noka 1995); (2) The structure of the Gjegjani formation is westward overturned and the age of the formation is Upper Jurassic (Kodra 1976). During the period 2008-2009, the Geological Survey of Albania undertook a study entitled "The geotectonic position of Gjegjani deposit and the prospect for finding other copper ore bodies" (Hysenaj and Naço 2009). The result was a new geotectonic model for the structure of the Gjegjani formation. Based on our investigations it results that: (i) The limestones and serpentinites occurring within the Gjegjani formation do not constitute a defined stratigraphic level. They are heterogeneously distributed and occur in various stratigraphic levels within the formation. Hence, we consider the so-called "blocks in matrix" *mélange* part of this formation; (ii) The limestones and serpentinites that occur within the formation represent olistoliths. The Gjegjani formation was formed later than the serpentinites (Middle Jurassic-Upper Jurassic) and limestones (Upper Triassic-Lower Jurassic) that occur within it. In addition, results given in other

studies of the dating of the amphibolites, should be cautiously interpreted because in our view they represent parts of the metamorphosed series.

The Gjegjan-Surroj formation (or the Gjegjan-Surroj tectonic unit) crops out in the deepest parts of the erosional section (in the banks of Fierza-Surroj lake), underlying all other formation in the form of a "tectonic window". The other units in the west and in the east direction, represent tectonic nappes overlying the Gjegjani-Surroj formation. As also given by previous studies, genetically the copper-bearing horizon of Gjegjani deposit is syngenetic with the volcano-sedimentary rocks. Our observations, confirm the interpretation given by previous studies, that the Bardhoci sector is the most prospective for locating other Cu-rich ore bodies. This due to fuller section in this sector and five levels of basalts in the volcano-sedimentary unit. We do not limit the prospective area only in the east or west direction. All the area of the extent of the Gjegjani formation is prospective for locating other Cu-rich ore bodies.

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## GOLD DISTRIBUTION IN SULFIDE-RICH DUMPS OF NORTHERN ALBANIA

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### Abstract

Gold is known to be included in the structure of common sulfides as inclusions smaller than 1000 Å, which are named "Invisible Gold". The latter is often found within pyrite structure as structurally bound or as superficially bound in nanosized nonautonomous phases. In addition, the highest Au concentrations are usually associated to fine-to-very fine pyrite grains that exhibit size lower than 100 µm (Simon et al. 1999). Gold distribution in 15 samples from 5 different sulfide dumps localities of Northern Albania was studied using INAA analyses. Mines of Mirdita district were strongly exploited for chalcopyrite and pyrite. Sulfide ore bodies have been classified as VMS deposits and are hosted within the Jurassic Eastern Ophiolites Type (EOT) of Albanides, where they form massive and disseminated mineralization in the volcanic sequence. As a consequence of copper extraction and recovery, big waste rock and tailing amounts were generated and stored close to main mines and processing plants.

Samples were taken from landfill sites of Rreshen (Rreshen1 and Rreshen2), Reps (Reps1 and Reps2), Spaç, Prosek and Kurbnesh. Tailing samples show fractured and strongly altered sulfides with high pyrite content and minor chalcopyrite in a silicate, sand-to-clay matrix. Grain size distribution of the sampled material (less than 2 mm) shows about 30 % of 250 to 38 µm and a finer fraction, lower than 38 µm, that constitutes 2 to 10 wt.% of the total material. Landfills are usually covered by natural screen material, made of sand and lime fraction. From every dump site, several specimens have been extracted then crushed and mixed to create a powdered representative sample. A sample size of 5 to 50 g was prepared and treated with Fire Assay method, using Ag as collector, to create beads which can immediately be used to determinate gold concentration. INAA analyses show that Au values range between 23 (Reps1) and 1260 (Prosek) ppb, with an average value of 358.6 ppb. Also between two samples from Reps2 a great difference in gold concentration is shown: the first sample (R2 – 684 ppb) is made only of pure tailing dark gray material, while the second one (R2T – 352 ppb) is yellow coarser and poorer in sulfides.

In addition, shaking table tests were made on Prosek and Reps2 samples, in order to obtain a "Pyrite Concentrate" and to extract the finest portion, lower than 38 µm. Reps2 "Pyrite Concentrate" lights out 759 ppb Au, with a Concentration factor of 2.13, and the finest fraction 577 ppb, with a Concentration Factor of 1.62, but the highest values are found in Prosek "Pyrite Concentrate" and Prosek finest fraction, where gold concentration is respectively 3730 ppb, with a Concentration Factor of 2.96 and 6070 ppb, with a Concentration Factor of 4.82. Gold shows a very good positive linear correlation with Ag, Zn, Cu, As and Pb that anyway probably reflect its good correlation with S and hence with pyrite content. As a whole data confirm that gold distribution in mine dumps of northern Albania is directly linked with pyrite/sulfide concentration, and its values could intensely increase where pyrite grains size is smaller than 38 µm. Within this frame, Prosek site shows an anomalously high Au content that does not fit the linear correlation of other sites. This anomaly could reflect an original high Au content of the primary mineralization or a different history during processing of sulfide ore.

Sulfur content is the highest Reps2 (11.70 wt.%) and Prosek (17.18 wt.%) in agreement with gold data and, in some selected samples, can reach values higher than 25 wt.%.

Our preliminary enrichment test with shaking tables increased Au content of concentrate up to 5 times that of feed, but metal recovery is too low, ranging between 20 and 50 %, so that further tests are required in order to maximize gold concentration and recovery.

Starting from these results, re-treatment of Mirdita zone mine dumps could be evaluated, where tabling could be followed by floatation, grinding, roasting and carbon-in-leach (CIC) processes, that are able to recover up to 90 % of the gold.

Calculations based on a 3D reconstruction of Reps2 dump give a volume of 351,989 m<sup>3</sup>, the waste material average density, measured on three samples with water picnometer is 2.849 gr/cm<sup>3</sup>, giving a total estimated tonnage of 972,527 t. This corresponds to around 345 kg of gold just for Reps2 dump and confirms a possible economic return for gold extraction.

## STRUCTURES AND TEXTURES IN THE QUARTZ-SULPHUR MINERALIZATION ORE BODIES FROM KAPTINA MASSIF

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### Abstract

The gabbroic massif of Kaptina is a part of the eastern belt of the Albanian ophiolite complex and is supposed to be formed in a supra-subduction zone (SSZ) setting. This massif is characterized by a very complicate geology mostly consisting of gabbros, norites and gabbro-norites hosting numerous copper ore bodies of quartz-sulphur mineralization.

The factors controlling the sulphur mineralization are tectonic (structural), magmatic and lithological, the most important role being played by the tectonic factor because it seems that sulfur mineralization is concentrated along the so-called weakened zones - tectonic faults separating different types of rocks.

The quartz-sulfur mineralization which is the principal mineralogical type of Kaptina massif, consists of two subtypes a) Quartz-sulphide type which consists of quartz, pyrite and chalcopyrite and b) Quartz-chlorite-sulphide type which consists of quartz, chlorite, pyrrhotite and pyrite.

The quartz-sulfur ore bodies show variable morphological features changing from lenses and veins to limited extension layers. The extension and inclination of these layers change both in their azimuth and dipping angle.

The structures and textures of these ores are conditioned by the deposition of mineralization from hydrothermal solutions within gaps of different morphologies. In some places, the ore bodies display banded structure (Thirra and others). Here the lateral parts of the mineralization consist of symmetric belts (parallel quartz-chlorite- chalcopyrite veins), while the central parts which in some cases are very thick, are composed of milky quartz with rare chalcopyrite disseminations. In this quartz mass are intruded ore fragments (quartz-chalcopyrite) and chlorite xenoliths. Within the ore bodies are also observed very large xenoliths consisting of altered gabbros. In addition to compact structure of quartz mass, some veinlets with denticular structure are

observed. Within the quartz mass, which is the main component of different ores, the sulfur and chalcopyrite is often found as stains and nodular forms among very large quartz crystals. The cemented structures are very characteristic for the quartz-pyrite ores is very characteristic, where quartz fragments with chalcopyrite disseminations are cemented by nodular calcite formations. We can mention also pyrrhotite-chalcopyrite ores with almost compact structure, where early oval quartz fragments are cemented. In some ore bodies of this massif, the disseminated structure is also observed.

Within the chlorite-epidote mass, the pyrite disseminations are present, whereas the chalcopyrite disseminations are found within the quartz or calcite masses.

The following main textures and structures were described:

1. Veined textures. They are formed by filling the tectonic fissures of gabbroic rocks with ore-bearing solutions deposited by hydrothermal solutions;
2. Veined-lenticular textures. Such structures are formed by the deposition of minerals along some stages or in some parallel fissures within gabbroic rocks;
3. Brecciated textures. These textures are characterized by the cementation of the altered gabbroic fragments (xenoliths) by a quartz-sulphide matter with sizes from several cm to several meters. Characteristic are following structures;
4. Disseminated structures. They are characterized by the distribution of sulfur mineralization like stains and grains within the quartz mass;
5. Spotted-nodular structures. This type of structures is represented by stained and nodular chalcopyrite concentrations within the quartz mass.

## GEOLOGICAL SETTINGS AND FORMATION CONDITIONS OF THE LESSER CAUCASUS FOLD SYSTEM METAL DEPOSITS

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### Abstract

The Lesser Caucasus has been formed as a result of convergent interaction between the South Caucasus (the southern margin of the Eurasian continent) and the North Iranian (the northern part of the Africa-Arabian continent) lithosphere plates at the place of the Tethys ocean branches.

In the Lesser Caucasus five metallogenic zones are distinguished: Adjara-Trialeti Paleogene gold-bearing zone; Bolnisi-Kazakh Cretaceous one, hosting copper, zinc and gold deposits; Somkhit-Karabakh Middle Jurassic-Early Cretaceous zone with copper-, barite-polymetallic-, gold and skarn-iron ore; Amassiah-Akera gold-bearing zone (obducted Cretaceous sediments which have been activated in Neogene); Daralagez copper-molybdenum-gold-bearing.

The western ending of Adjara-Trialeti structure is composed of Paleogene subalkaline and alkaline volcanic-plutonic complexes, which are associated with copper and gold mineralizations.

Within the Bolnisi-Kazakh zone, in the fragments of geodynamic complexes of the Cretaceous back-arc paleobasin are placed volcanogenic complexes of Madneuli gold-copper, Sakdrisi-gold-, Tsitelisopeli and Kvemo Bolnisi - old-bearing and copper-, and in Azerbaijan (Kazakh district) is known Daskesaman gold-sulfide ore.

Southward of Bolnisi-Kazakh structure is located Somkhit-Karabakh zone paleoisland arc, where epigenetic copper ores are located in Bajocian andesite-dacitic complex, mainly in the upper part of the complex – in the horizon of hyaloclastites epigenetic copper ores in Bajocian andesite-dacitic complex - mostly in its upper part - in the horizon of hyaloclastites (Alaverdi, Shamlugh, Kafan, Kedabek), copper porphyry deposit (Tekhut, Kharkhar etc.), and Dashkesan iron-ore skarns.

Gold-ore and mercury paleosystems are manifested within megastructures, which experienced intensive tectonic stress (gold ores – Zod, Megradzor, mercury – Agyatag, Lev).

In the southern part of the Lesser Caucasus – in

Daralagez block of North Iranian microplate molybdenum-porphyry and copper-molibdenum-porphyry deposits are known (large Kajaran, medium-sized – Agarak, Lichk, Dastakert in Armenia; Geydag, Gay-Gel, Paragachay, Kapudzhikh, Diakhchay etc. in Azerbaijan).

**Keywords:** *Lesser Caucasus, ore, gold, polymetallic.*

The Lesser Caucasus has been formed as a result of convergent interaction between the South Caucasus (the southern margin of the Eurasian continent) and the North Iranian lithospheric micro-plates at the place of one of the Tethys Ocean branches. Geodynamic complexes, composing the Lesser Caucasus, variously at some areas were subjected to intense epigenetic endogenous processes, and in the result massive deposits of base and precious metals were formed.

In the Lesser Caucasus five metallogenic zones are distinguished: Adjara-Trialeti Paleogene gold-bearing zone; Bolnisi-Kazakh Cretaceous one, hosting copper, zinc and gold deposits; Somkhit-Karabakh Middle Jurassic-Early Cretaceous zone with copper-, barite-polymetallic-, gold and skarn-iron ore; Amassiah-Akera goldbearing zone (obducted Cretaceous sediments have been activated in Neogene); Daralagez copper-molybdenum-gold bearing.

Development of endogenous ore-forming systems is considered in the view of processes occurring at the boundaries of tectonic microplates. Fluid systems are identified with dissipated systems that are in constant interaction with the environment. Attention will be given primarily to macroelements of fluid-magmatic systems - the area of fluids origin and discharging. More than 60 copper- and 70 gold-bearing sulfide mineralizations are known in the Lesser Caucasus

The northernmost structure of the Lesser Caucasus - Adjara-Trialeti has an intraplate rift nature; its western part is composed by Paleogene subalkaline and alkaline volcanic-plutonic complexes, which are associated with copper and gold ore manifestations. There are allocated several ore



nodes, general gold potential of which is estimated at 90 t of metal. According to the geological conditions, in the western part of the zone are manifested ore bodies characteristic for supra-ore levels of copper-molybdenum ore-magmatic paleosystems. Here are found narrow, often discontinuous, mineralized zones of gold-quartz-sulfide (sometimes with barite) composition. Vein zones are located in small-scale syenite-porphyric bodies or in their exocontacts.

Within the Bolnisi-Kazakh zone, the richest with metallic manifestations is the Bolnisi ore district (Georgia). Here the fragments of the Cretaceous backarc paleobasin are placed Madneuli volcanogenic complex gold-copper, Sakdrisi – gold -, Tselisopeli and Kvemo Bolnisi - gold-bearing-copper -, and David Gareji - silver-polymetallic deposits. To the east, in Azerbaijan are known gold-sulfide ore mineralisation - Daskesaman, probable gold reserves of which are estimated at 10-12 t.

At major Madneuli deposit, localized on the slope of a large volcanic edifice under the screen of radiodacite extrusions and ignimbrites, are marked isolated in space stockwork gold bearing copper-, coarse-crystalline barite-polymetallic-, massive and vein barite-, and in secondary quartzites fine-dispersed gold ores (initial reserves amounted: Cu - 800 th.t, Zn - 137 th.t, Pb - 28 th.t, Au - in secondary quartzites - about 20 t, BaSO<sub>4</sub> - more than 5 million tone). Here, ore bearing heteroclastic tuffites were subjected to explosive brecciation and transformation. On the upper level of secondary quartzites are spread gently sloping barite and barite-polymetallic veins, below and to the south mainly in quartz-chlorite metasomatites - pyrite-chalcopyrite (with traces of sphalerite) stockworks and veins. The border between brecciated quartzites and quartz-chlorite (with sericite) metasomatites is marked by tectonites (as breccias and slickensides), which at some places and ferrous and contain gypsum.

Southward of Bolnisi-Kazakh structure is located the paleoisland arc of Somkhit-Karabakh zone, and to the south-eastern - displaced along the submeridional fault its block - Kafan (here are accommodated mined for a long time Kafan copper deposit and Shaumyan gold-sulfide deposit). The above noted blocks of paleoisland arc structures preferably are composed of Bajocian- Late Jurassic volcanics, which are complicated by the Middle- and Upper Jurassic and Early Cretaceous granitoids; they are characterized by gold-bearing copper-pyritic and copper porphyry deposits.

In the western part of Somkhit-Karabakh zone (Armenian part) are located epigenetic copper ores in Bajocian andesite-dacitic complex - mostly in its upper part - in the horizon of hyaloclastites (Alaverdi, Shamlugh) and Tekhut copper porphyry deposit (reserves - 888 million tone of Cu). On Tekhut copper-bearing tonalite porphyry stocks occupy the apical part of the large Early Cretaceous quartz-diorite-tonalite intrusions. Steeply dipping zones with stockwork-impregnated mineralization are located in the exo- and endocontacts of porphyry bodies among quartz-sericitic (often with anhydrite) metasomatites.

In Azerbaijanian, part of the structure are known gold-bearing Middle Jurassic copper porphyry deposits (Kharkhar, Dzhangirchay, Shamlug, Gadzhilar, etc.), the extent of mineralization of which remains to be determined. Manifestations are associated with diorite porphyries, complicating Middle Jurassic diorite-plagiogranitic complex; copper content in zones varies from 0.3 to 0.6 wt.%, gold about 0.4 g/t, and silver - up to 50 g/t. Middle Jurassic deposits of paleoarc like Kharkhar represent so-called Hollister "dioritic" model (Titley and Beane 1984). Unlike of Middle Jurassic copper porphyry ore manifestations, deposits of the Lesser Caucasus paleoisland arc late stage development such as Tekhut, is characterized by an extremely low content of gold in ores. Introduction of tonalite intrusions and operation of copper porphyry paleosystems are linked to Early Cretaceous.

Magnetitic skarn deposits are concentrated in paleoisland arc and precollisional structures. Their typical representative in the Lesser Caucasus is Dashkesan deposit (Sokolov and Grigoriev 1974). It is connected to synclinorium composed of Middle Jurassic volcano-sedimentary rocks. Volcanites contain Neocomian polyphase intrusion, consisting of gabbro, quartz diorites and tonalites. Magnetite deposits are placed in Late Jurassic carbonate skarn deposits - garnet-pyroxene and Dashkesanite skarns.

Gold ore paleosystems are manifested in megastructures that experienced intense tectonic stresses. They are located on the activated areas of microplates, in zones of obducted oceanic complexes (Zot), and in the activated marginal parts of Daralagez block (Meghradzor).

Zod deposit, with reserves about 100 tone of gold, is located in obducted basic-ultrabasic complex of the Lesser Caucasian suture zone. Here outcrop Precambrian schists and Early Senonian rhythmically bedded volcano-sedimentary rocks.

Allochthonous block is composed of serpentized ultrabasites and gabbroids, intensely desintegrated and complicated by intruded granodioritic porphyry dikes. Near the latter are manifested mineralized zones, ores of which are attributed to gold-quartz-tellurium geochemical type (Konstantinov and Bochek 1984).

Megradzor deposit is located on the edge of Daralagez block. Here Precambrian metamorphic schists are covered by Cretaceous carbonate-terrigenous flyschoid formations, which, in turn, upward are replaced by Eocene volcano-sedimentary flyshoids. The last are saturated by sienites, monzonites, nepheline sienites and lamprophyres. Some of lamprophyre bodies are ore bearing. Gold-bearing bodies represent narrow, but extensive zones of argillites. The deposit is characterized by ore columns with high grade gold (up to 500 g/t).

Representative examples of Sevan-Akera suture zone are Agyatag and Levski deposits in Azerbaijan.

At Agyatag, deposit mercury zones are located in Early Cenomanian sediments and their contact with listvenitized serpentinites. At deposit Levski one antimony- and five mercury bodies are identified in Campanian sandstones and limestones

In the southern part of the Lesser Caucasus (in both Armenia and Azerbaijan) are known molybdenum-porphyry and copper-molibdenum-porphyry deposits (large Kajaran, medium-sized – Agarak, Lichk, Dastakert in Armenia; Geydag, Gay-Gel, Paragachay, Kapudzhikh, Diakhchay etc. in Azerbaijan), near which are located the gold-polymetallic “satellite” manifestations. The most representative is the Kajaran copper-molybdenum deposit in Armenia (reserves: 4.5 million tone of copper and 450 th. tone of molybdenum). The mineralization here is confined to the contact zone of Oligocene monzonite-sienites with younger porphyritic granodiorites. Within the ore-bearing stockwork are allocated pre-ore amphibole-biotite, molybdenum-bearing quartz-feldspar and copper-bearing (with molybdenum) sericite metasomatites. Around porphyry intrusions manifest explosive breccias and phaneritic frame experienced volumetric “steaming” - quartz-feldspar alteration. The copper content amounts 0.2-1 wt.%, molybdenum - 0.03-0.15 wt.%. From Kajaran deposit are extracted gold, silver, rhenium, selenium, tellurium, bismuth.

From above, it's obvious, that the Lesser Caucasus ore potential determines, shown here copper-molybdenum-porphyry, volcanogenic copper and

gold, the actually gold-ore and iron-skarn deposits. With respect to genetic understanding of the development of ore-magmatic systems prevailing in the present, they are briefly as follows.

In the Lesser Caucasus as in the other parts of the world porphyry deposits are example of the closest approach, and sometimes overlapping, areas of discharging fluid systems with their power sources. Porphyry intrusions were located at depths of 1 to 3 km from the surface during the functioning of fluid systems, and their crystallization occurred at 1230-800 °C (Titley and Bean 1984; Krivtsov et al. 1987). Areas of formation of phaneritic intrusions were deeper (5-10 km) zones of the earth's crust.

Based on isotopic-geochemical research (Titley and Bean 1984; Krivtsov et al. 1987; Krivtsov 1989; Zvezdov et al. 1989) the components having both magmatic and exogenous sources were involved in the ore process. Mineral forming is conceived as a process occurring in a whole pore-water space around the intrusions, within which ore components migrated diffusively and precipitated as sols at critical temperatures. At the thermal barrier metal complexes were destroyed by increasing the temperature and thus increase the degree of association of acid components ( $H_2S$ ,  $HCl$ , etc.). It is assumed that the fluid system functioning was preceded by the following events: cooling of porphyry intrusions (800-450 °C) with the arrival of a supercritical fluid into contraction fractures (frontal zones), and then fluid boiling (450-4000 °C and 70-80 MPa), with its division into highly mineralized brine and gas-water mixture. At brine concentration level (or zones of fluid alkalinity as a result of gaseous constituents separation) were formed quartz-feldspar metasomatites, and in the neighboring areas under the influence of acid gas mixture and with participation of previously formed captive solutions – zones of medium-temperature propylites. Based on thermobarogeochemical research (Rekharsky et al. 1983; Titley and Beane 1984; Ratmann et al. 1985; Arevadze 1989) propylitic and quartz-feldspar zones were formed almost synchronously at 450-300 °C temperature range. In the beginning of the mineral formation, at copper deposits simultaneously with quartz, stands out anhydrite (380-340 °C). Stable ore accumulation took place at 300-200 °C, at about 50 MPa.

According to the materials on Tekhut and Kajaran deposits, it can be concluded a stepwise formation of the “porphyry” ores. These conclusions are proved by geochemical data. In the preparatory phase magma melted from the lower crust and

upper mantle; magma plumes then moved to the surface and crystallized at depths of up to 3 km. In the final phase porphyry bodies introduced in hardened phaneric massif, under the influence of the thermal field and volatile components released from them. While interaction with the saline pore waters originated and operated "porphyry" hydrosystems.

Many researchers assume that the hydraulic systems of volcanogenic deposits of nonferrous metals developed according to the principle of convection model, which implies the involvement of exogenous water under the influence of the intrusion thermal field in hydrothermal process (Franklin et al. 1984; Ovchinnikov 1988; Krivtsov 1989). Thus, there is a problematic issue of near-ore space "specialization". In the case of copper-zinc deposits, the primary sources of metals could be volcanics and intrusions within which during their solidification ore elements dissociated, because of their geochemical properties in mineral-concentrators or ore liquats. From the "specialized" magmatites, metals were extracted by overheated exogenous water (often sea water). In the case of gold-ore manifestations in volcano-plutonic belts or in the area of microplates, which have experienced tectono-magmatic activity, as the set of paragenetic igneous rocks (subalkaline and alkaline rocks, lamprophyres), the origin of fluid-magmatic systems at subcrustal depths is highly probable.

Gold source of suture zone deposits should be found in the near-ore area of basic-ultrabasic rocks, subjected to intense serpentinization and post-collisional propylitization due the intrusion of small granitoid bodies that was followed by fluid flows.

Skarn-iron ore systems have been functioning as at near-surface, as well as at abyssal levels (Einaudi et al. 1984; Sinyakov 1986). In the beginning the system was closed, and then (retrograde stage) it has been exchanging energy and matter with its surrounding environment. Ore forming process involved meta-morphogenetic waters. Ore precipitation occurred as during the skarning process, - against the fluids acidity reduction.

The above discussed fluids and fluid-magmatic systems from thermodynamic position refer to isobaric thermogradient with perfectly mobile components. Decrease in the free energy is due to change in the composition, as well as is a result of their influence on the environment. From the above, it can be concluded that fluid systems naturally arise at certain stages of the

development of mountain-fold belts. The scope of the fluid-magmatic systems, as it is evident from the nodal distribution of ore fields in mountain-folded structure, were the zones of influence of "conservative", periodically tested for tectonic cycle activation, transform structures.

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## MIRDITA OPHIOLITE BELT (EASTERN ALBANIA) AND ITS OIL AND GAS-BEARING PERSPECTIVE

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### Abstract

The ophiolites of the Mirdita Belt, by all geologists, are accepted to be originated in the ocean. In this contribution, the Mirdita ophiolites are considered like formations of a continental marginal back-arc basin behind the volcanic arc of Korabi. This basin was not opened at any time as an ocean. Ultrabasic massifs are considered like large diapiric structures. Below the ultrabasic massifs the structures of the piercing should be present. These piercing carbonate structures are of interest for oil and gas.

**Key words:** *Mirdita ophiolites, diapiric structures*

### Introduction

The ophiolites of the Mirdita Belt, by all geologists, are considered formed in the ocean (Robertson and Shallo 2000; Geology of Albania 2002; Bortolotti et al. 2005; Dilek et al. 2007 etc.). Some authors accept that the ophiolites have come from the east (Bortolotti et al. 2005 a.o.), whereas others accept the opinion that considers them autochthonous and formed in the Pindos-Mirdita ocean (Robertson and Shallo 2000 a.o.). Volcanics of Mirdita are divided into western type (MORB) and the eastern type (MORB-IAT, IAT and boninites). The volcanics of the eastern type are considered like the intraoceanic suprasubduction zone formations (SSZ type), but the volcanics of this type presently occur also in the continental marginal back-arc basin of Okinawa. In fact, in the Mirdita Ophiolite Belt there is no evidences of suture. So, no subduction has happened.

### Materials

Since a few years ago the author of this contribution has argued that Mirdita Ophiolites are originated in a continental marginal back-arc basin (Kici 2011a, 2011b, 2013). Mirdita ophiolites are not formed in the ocean. The author is based on stratigraphic studies of the deposits at both sides of ophiolites

and of the deposits on Jurassic volcanics. Based on deep and shallow marine facies palaeogeographic reconstructions are made (Kici 2011a, 2013). Palaeogeography and various geological surveys show that ophiolites in the Mirdita furrow are formed.

### Results and discussions

Ophiolite Belt of the Mirdita-Kosovo (M.K.O.B.) is presented in Fig. 1. On both sides of the ophiolites, the Triassic-Jurassic limestones (western and eastern carbonate belts) lie. The two carbonate belts represent monoclines, that successively become younger, towards the ophiolites. The top of carbonate stratigraphic column is represented by some meters red pelagic limestones with reduced thickness. Their geological age is Middle Toarcian-Middle Jurassic. These are slope deposits on both sides of the Jurassic furrow of Mirdita. So, since the Middle Toarcian up to the end of Valanginian the furrow of Mirdita has existed, similar to the current furrow of Okinawa in Japan. Mirdita basin has represented an intracontinental marginal back-arc basin behind the continental volcanic arc of Korabi. Volcanic arc is represented by the volcanics rocks of Korab-Pelagonia zone, that are found in western Macedonia (Petkovski 1973-1978). During the Middle Jurassic Mirdita furrow has been in retreat from both sides (extension). In the furrow cracks and faults were formed. The strike of these cracks and faults has been along the axis of furrow and parallel to it. In these cracks and fractures had different volcanoes. The lavas of type MORB and of type MORB-IAT, IAT and boninites, perhaps, are of the MBB type, because they are similar in their geochemistry (Tarney 2006-2009) and can be confused with each other. Up to Bathonian-Callovian, volcanics and red limestones with reduced thickness on both autochthonous carbonate belts were overlain by red radiolarian cherts. Thus, volcanics are autochthonous, because lie under the autochthonous cherts. More active mantle diapirism occurs in back-arc region, as in Mirdita basin. Ultrabasic massifs have emerged like diapirs, on the basins



floor, in the Late Tithonian. This emergence of the massifs is argued by the finding of ultrabasic clasts in the sedimentary rocks (Kici 2011a, 2011b, 2013). These large diapirs should have originated the piercing structures, that are of interest for oil and gas. In Hauterivian Mirdita basin became continent.

## Conclusions

Volcanics of the Mirdita Belt should be formed in the basin behind the arc of Korab. The ultrabasic massifs represent diapirs with interest for oil and gas in the piercing structures.

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## BËNJA LOW TEMPERATURES GEOTHERMAL SPRINGS A COMPETITIVE ENERGY RESOURCE

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### Abstract

In the Bënja of Përmeti village, in the Lëngarica creek are found eight springs, known and used for their curative values since the time of the Roman Empire. This springs blow out mineral water with temperatures in the range of 23-30 °C and yields in the range of 8 up to more than 40 l/s. These waters, even though of the low enthalpy represent a competitive energy resource. Their flow direct to the river, as in the case of the other geothermal resources of Albania can be “translated” as throwing in the creek of considerable monetary values, delay in the economic development, infrastructure and also social of the area. Below will be showed that these waters are not only a competitive energy resource, but they can be efficiently used for greenhouses, aquaculture and mineral salts extraction (Kodhelaj 2011; Kodhelaj et al. 2012a, 2012b).

**Key words:** Geothermal, Bënjë, temperature, heat exchanger, combined

### Introduction

Albania is a small country of only 28,787 km<sup>2</sup> surface area and around 4,500,000 inhabitants, situated in the southwest part of the Balkan Peninsula. Like the other Balkan countries, Albania is located next to the subduction boundary between the African plate and the Euro-Asiatic plate. This setting makes the presence of geothermal resources possible (Aliaj et al. 1996). Surface manifestations of geothermal resources are found throughout Albania, ranging from the region of Peshkopia in the northeast, where hot springs with water temperature of about 43°C and inflow above 14 l/s are found, through the central part of the country with different sources with temperatures above 66°C, to the Peri-Adriatic depression with a number of wells, producing water

with temperatures around 40 °C and variable flow rates (Frashëri and Čermak 2004). The thermal waters in Albania are only used for balneology. So far, the geothermal resources have not been utilized for other purposes, such as space heating (Hyseni and Melo 2000). This paper is aiming to give some calculations that show that these resources, not only fulfil all the requirements for direct utilization, but if combined through hybrid systems they are fully competitive compared with the conventional resources.

### 1 Materials and Methods

#### 1.1. Katiut Bridge (Ura e Katiut), Lëngaricë-Përmet geothermal springs

In the village of Bënja, there are 8 springs with temperatures 23-30 °C and yields in between 8-40 l/s each. They are linked with the regional dissociative tectonic of the Bodar-Postenan anticlines chain. The limestone's layers sink toward west with an angle of nearly 20 °C and azimuth of 210-215 °C. These limestone's layers are karstified, especially in the right bank of the river where some caves or cavities can be found. In a 500m long belt, in both sides of the river are found the geothermal springs: 4 in the left side and 4 in the right side. The water generally blows out in the water level, below or even 1-2.5 m above it. Their placement is (Kodhelaj 2011; Kodhelaj et al. 2012a, 2012b):

- **Spring 1** is 25-30 m further down the bridge, 20 m far from the riverbed. Its temperature is 26°C;
- **Spring 2** is 8 m beyond the bridge and blow out below the water level. It can be seen by its blue with some white tint color on the limestone's surface, by whose fractures the waters blows out;
- **Spring 3** is 25 m beyond the bridge, in the water table but 15 m far from the river shore. They

blow out as three very potent griffons. The water temperature is 26 °C and the yield about 8 l/s;

- **Spring 4** is 150-200 m beyond the bridge, where the canyon width is over 20 m. they blow out as two griffons. The most important about 15÷20 cm height, blow 0.5 m above the water level, have a yield 8-9 l/s and temperature 23 °C. Approx. 30 m beyond is the second griffon with yield of 4 l/s and the same temperature.

The other four springs are placed in the left bank of the river. Their main characteristics are given below:

- **Spring 5** is 300-400 m beyond the bridge, before the canyon whose is 10-12 m wide and 40-50 m height. Some powerful water blow out by the limestone fractures have yields of 30-40 l/s and temperature 30 °C;
- **Spring 6** is at the bridge pier, 0.81 m above the water level and 4 m away from the river. Its yield is 30 l/s and the temperature 30 °C;
- **Spring 7** is 7 m further down the bridge, in the water level and 2-3 m away. The yield is 30-40 l/s and the temperature 30 °C;
- **Spring 8** is the biggest one. This spring is 20-25 m further down the bridge, 1-1.5 m above the water level and 8-10 m away from the river. The yield is over 40 l/s and the temperature is 30 °C.

## 1.2. The geothermal complex-Katiut Bridge (Ura e Katiut), Lëngaricë, Përmet

The demonstrative geothermal complex for the integral and cascade use of Katiut Bridge, Lëngarica, Përmet assume that the construction will be completed step by step in order to decrease the value of the initial investments (Kodhelaj 2011; Kodhelaj et al. 2012a, 2012b). In the design phase of the center should be considered several factors and parameters as: orientation, approach with different environment, thermo insulation of the walls, floor, windows, sealing etc. Based in the yield of the geothermal spring is possible to be installed a capacity of 10,040 kW. Due to the fact that their temperature is low for optimizing their utilization should be used the complex and cascade scheme that includes the hybrid system through combining of geothermal with solar

panels and water-water geothermal heat pumps and heat exchangers, as it is shown in the Figure 1 (Kodhelaj 2011).

## Cost calculation and economic analysis of the proposed center

In the table 1 is presented the detailed cost for the construction of the proposed center. There is clearly seen that main investment goes for the main building (40.27 %) while the total investment goes about 3,024,645 Euro (Kodhelaj 2011; Kodhelaj et al. 2012a, 2012b).

**Table 1.** Cost analysis of the proposed center based on the constituent.

Constituent	Investment [€]
<b>Property (land)</b>	370 980
<b>Hotel-Clinic</b>	
- Building	1 812 280
- Acclimatize system	354 560
- Furniture	129 670
<b>Greenhouse</b>	86 710
<b>Spiroline cultivation center</b>	154 085
<b>Aquaculture installations</b>	116 900
<b>Total [€]</b>	3 024 645

Due to the fact that for the proposed area there are some WB programmers, the construction will be released through a bank loan with interest of only 2 %/year. Based in this information the ROR results:

$$ROR = \ln \left( \frac{\text{Final Value}}{\text{Investment}} \right) = \ln \left( \frac{4051504.93}{3024645} \right) = 0.2923 = 29.23 \%$$

A detailed economical analyzes is completed to find out the viability of the installation. This analyzes was based in the Present and Net Present Values Calculation. The results showed that NPV become positive for income not lower than 250,000 €/y (Kodhelaj 2011; Kodhelaj et al. 2012a, 2012b).

## 2 Results and discussion

By the economic analysis, can be clearly seen that NPV become positive for income not lower than 250,000 €/y. To go a little bit deeper on this analysis, the PV and NPV graphs were designed, as shown in the figure. Their analytic processing proves that the NPV is equalized to zero for yearly income of 220,893 €/y. The business plan based in the Albanian touristic market and it prices evaluate that the yearly CF will be around 237,000 €/y, so

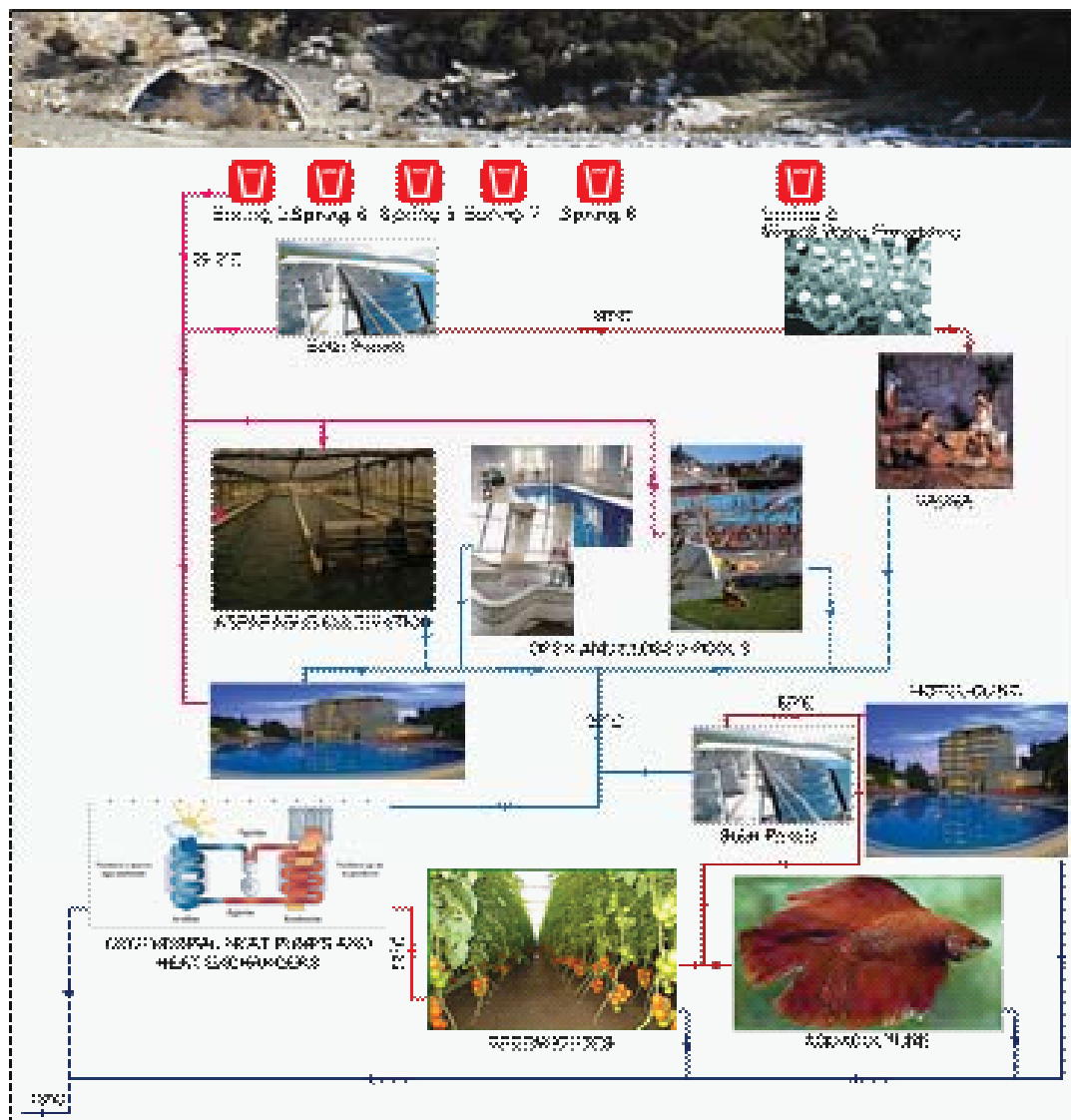


Figure1. Bënja, Përmet geothermal springs utilization sketch.

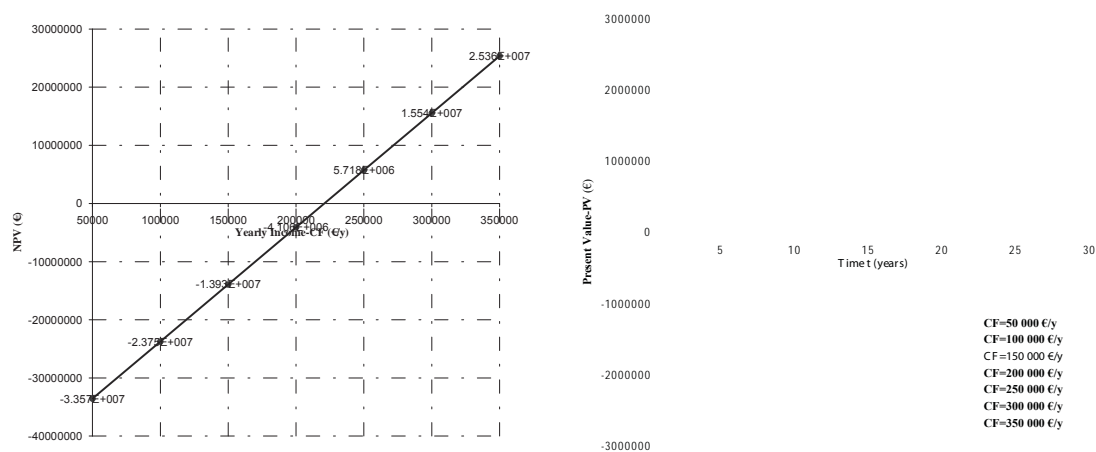


Figure 2. Economical analysis of the Bënja-Përmet recreational geothermal center.



7.29 % higher than the minimal calculated value (Kodhelaj 2011; Kodhelaj et al. 2012a, 2012b).

### 3 Conclusions

Based on the calculations presented in this report the following can be concluded regarding utilization of the hot springs in Albania:

- Albanian geothermal regime allows different scale borehole heat exchangers applications;
- Use of the low and middle enthalpy geothermal waters is economically viable in Albania and they can be successfully used;
- Use of the low enthalpy geothermal waters in Albania can mitigate the economic problems, improve the living standards of the communities and diversify the energy resources;
- The Bënja springs, water temperature is suitable for the supply of a recreational center, including geothermal indoor and outdoor pools;
- The water temperature is suitable for feeding of two cascades;
- The hybrid system will improve the economic efficiency of the project;
- The construction of the center will improve the energetic balance of the region;
- The construction of the center will help on diversifying the energy resources in Albania;
- The degasified and desalination line will improve the environmental status of the area, as actually is highly polluted;
- It will improve the living standards of the community of the Bënja village;

- The economic analyses shows that it is feasible;
- The electricity generated by the combined scheme will improve its efficiency;
- The geothermal systems are environmentally friendly;
- Direct utilization of the low enthalpy geothermal resources of Albania will help in diversifying of the energetic resources mitigating so the supply problems faced in the near past.

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## REVISORY EVALUATION OF POTASSIUM SALTS RESOURCES IN UKRAINIAN PART OF CARPATHIAN FOREDEEP

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### Introduction, actual state of the problem

In the Ukrainian part of Carpathian foredeep there exist deposits of potassium-magnesium salts characterized by unique sulfate composition, suitable for production of high quality non-chlorine fertilizers. In the former USSR two large combines (Stebnyk and Kalush) have operated on the basis of these deposits. Nowadays the operation of these combines is completely stopped. Within the Kalush industrial zone, the ecological emergency situation has been stated. The results of this situation are as follows: the closing of mines (and their flooding), earth surface deformations, gaps; aquifers salinization and flooding of Dombrovo open pit (quarry) with possibility of brines intrusion into a river with a prospect of transborder spread of contamination. The partial flooding of Stebnyk mines also has taken place.

### The concept of subsequent use of potassium salts resources.

The purpose of this study is the revisory evaluation of potassium-magnesium salts resources aimed at restoration of potassium (and magnesium) industry considering actual ecological state and ecological safety standards as well as modern technological possibilities. The actual state resources balance on potassium (and magnesium) salts comprises a number of large, average and small deposits. One of the most significant is Rozsilna-Markova group of deposits located in neighborhood of Kalush combine. Our working team has compiled the concept for potassium-magnesium salts resources use.

This concept includes two main topics:

1) The industrial exploitation of Rozsilna-Markova group of deposits by traditional mining (by two variants: creation of the new combine or by means of existing Kalush technologic basis use);  
2) Exploitation of the mediate and small deposits by means of modern technologies of underground leaching. The last method meets any requirements of ecological safety. Our working team disposes a database on salt deposits which have been compiled in the frames of special contract of the State survey for geology and bowels of Ukraine. Basing upon this data, a number of target oriented digital structural-lithological models of promising deposits have been developed. These models are an efficient tool aimed at information supervision for exploration and exploitation of deposits.

### Conclusion

The presented concept can be transformed into a scientific-technical program for industrial exploitation of potassium-magnesium salt deposits aimed at potassium industry restoration, comprising wide international cooperation, including investment projects.

## GEOGRAPHIC DISTRIBUTION, INDUSTRIAL USE AND THE CHARACTERIZATION OF VOLCANIC GLASSES IN ALBANIA

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### Abstract

#### Background of the study

By the years 1960-1964, volcanic glass was mentioned as volcanic facies in Munella region, but in later years the studies also focused on their practical assessment, particularly for increasing the production of cement, in particular in the pozzolanic brand value. Therefore, the work for evaluation of volcanic glass in territory of Puke and Mirdita districts, had started.

In general were conducted studies and assessments for all volcanic glass in Mirdita area and were performed research and exploration works to determine and evaluate the deposits of Lumbardhës, Qafë Bari, Lumziut, and Letitnës. Other object of volcanic glass are known in Korav, Përbibaj, Munelle, Guri i Korbit-Qafë Bari Jugor, Qafë Lisi, Sukë Pelë - Gurth, Kodër Spaç, Beqiraj, Shebe, etc.

#### Geological features

Volcanic glass in Albania are associated with basalt-dacitic series of ophiolites in Mirdita zone. Volcanic glass of the Lak Roshi-Lumbardhit-Qafë Bari, Lumzi until Gurth Spaç are mostly of medium-acidic composition, to medium, the Lëtitën-Mollë, Kodër Spaç are of medium-basic composition, while in Shebe, Beqiraj, Shpërdhazë, Vjedhës, Roshaj, are mostly basic composition.

In Lumbardhë, Imsht, Qafë Bari and Guri i Korbit-Munellë, Kimëz-Qafë Lisi, Sukë-Pelë and Gurth-Lëtitën, volcanic glass bodies have an average thickness of 20-30 m, 150-250 m and rarely up to 300-400 m, dip length of 20 m, up to 50-60 m. Medium-acidic glass have black-dark color, almost green to black, shiny up to greasy, amorphous, and spherical-parallelepiped parting, angular fracture, glassy to Porcelanic.

#### The Lumbardha Deposit

Body 1, including 70 % of the deposit reserves, has a length from 120 to 150 m, 10-50 m thickness with distention in its central part, followed in dipping depth of 50-60 m.

Chemical composition: SiO<sub>2</sub> 64.88 wt.%, TiO<sub>2</sub> 0.46 wt.%, Al<sub>2</sub>O<sub>3</sub> 10.61 wt.%, Fe<sub>2</sub>O<sub>3</sub> 2.54 wt.%, FeO 2.50 wt.%, MgO 0.81 wt.%, CaO 4.72 wt.%, Na<sub>2</sub>O 1.41 wt.%, K<sub>2</sub>O 0.93 wt.%, MnO 0.12 wt.%, H<sub>2</sub>O' 4.08 wt.%, H<sub>2</sub>O<sup>+</sup> 4.78 wt.%, LOI 0.34 wt.%. Physical properties: specific gravity 2.37 gr/cm<sup>3</sup>, 2.25-2.36 gr/cm<sup>3</sup> volume weight (fresh type and altered). There are produced 266,000 tone of volcanic rocks and exploited every year 10 to 20,000 tone for cement in factories of Fushe Kruja, Vlora, Shkodra and the Perlit Plant in Ballsh.

#### The Qafë Bari deposit

Localized in the upper levels of dacite-rhyolite sequence, this deposit occupies a surface of 0.5 km<sup>2</sup>. More intensive development has in 1100-1350 m quotes,

Chemical Composition: SiO<sub>2</sub> 63.40-66.20 wt.%, Na<sub>2</sub>O 1.40-2.0 wt.%, TiO<sub>2</sub> 0.46-0.59 wt.%, K<sub>2</sub>O 0.27-0.94 wt.%, Al<sub>2</sub>O<sub>3</sub> 10.26-10.66 wt.%, P<sub>2</sub>O<sub>5</sub> 0.01-0.08 wt.%, Fe<sub>2</sub>O<sub>3</sub> 1.96-2.97 wt.%, H<sub>2</sub>O 3.75-6.36 wt.%, FeO 1.72-3.08 wt.%, H<sub>2</sub>O<sup>+</sup> 5.34-7.0 5 wt.%, MgO 0.40-0.90 wt.%, LOI 0.27-0.72 wt.%. In this Deposit, reserves are estimated 21.7 million tone.

## THE CONTINUING EDUCATION “OFFENE HOCHSCHULEN” PROJECT AND ITS OUTCOMES RELATED TO GEOSCIENCE EDUCATION AT THE UNIVERSITY OF BREMEN

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### Abstract

In Germany, Continuing Education (CE) has a strong tradition: in 2007, 69 % of the population was actively involved in formal, non-formal or informal education. As coherent higher education contribution to CE, in 2010 the federal government has launched the 250 million Euro “Aufstieg durch Bildung: offene Hochschulen” project. In order to underpin the chances for local applications to this Call, the state of Bremen initiated the “Offene Hochschulen” (OH) project (2012-2014). The main goals were to design study programs beyond the classical academic offer, mainly addressing working professionals.

In Geosciences, the OH project represented an opportunity to test the timeliness and issues related to designing a professional Master program (Bologna sense) at the University of Bremen. As starting model, a “Geoscience Certificate Program” (GCP) was proposed. GCP was designed as a set of four professional modules, each of 15 ECTS and finalized with a university-accredited certificate. The didactic method of choice was blended learning, including both on-campus and off-campus components. However, based on the feedback from the industry and on the evaluation of internal resources, the original goal had to be redefined. The new outcome, i.e., recasting existing geosciences master programs through the development of E-Learning components represents the most straight forward benefit in the frame of the current educational offer.

The adult education system in Germany has some peculiarities that influence the implementation of full professional Master programs. On the one hand, there is a large number of private companies involved in professional training; on the other, professional Masters involve high tuition fees. In

Geosciences, the time does not seem to be ripe for this goal. Nevertheless, preparatory outcomes such as designing and implementing E-Learning elements, focusing on applied aspects and developing practical skills represent a starting point for further Geoscience professional Masters.

**Key words:** *Continuing Education, professional master, geosciences, Germany*

### Introduction: Adult education in the EU, with focus on Germany

Lifelong learning (LLL) is a relatively newly coined concept that can be synthesised as “ongoing, voluntary, and self-motivated” (\*\*\*, 2000) pursuit of knowledge related to either personal or professional development. More restrictively, continuing professional development (CPD) or continuing professional education (CPE) address the means used to improve professional knowledge and skills during lifetime. Starting with the 1990es, a lot of political momentum in the EU was dedicated to define terms, to develop, implement and assess initiatives related to adult education. In 2009, the strategic framework for European cooperation in education and training (“ET 2020”) set a benchmark for minimum 15 % of the adults (age group 25–64) participating into LLL by 2020, as compared to the current 9 %.

Continuing education (in German: “Weiterbildung”) has a strong tradition and a complex profile in Germany. In 2008, about 25,000 institutions were competing in offering general and vocational programs for various age groups; 69 % of the German population was actively involved in formal, non-formal or informal education (Brandt 2010). By 2015, the federal government aims to increase the participation rate in all forms of CE from about 44 % to 50 % of the 19 to 64-year-olds segment. Currently, Germany spends about



1.2 % of its GDP on adult education: in 2007, this was approximately 28 billion Euros. In the last years, the federal government and the states have funded more and more structural and model LLL projects. Nevertheless, in most of the cases, the participants to LLL programs cover the direct costs themselves. Companies and public sponsors (in total 39 %), and public funds (about 11 %) are the other contributors to the costs. As of 2007, in 84 % of the cases participation was related to occupational topics. Among these programs, 60 % were organised by private companies and 24 % by individuals (Brandt 2010). Professional CE involves high tuition fees that nevertheless do not fully cover the real costs, in the absence of government subsidy (Davies 2009).

In order to provide a coherent higher education contribution to adult learning, in 2010 the German Joint Science Conference (Gemeinsame Wissenschaftskonferenz, GWK) has initiated the national-scale “Aufstieg durch Bildung: offene Hochschulen” initiative. The aim was to foster CE for working professionals in the form of university-accredited programs. This 250 million EUR project funded through the Federal Ministry of Education and Research (BMBF) had two calls, in 2011 and 2013 respectively. The projects approved during the second call will start in August 2014; following a successful evaluation in 2018, the funding would continue until July 2020.

The University of Bremen, through its “Academy for Continuing Education” (Akademie für Weiterbildung), obtained local funding from the Bremen Senator for Education and Science office (SfBW) for the preparation of successful applications for the second federal call, in 2013. This “Offene Hochschulen” (OH) project offered the interested departments from four higher-education institutions in Bremen and Bremerhaven a fast-track access framework to design and develop new LLL offers in the period June 2012–June 2014. The main goal of the OH project was to initiate study programs beyond the classical offer, addressing working or unemployed professionals, or returners to studies after interruptions related to personal reasons (such as family/health issues, maternity leave) etc. These traditionally not-addressed target groups by the academia were thus offered opportunities to study full- or part-time towards obtaining a full-cycle degree (Bachelor- or Master-level) in presence-, or blended-learning formats.

In the area of Geosciences, the OH project was seen as an opportunity to test the timeliness and issues related to designing and developing a professional study program at Master level, at the University of Bremen. This challenge was assumed by the Studies Office of the Faculty of Geosciences with the proposal for a “Geoscience Certificate Program” (GCP). GCP was designed as the foundation element towards the realization of a full geoscience professional Master program.

### **Professional Master programs in the frame of current trends and needs**

University lifelong learning (ULLL) is only one component of the CE, but nevertheless the most important when it comes to training professionals in highly specialized fields, such as geosciences. In general, in ULLL there is a clear separation made between “continuation, consecutive (or just young)” students and “mature, or lifelong” students, with most of the prestigious universities being “youth-focused” (Teichler 1999). As a rule, for the second target group short, multi-modal or customized courses that are outside the universities regular Master programme portfolios are offered (Davies 2009).

The concept of “Professional (Science) Master” (PSM) was coined in the US, in 1997. With the support of the Alfred P. Sloan Foundation, two-year cross-disciplinary programs including business and legal topics were designed as an alternative to traditional research-based graduate education. According to Davies (2009), there is nothing in Europe quite as targeted as the American PSMs. The European terminology concerning Master programs for professionals is rather ambiguous: “professional Master” is still used sometimes to designate degrees awarded by non-university higher education institutions, as opposed to academic Master programs. At the same time, there is a strong practical component in most of the “regular” European Masters, especially into those offered by Applied Sciences Higher Education institutions. It is therefore hard to predict the future for the “professional Master” in the wider European and international recruitment market (Davies 2009).

In Geosciences, Rice University (Houston, US) delivers one of the most successful PSM programs, “Subsurface geoscience”, addressing the needs of the oil industry. The curriculum is mainly

overlapping that of the consecutive masters, so that only a limited number of new courses had to be specially designed. All the taught components take place on-campus (presence learning); the rest is represented by practical stages and thesis work in industrial environments. In Germany, there is currently only one similar academic offer: the Bremen Jacobs University's Executive Master program in "Basin and Petroleum System Dynamics" (BPSD). This, in spite of the fact that according to labour market estimates, there is a high demand for well-trained and experienced geoscientists in other areas such as environment, off-shore industry and advanced materials-related industry. In addition, according to the German Professional Association of Geoscientists (BDG), the economic crisis led to an increase of about 5 % unemployment rate in Geoscience-related jobs in Germany; professional reorientation could open new job opportunities.

### **The Geoscience Certificate Program: A case study on the timeliness for German professional Masters in Geosciences**

As solutions to the integration of the Master-level CE activities with the mainstream academic provision, the report of the EC, Directorate-General for Education and Culture (\*\*\*, 2011) suggested two models: a). "building up", and b). "dividing up". The first model consists of short CE courses that can be aggregated into a Master qualification. The second one is represented by the breaking down of an existing Master program into units suitable for being used in different training environments.

The Geoscience Certificate Program (GCP) proposed in the frame of the OH project embedded both these models into an original concept, progressively developed as learning-by-doing process. The original design of the GCP consisted of four modules, each of 15 ECTS and finalized with a university-accredited certificate. A full Master degree (120 ECTS) could be obtained following the finalization of all these modules, together with a research thesis (30 ECTS). The selected topics represented the Bremen specialty in geosciences: from traditional ones such as Marine Science, to newly emerging ones like Applied Mineralogy. Additionally, as indicated by our industry survey (see below), soft-skills training had to be added to the curriculum. GCP addressed two distinctive target groups: the local industry

and the international professional community. Blended learning including both on-campus and off-campus (online-, distance-, E-Learning) components was the didactic and logistic choice.

In order to evaluate the real need for such a program, in June–August 2013 we have invited about 500 representative Geosciences-related industrial companies, research and academic institutions, governmental agencies etc. to participate to an online survey. The response rate was only 6 %; nevertheless, 83 % of the answers confirmed an interest in the GCP. Critical evaluation of the beneficiaries' survey results, as well as detailed analysis of the available resources (staff and time) as indicated by a previous, internal survey followed. The conclusion was that the original main goal of GCP had to be cancelled. A new outcome, i.e., recasting existing Geosciences Master programs through development of E-Learning components was considered the most beneficial outcome of the OH under the given circumstances. This revised approach embodies a first stage of the "dividing up" model presented above. The example of GCP shows that there is no single pre-defined path in designing professional Master programs.

### **The new GCP outcomes: Developing E-Learning objects in Geoscience subjects**

Four representative courses from the current Master programs, having a relatively strong applied character were selected: Marine geotechnology; Petrology and crust dynamics; Introduction into geophysical methods: seismology, gravimetry and magnetic, and Introduction to mineralogy. For these courses, the content and the practical realization was evaluated, in order to cope with the foreseen requirements of professional training. The "test E-Learning platform" could be further expanded into efficient professional modules. In this way, a solid basis for the future is built, while the current Geoscience educational offer is qualitatively improved. Until June 30, 2014, new E-Learning objects and scenarios will be integrated into the selected courses, by using the learning platforms available at the University of Bremen (StudIP and ILIAS). The E-Learning objects of choice: learning modules, videotutorials (slidecasts), formative self-evaluation tests, summative assignments, blogs/forums, E-Portfolio, and glossaries will be embedded in various learning scenarios.

## Conclusions

As positive experience related to Geosciences in the frame of the “Offene Hochschulen” project, we can mention:

1. Developing new E-Learning components has a double-benefit: it creates a didactic basis for distance learning that can be further used in professional programs, and it responds to the Bremen university’s call for implementation of modern didactic methods. The E-Learning objects could also be used during lecturers’ periods of absence (research trips, sabbaticals etc.);

2. Implementing E-Learning turned into a continuous learning process for the lecturers themselves.

The learning-by-doing experience accumulated while working for the GCP project has shown that a full professional Master program in Geoscience at the University in Bremen is not yet an efficient investment: the industry does not seem to be interested in providing enough input students, while the academic resources (staff, time) are limited. Nevertheless, outcomes such as designing and implementing E-Learning elements focusing on applications and developing practical skills contribute to building a healthy foundation for the further development of Geoscience professional Master programs in Germany.

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## “PLANNING - A NEED FOR SUSTAINABLE USE OF AGGREGATES”

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### Abstract

Albania is a rich country in mineral resources as well as with primary aggregates, evaluated to be of enormous reserves. During the fifty years period until 1990, the use of aggregates has been limited and conditioned by a centralized planning governed by rules of centralized economy.

At the beginning of the last two decades when Albania faced the free market economy rules, the mining industry almost went in collapse. In 1994, the application of the new mining law and restructuring policy for the mining industry, which enabled the transition from an economically centralized type of ownership, planning and operation, the mining industry kept the state ownership and operation is left to private companies. Planning of mining activities is realised through and interactive dialog between the state and interested groups. From that time this industry began to play an effective role in improvement of the quality of life and on the sustainable economical growth of the country.

Albania already has a mining strategy and a new package of mining legislation. In the present mining strategy, the aggregates take a big attention due to the fact that the production of primary aggregates actually, occupies up to 83 % of the total mining products. On the framework of the SNAP project a consultation with the participation of main stakeholders from aggregates sector is done. The necessity of a new specific strategy taking into account all its elements as an integrated strategy for use of aggregates in Albania, is revealed with a great importance. The mining strategy and different reforms that have been undertaken by the government, still does not give a proper answer for integrated planning process and activities on the aggregates exploitation. Roundtable consultation has shown the importance on planning process. From this consultation is expressed the idea that it is the time, for a new sectorial strategy for the aggregates. This strategy shall overcome the difficulties generated by management of aggregates into two legislations and between three institutions AGS, NANR and NCW. Such division creates

difficulties in planning process, in the management from central state and local institutions and in the use of aggregates. Definitely, it is the time to harmonize and improve the aggregate planning policies, by greater policy coordination within and among central and local state authorities, followed by a wide consulting and discussion with all the stakeholders. Consulting activity accomplished under SNAP-SEE project was the first effort in beginning the debate forum for planning process of aggregates and a part of the several topics related to planning, exploitations, rehabilitation of quarries, improvement on Albanian legislation, investments on mining sector and environments, mining legislation and policies, needs for a cooperation among ministries and relevant institutions on permitting, monitoring and control, etc. The important topics are emphasized also in this consultation such as the harmonization of laws; creating an investment environment with appropriate international standards by fighting corruption, increasing transparency and better informing about the impact of exploitation of mineral resources to the environment, to facilitate the availability of information; encourage the establishment of domestic association of operators in the aggregate business; strengthening of the institution to correctly applying the law; progressively environmental rehabilitation of operating quarries to avoid some major related environmental impacts; a reassessment of aggregate resources based on international standards is a condition for a good planning.

Results of the first open debate with key stakeholders, topics raised during discussion, ideas for performing a wider participating process in the planning of aggregates, reveals once more the importance of such a consultation and at the same time it ensures that a plan done with all the stakeholders has more chances to be successful than any other plan done just only from the authorities which approve such plans. At the end of SNAP-SEE project we aim to prepare a national plan on aggregates.



## **MINING WASTES OF ARTANA - A POSSIBLE SOURCE FOR THE RECOVERY OF NON-FERROUS METALS**

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### **Abstract**

Industrial waste stockpiles have been created since the commencement of mining activities in Trepca (1930). These wastes have never been treated technically.

Therefore, the recycling of these wastes and the rehabilitation of their stockpiles would have an effect not only in the improvement of the health, but also in the development of environmentally clean businesses, in accordance with international standards.

Chemical analysis presented in this study, including the analysis of relevant studies ("Minetek", "Korov" a.o.), as well as the studies conducted by Trepca experts, have shown relatively high content of these metals: Pb - 0.76 wt.%, Zn - 1.2 wt.%, Ag - 30 g/t, Au - 1.3 g/t including precious metals Au and Ag in the waste mineral stockpile in Artanë.

Considering the increasing demands of the global

market for non-ferrous metals and the continuous increasing prices of these metals in international exchanges, it is necessary the detailed study for the recovery of these metals from mining wastes. Considering the advancement of the modern enrichment technologies of minerals and waste recycling it is possible that a part of the Trepca mining waste, such as those in the two deposits of Artana, undergo a recycling process, namely an enrichment process, with considerable economic interest.

From 850,000 tone of these wastes which, according to studies, are considered of economic value, the outcome would be 20,000 tone of zinc and lead concentrate, after processing (melting) of which, 10,000 tone of pertinent metal might be acquired approximately.

**Key words:** *Industrial waste, deposits, recycling, concentrate, lead, zinc*

## DISCOVERY AND DEVELOPMENT OF OIL AND GAS FIELDS IN ALBANIA

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### Abstract

Hydrocarbon exploration is a difficult undertaking. Deep knowledge on geology, seismicity and geochemistry are necessary for a given region. Opinion on oil field types up today discovered, main features of the general structural model of the Ionian zone, the exploration prospect for oil and gas in the carbonate deposits of the Ionian zone, are presented in this paper.

**Key words:** *source rock, hydrocarbon potential, Ionian zone, carbonates, oil field*

### Introduction

Many geological-geophysical studies, numerous wells data, as well as the discovery of many hydrocarbon fields, clearly show high prospect of the Ionian zone and an evident hydrocarbon potential. From the geological-geochemical view point the problem of source rocks is resolved, so that the concept of researching only the trap has become usual in our practice, considering indisputably

the hydrocarbon presence. There are five source rock levels in the Ionian zone carbonates. They are in the Upper Triassic deposits, in those of the Triassic-Jurassic boundary of Toarian, as well as in those of Jurassic and Cretaceous age.

It should be mentioned that all carbonate oil fields, with any rare exception (Ballshi, Visoka) have their trap filled with hydrocarbons, thus arguing indisputably an important hydrocarbon potential of the carbonate section. Not full with hydrocarbons of the Ballshi 's (up to its 70 %) is related to its structural plane change in younger times. Whereas not filling of the Visoka 's trap is related to oil field destruction in active hydrodynamic conditions.

So, we have not any restricted potential in these two traps. As a seal in the carbonates case are flysch deposits of Oligocene with a regional spread and with good sealing features. High reserves Messinian - Tortonian sandstones are generated from underlying carbonates and migrated later (e.g. Patos - Marineza's and Kuçova's).

### Oil field types up today covered.

There are three oil fields types discovered so far:

1. *Oil, gas condensate fields concentrated in top of the anticlinal structures.*

The oil fields Gorisht-Kocul's (Fig. 1), Cakran-Mollaj's, Amonica's, Finiq - Krane's, Delvina's etc, belong to this type. The structures have western asymmetry, with western flank overturned and faulted. Their internal model is presented of hump form, individual axe of which forms an angle of 25-30° with general trend. The dimensions are considerable and range from 3-8 x 1-4 km. Generally they have very dip eastern flanks and sometimes overturned. In their top the terrigenous deposits are condensed and, there generally two unconformities are distinguished, that of Burdigalian and Hatian - Aquitanian. The thickness changes from flank to the top structure in the ratio 10:1 and it is

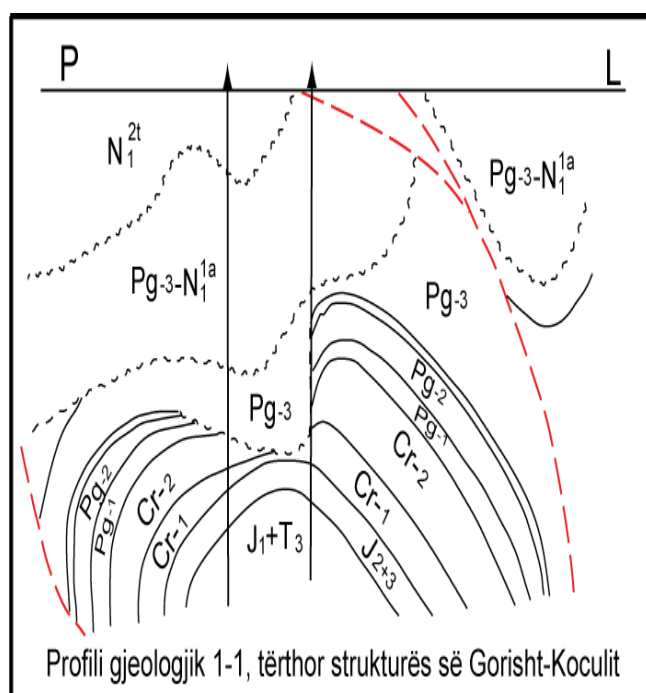


Figure 1. Gorisht-Kocul oil field.

associated with lithological changes.

## 2. Oilfields of carbonate tectonic blocks.

A typical field of this kind is Karbunara's oil field (Fig. 2), where the tectonic blocks are of "wedge" form with eastern dip. They are set one over other and are separated by some ten meters flysch. They are formed as a result of a cutting up of the western structure from that eastern one during the thrusting process (chiefly in and past Tortonian). The carbonate blocks dimensions are relatively small, but the well production flows are considerable due to high fractures (fissures).

## 3. Oilfield of combined traps (structural-hydrodynamic - reservoir - traps)

Part of this type are Visoka and Kallm oil fields (Fig.3). These fields are related with the big structure Patos-Verbas and are located in its near top or in its periclinals. They belong, to Cretaceous-Eocene carbonates, sometimes eroded and covered by Tortonian deposits.

Reservoir feature of the carbonates change,

especially those of Eocene, as well as an active waters movement create traps of combined (structural-reservoir - hydrodynamic) type along the strike direction of Patos-Verbas. The dimensions of these fields are different from relatively small to large, with considerable oil reserves.

The joint characteristic of all above traps is their location on or near the top structure in old structural lines, associated by the consedimentation event. This characteristic has led up today to the exploration criterion according to the continuation of the anticlinal carbonate lines. This criterion is principal for the future as well.

## Main features of the general structural model of the Ionian zone

Two main features have strongly affected the structural-tectonic model of this zone:

a - The presence of the evaporites as a substratum of the carbonates complex and their diapiric

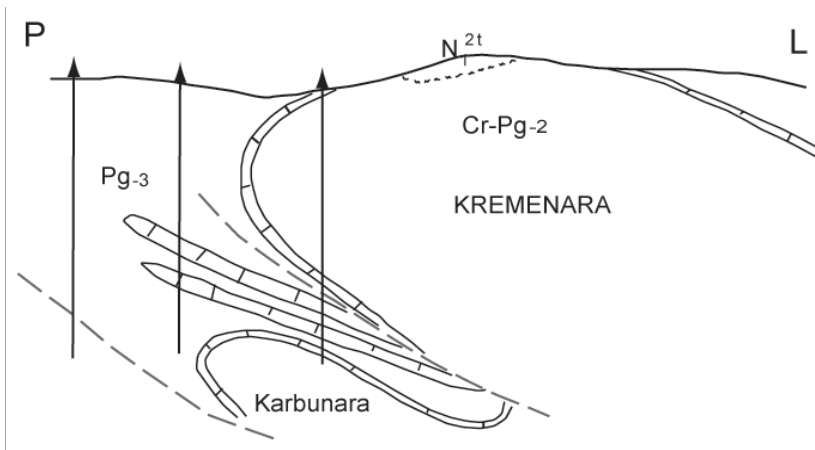


Fig.2. Karbunara oil field

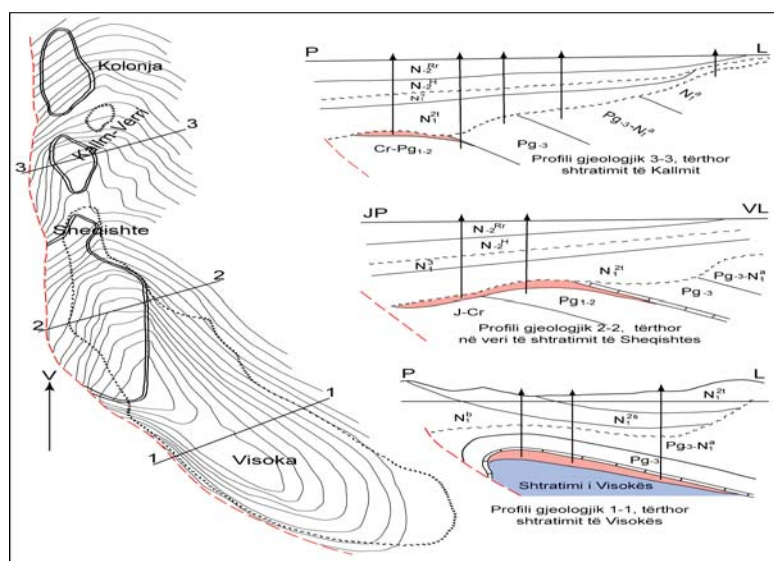


Fig.3. Visoka and Kallm oil field

development.

**b** - High westward thrusting rate of the internal Albanides zones and Ionian zone.

*a* - *On the Ionian evaporites and their role in structuration.*

Evaporitic outcrops in Albania, such as in Dumrea, Bogaz, Kardhiq, Matogjin etc., as well as those of Greece territory, show that they must represent a sedimentary formation of a general spread in the Ionian zone. As they are tectonically encountered under the Upper Triassic carbonates, they should belong to upper Triassic and older ages, thus showing the platformic phase of the further nearly undifferentiated Alpin orogen. Based on their huge volume (1000 km<sup>3</sup> in the Dumrea's) their thickness is to be some kilometres.

Such a big plastic mass has played a great role in favoring the westward thrusting. On the other hand the diapiric movements have also affected the structural model. So the evaporites have westward moved to small pressures along the western faults and causing new faults in the top of the structures and some time in their eastern flanks. In this last case of eastern flank, fault, a backthrust happens and sometimes the structure takes a fan form.

*b* - *High westward thrusting rate of all internal Albanides zone and especially that of Ionian zone.*

Within our country territory the facts like the presence of flysch tongue of the Krasta deposits under those of the Mirdita's and the encounter of the three tectonic zones Mirdita's, Krasta's and Ionian's at the same place in Leskovik, show an over 50 - 60 km overthrusting of the internal zones west-south westwards.

Based on the complex geological-geophysical data there exists these considerations: The Kruja zone overthrust in the Elbasan-Laç sector is of over 40-50 km.

The Marak's thrust (above Dumrea's) is estimated over 15 km, the Tragjas anticlinal above that Vlora's is of 25-30 km.

The westward Ionian zone overthrust has to be greater than their individual structural lines, so it may be of 30-40 km.

The backthrust model of the structures is created due to the resistance encountered during thrusting the eastern structures through/above the adjacent western structures. The eastward movement in this case is relative or apparent because the structures really move only westward.

The backthrust faults are developed there, where

the structures are more approached with each other (Goliko-Kurvelesh, Kurvelesh-Mali i Gjere etc, which is expressed on the surface, whereas in depth it may be separated as a duplex backthrust

They are less developed there, where the structures are away from one another and. the backthrust event in this case is expected to be only in depth and of a less amplitude (Ftera, Cika).

The horizontal throw of these backthrusts is of a range of some kilometers and because of thrusting the eastern structures an apparent view of closing the synclines have created but in depth we have an open sector of triangle zone model

As a conclusion, based on the above analysis of "backthrust" faults, the thrusting amplitude of the Ionian zone has to be of the range of tens or more kilometers.

### **The exploration prospect for oil and gas in the carbonate deposits of the Ionian zone**

The main exploration prospect in the carbonates is related to anticlinal lines.

Based on the tectonic style of the Ionian zone the expected carbonate structures are related to:

1. Continuation of existing structural lines underlying the adjacent structures and under the evaporites.
2. Continuation, of the structural lines of the Ionian zone northward in the square Durres-Laç-Paper-Lushnje.

Numerous structures, which are predicted by geological-geophysical data, are included in the first group. So, by same particular seismic lines, a structure (Sevaster's anticline ) is notified as a southern continuation of the Kremenara, but it is lied under the Griba anticline. Also, south of Gorisht-Amonica-Amantia, the Velça structure is now being explored and more to south another structure (Bolena 's ) is notified by seismic lines. It is expected partly masked by the Fterra anticline.

The northern continuation of the Berati belt structure (Kasithiari's, Greece) is only as geological prognoses. Of this study kind (only geological) is also the northern continuation of the Borsh anticline under the Fterra's thrust.

Some more prepared by geological-geophysical data are the carbonate plays of the Dumrea, Sqepur, Vlora etc.

The first group structures are with considerable dimensions, with setting depth of 2000-5000 m, complicated from structural and tectonic viewpoint.



In the second expecting structures group are involved those, whose existence is related with the problem of continuation or not continuation of the Ionian zone under the molasse unconformity. This problem is also related to the conception on the Vlora-Elbasan strike-slip.

Since the carbonate structures of the Tragjas-Selishte, Kreshpans, Patos-Verbasi, are technically interrupted northward, and the general geological picture in this sector suffers a considerable plunge due to the southern Adriatic Basin plunging there, the carbonate level of the Ionian zone is expected to be relatively deep, but above that of the Adriatic basin. That's why seismic information in this sector is not sufficient.

The interruption of the structural units of the Kruja zone, due to the Vlora-Elbasan transversal fault, shows only a change in structural-tectonic model, but the structures continue. That is an argument that the structural lines of the Ionian zone must continue northward. From the tectonic point of view there are other strike-slip faults like that Vlora-Elbasani in the Ionian zone, such as: Krongji-Paleokaster's, Kremenara-Shendelli's, that north to Sazani's, etc. They are always associated by a northeastern bounding and by a northward shift of the structural model.

The analysis of the western margin of the orogen starting from the Mediterranean Sea (Greece) and northwards shows that the most western structural lines are tectonically closed northwards, but gradually and one by one. In an analogue manner, north to the Vlora-Dumrea sector, we ought to expect that only the western anticlinal line of Cika-Tragjas' has to finish, whereas they more in east (the Berati and Kurveleshi belts) have to continue but relatively deep. At the same time their structural and tectonic model must change, dictated by the partly joint geological history with that of South Adriatic, the carbonates of which are in depth of 12-13 km.

The opinion on the northwards continuation is supported by the seismic data which give signals on deep carbonate structures presence such as the ones Mlik's, Shenkollas's etc. The structures of this group are expected to be of big dimensions, with a less developed tectonic and a setting depth of 5000 m range.

## SPATIAL DISTRIBUTION OF RARE EARTH ELEMENTS (REE) IN STREAM SEDIMENT OF KOSOVA

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### Abstract

The rare earth elements (REE) are a group of chemical (metallic) elements belonging to the periodic table. The group consists of the 15 lanthanide elements along with yttrium and scandium. They share many similar properties, which is why they occur together in geological deposits.

The REE are often associated with other incompatible elements, the most common of which are zirconium (Zr), niobium (Nb), cesium (Cs), tantalum (Ta) and thorium (Th). REE also naturally occur related to the phosphate, beryllium, barium, fluorine, gallium, and tantalum minerals in various geologic environments.

Results on stream sediment geochemical analysis were taken by the Independent Commission for Mines and Minerals (ICMM) and they belong to the entire territory of Kosovo. There is a total of 3240 collected and analyzed stream sediment samples.

The geochemical analysis provide data on a range of elements such as lanthanum (La), cerium (Ce), yttrium (Y), scandium (Sc), zirconium (Zr), niobium (Nb), cesium (Cs), tantalum (Ta) and thorium (Th).

The comparison of the assayed REE values versus their average composition of the earth's crust ("Clarke value") have been used to highlight their distribution in the surveyed area.

The analytical data have been statistically treated, processed using Surfer software and represented by respective maps showing the areas where the elements have higher contents than their average

composition.

The statistics show that the REE mean and median values of the stream sediments from the surveyed areas are lower than crustal average for element such as La, Ce, Y, Sc, Zr, Nb and Ta. In contrast, the abundance of Cs and Th exceeds the crustal average. A maximum value exceeds the Clarke values by the factor 3.58-26.9. The REE values range over several orders of magnitude with larger variations. The coefficients of variation of elements except La and Th (0.44), are more than 0.50 and the coefficient of variation of Cs is the highest one (1.14).

Correlation analyses indicates that there is a significant correlation between Nb and Ta, La and Th, La and Ce, Y and Nb and a moderate correlation between Nb and Ta, La and Y, La and Nb. Correlation matrix shows a positive correlation between selected elements.

Spatial analysis or spatial statistics includes a series of techniques for analyzing spatial data. The initial procedure of analysis includes the set of generic methods of exploratory analysis and the visualization of data, generally by maps. Software for application of this spatial analysis requires access to the data characteristics: their location and their attributes.

This study attempts to achieve the numerical characterization of the anomaly, and its differentiation from the background. In this work raw data after pre-processing have been mapped as post and 3D surface maps. The illustrated maps are interpreted to identify the target area for the considered elements.

## DIVERGENT RIFTING SEPARATION OF ADRIATIC-DINARIC AND MOESIAN CARBONATE PLATFORMS WITNESSED BY TRIASSIC MVT AND SEDEX DEPOSITS, METALLOGENETIC APPROACH

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### Introduction

Metallogenesis brings together knowledge of regional geology and ore petrology. Their mutual interfering is beneficial to interpretation of plate tectonic models of orogenic processes. The Alpine-Balkan-Carpathian-Dinaride (ABCD) metallogenic and geodynamic provinces are result of the Wilson cycle, which includes phases of rifting, oceanization, subduction and emplacement of ophiolites, collisional and postcollisional deformation events with synkinematic granite plutonism. The rifting and oceanization processes took place almost synchronously within the vast circum ABCD area, in the Mid-Triassic time, creating symmetrical emplacement of Adriatic-Dinaric and Moesian carbonate platforms, on the passive continental margin of Gondwana and Euroasia. The symmetry was emphasized by deep marine basins in between, gradually developing into oceanic crust of the Tethys. The scenario is outlined by symmetrical distribution of ore deposits characteristic for the rifting metallogenesis, MVT Pb-Zn ores in carbonates (Bleiberg-Mežica type) and SEDEX iron-manganese-polymetallic ore sediments (Read sea type). The early symmetry of the tectonostratigraphic and metallogenic phenomena along the line of extension and opening of the future Tethys was subsequently "spoiled" by continental convergence of Africa and Euroasia mainly from the Cretaceous to the present. It developed complex geometry of the collisional interfaces, with interfingering microplates giving rise to discontinuous sutures, diachronous magmatism, subduction of continental crust, leading to variable thickening, followed by extension and collapse (Heinrich and Neubauer, 2002).

The paper gives a brief description of MVT and SEDEX deposits, in the two carbonate platforms and rifts in between, formed synchronously and in similar manner on opposing side of the diverging continental margin.

**Key words:** *Triassic MVT Pb-Zn deposits, SEDEX deposits, Adriatic-Dinaridic-Moesian carbonate platforms, Tethyan rifting*

### The MVT and SEDEX deposits, markers of Triassic rifting processes

Triassic carbonate-hosted lead-zinc deposits (Alpine-type/MVT) in the Alps and Dinarides are placed within the Adriatic-Dinaridic carbonate platform, a passive continental margin of Gondwana. Carbonate-hosted, low-temperature, Pb-Zn deposits are contemporaneous with the advanced Tethyan rifting in the Middle Triassic. The most important deposits are Bleiberg-Kreuth (A), Mežica (SLO) and Topla (SLO) in the Eastern Alps, Raibl and Salafossa (I) in the Southern Alps. These deposits so far provided more than 10 Mt of Pb-Zn metal. The mineralization is generally stratabound in carbonates of the Ladinian and Carnian stage. Usually they are combined under the term "Bleiberg type" and have often been compared with MVT deposits (Ebner et al., 2000).

The discussion of the origin of the Pb-Zn ores is still controversial. There is a general agreement on their formation by low temperature fluids. The lead model ages older than the host rock may be derived from Palaeozoic sediments. However, the derivation of metals and the concentration mechanisms of Pb-Zn metals for these deposits are not yet fully understood.

Apart from the above "majors", there are more than 200 similar Pb-Zn occurrences known in the External Dinarides, the Southern Alps and the Eastern Alps. Some of them are shortly reviewed in the following.

Sv. Jakob Pb-Zn deposit hosted by non-metamorphosed dolostones is situated in the

Medvednica Mt. in the south-western part of the Zagorje-Mid-Transdanubian zone. The vein-type mineralization has a simple association of galena, minor sphalerite and pyrite with quartz and calcite as gangue minerals (Šinkovec et al. 1988). Pb isotopes are anomalous and may be classified as Bleiberg-type according to the Doe and Zartman model yielding 490 Ma (Palinkaš 1985). FI studies of quartz gave the following characteristics: NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O composition, 6-19 wt.% NaCl eq., temperature of homogenization ( $T_H$ : 80-230 °C, mean 130°C). The  $\delta^{34}\text{S}$  values of galena and sphalerite vary between +7 and +10 ‰ (Borojević Šoštarić 2004).

Pb-Zn deposits in the Middle Triassic carbonates occur also in the Ivanščica Mt., in the Ivanec deposit in the Zagorje-Mid-Transdanubian zone (Šinkovec et al. 2000), on the eastern slopes of Petrova gora Mt. in the Svinica deposit, and in the Srb deposit in Lika region. All of them are accommodated within the units which can be correlated with the Mesozoic carbonate platform of the External Dinarides.

The Olovo deposit, Central Bosnia, is hosted by Middle Triassic dolostones and limestones, evolved in reefal facies. The major ore minerals are Pb and Zn carbonates mainly cerussite and to a lesser extent smithsonite (Kubat 1988)

SEDEX Fe-Mn-polymetallic deposits, related to advanced Tethyan rifting, deposited by basinal brines.

Vareš metallogenic province in the Central Bosnia owes its ore load to processes during the advanced rifting in the evolution of the Tethys. Coeval magmatism produced spilites, basalts, keratophyres and diabases interbedded with Ladinian sedimentary rocks (Pamić 1984). The Vareš deposit with Smreka, Droškovac and Brezik deposits are taken as the locus typicus mineralization of the Mid-Triassic Tethyan rifting. The deposits contain hydrothermal, stratiform siderite-hematite-chert beds. The ore mineralization is intercalated into an Anisian and Ladinian sequence and distinctly zoned vertically, reflecting gradual changes of redox conditions in the depositional environment during the basin subsidence. The sequence began with bituminous, thinly bedded black shales with plenty of pyrite and base metal sulphides, overlain by barite and siderite, all of which were deposited under reducing conditions. Clastic rocks and oolitic limestone rest upon this metalliferous series and are succeeded by another metalliferous

series with hematitic shale and siliceous hematite beds, which in contrast to the footwall rocks were deposited under oxidizing conditions. The overall mineralization consists of siderite, Mn-enriched hematite, barite, pyrite, marcasite, chalcopyrite, galena, sphalerite, tetrahedrite and Pb-sulphosalts. The  $\delta^{34}\text{S}$  values of barite vary from +21 to +29 ‰. The chemical composition of fluid inclusions in sphalerite and barite may be described as a CaCl<sub>2</sub>-NaCl-H<sub>2</sub>O system which evolved under moderately high temperature, ( $T_H$  between 110 and 230 °C). Salinity ranges from 2 to 4 wt.% NaCl eq. In context with the Cl/Br ratio the fluids are assumed to have been derived from modified seawater (Palinkaš et al. 2003) (Fig. 1).

Triassic carbonate hosted Pb-Zn ore deposits on the Moesian carbonate platform resemble in many respects to those in the Alps and Dinarides (Minčeva-Stefanova 1972).

The Pb-Zn bed-like ore deposits in Bulgaria are found in the Balkanide region within an area of about 30 x 25 km. The host rocks are primarily dolomite of Anisian and partially of Rhaetian age. The ore bodies are elongated lenses, and veins mostly of metasomatic origin. The ore is represented by fine grained light-coloured sphalerite, pyrite, marcasite, galena, small amounts of arsenopyrite, bravoite [(Fe,Co,Ni)S<sub>2</sub>], and sporadic Ag-Sb-sulfosalts. Dolomite, barite, quartz and calcite are typical gangue minerals.

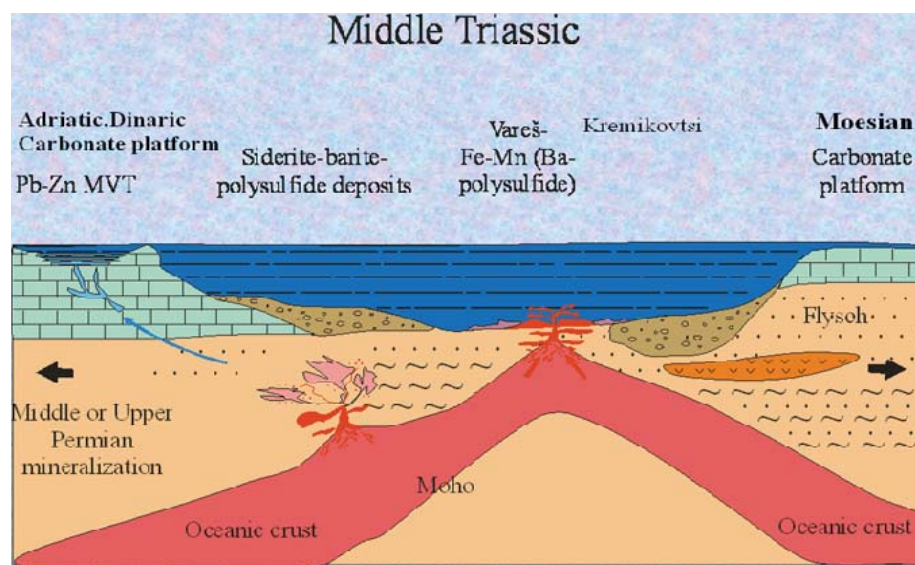
Kremikovtsi SEDEX deposit is situated app. 15 km NE of Sofia. It lies in the southernmost part of the Kremikovtsi-Vratsa ore district, in the Western Balkanides, a northern branch of the Alpine-Himalayan collisional orogenic belt. The deposit was produced by Middle Triassic metallogenesis in the graben shaped structure adjacent to the Moesian carbonate platform. The ore forming processes took place in an incipient rift-related extension. The deposit is of SEDEX type, consisting of stratiform pyrite and barite ore, and iron-manganese formation with low-grade sulphide mineralization. Primary zoning of the Kremikovtsi ore district extends vertically and laterally: pyrite, siderite, barite, ferroan dolomite, ankerite, and hematite. It has a prominent feeder zone with stockworks and veins of iron carbonates-barite-sulfide in the underlying rocks.



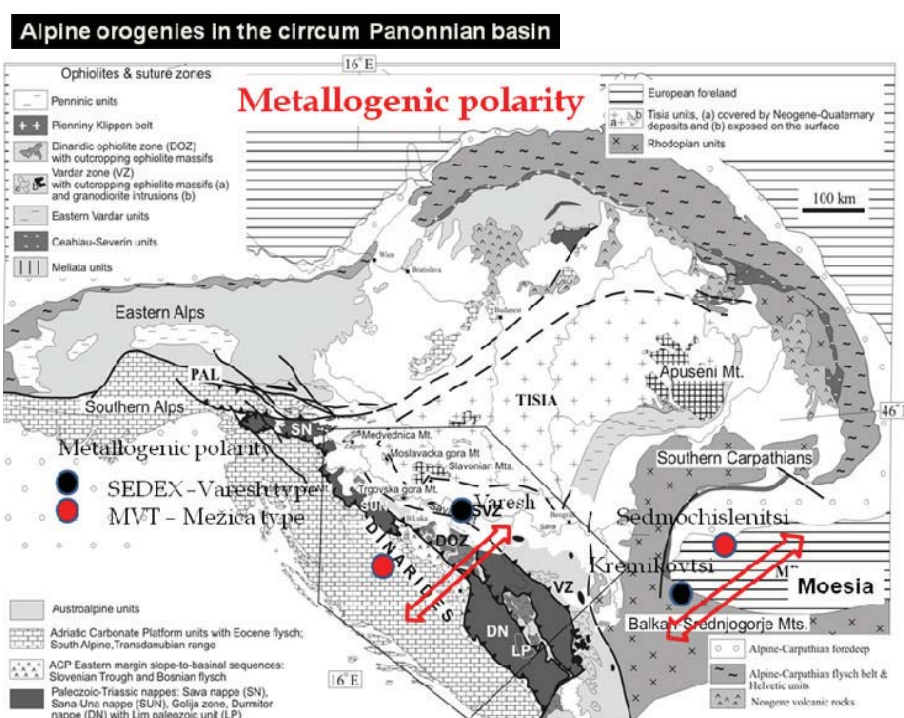
## Conclusion

ABCD area is a collage of variable crustal elements, a part of a long suture of the Tethyan ocean, squeezed between Gondwana and Euroasia continental blocks. Introduction of plate tectonic models greatly contributed to integrated interpretation of geological evolution in time and space. There are still, however, numerous disputes, in putting collage elements together. The crucial moments in interpretation is timing of incipient rifting and creation of Tethyan oceanic

crust. Number of oceanic slivers, recognized by Dinaridic, Western and Central Vardar ophiolites, makes firm conclusion blurred. Metallogenetic events, formation of MVT and SEDEX deposits, formed on the carbonate platforms and in intracontinental rifts in the Mid-Triassic time, define spatially and constrain timing of advanced Tethyan rifting. Symetrical polarity of MVT deposit positions on the flanks of the rift basin contributes convincingly to the suggested interpretation (Fig. 2).



**Figure 1.** Middle Triassic advanced Tethyan rifting. The drawing depicts formation of characteristic MVT type of deposits within the carbonate platforms. The SEDEX type deposits are formed in response to volcanic activity within a rift basin, like hydrothermal exhalation and deposition of sedimentary ore load.



**Figure 2 .**

Metallogenetic polarity of mineral deposits, related to the advanced Tethyan rifting. The two carbonate platforms, facing each other from the opposite passive continental margin of Gondwana and Euroasia, accommodate numerous MVT deposit in Alps, Dinarides and Moesia. The newly formed, deep water marine basin, with still continental crust (not the ocean) are the home of SEDEX deposit, formed by hot water, issuing their ore load primarily as sediments on the bottom of the Triassic sea.

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## MODELING OF ORE BODIES AND CALCULATION OF RESERVES WITH COMPUTATIONAL METHODS IN A QUARTZ - COPPER SULFIDE DEPOSIT IN CENTRAL MIRDITA

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### Abstract

Increasing the effectiveness of quantitative and qualitative exploitation of raw ore material in the mining industry, requires a precise spatial perception of ore bodies discovered by geological works, as well as high precision of ore reserves, estimated for certain economic elements. In previous practices of geological discoveries, calculation of mineral reserves in a certain deposit, has been accomplished manually, after elaborating of a numerous statistical and graphical materials; vertical geological section, where ore bodies have been outlined, horizontal and vertical projections of ore bodies depending on their dip, numerous tables of calculating of surfaces in section, of volumes between certain surfaces, of pondered contents of results of chemical analyses and after the determining of the volume weight of the ore, the geological reserves were calculated according to the relevant categories, as well as the amount of economic metal elements, all of these, for a period that lasted several months, one year or more.

The use of computer technology in recent years in data processing of geological modeling has made possible detection of ore bodies and carrying out accurate calculation of their reserves. In this article, will be given the real data on modeling and calculation of ore reserves in a quartz - copper sulfide deposit in Central Mirdita. These methods, as shown by the study, are a great help in exact designing of the opening mining works, reducing unnecessary expenses, and rational planning and extraction of ore reserves with minimal loss in quality and quantity.

**Key words:** ore body, database, outline, interpolation, extrapolation, modeling

## OLIGOCENE-PLIOCENE SEDIMENTARY CYCLES AND LIGNITE PHASES IN SE ALBANIA

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### Abstract

The main principles of coal accumulation and relation with marine molassic cycles or sedimentary cycles of intermountain basins are analyzed. Two Oligocene paralic lignite phases were followed by a third phase occurred during the early Aquitanian, which progressively evolved into a siliciclastic sequence in late Aquitanian, and was accompanied by important erosion. In the freshwater intermountain basins are formed Middle Miocene, Late Miocene and Pliocene lignite phases.

**Key words:** *Lignite phases, marine cycles, freshwater basins.*

### Introduction

The first geologic-palaeontologic studies of the Oligocene lignites and molluscs from Morave were reported during the second half of the 19-th century by Penecke (1896). Having an economic potential because of lignites, the Oligocene-Aquitania sediments of Albanian Thessalian Basin (ATHB) and Middle Miocene - Pliocene sediments of continental intermountain basins, has been subject of numerous detailed geological and stratigraphic investigations of lignite accumulations during the late 20<sup>th</sup> century. Many geologists have described and published the results of their investigations: Cossman and Bourcart and Cossmann 1921; Pashko et al. 1973, 2013; Pashko 1977; Dimo, et. al. 1982; Kleinholter 2004. The main factors for coal accumulation are palaeogeographic evolution of basin and climate, especially the humidity level, which define the type of sediment and their fossil fauna and flora. Therefore, analysis of tectonics, palaeogeographic reconstruction, facial analysis and biostratigraphic correlation of basin formations help for prognosis of lignite phases and for determining the possible potential sites for further prospecting – exploration of coal in the basin. In this paper are analysed the main principles of coal accumulations and their relation with marine cycles and sedimentary cycles

in intermountain basins of the southeastern part of Albania. Biostratigraphic, palaeogeographic and geological studies carried out in the Oligocene – Pliocene formations, have made possible to distinguish and correlate in their separate sedimentation basins, several paralic lignite phases formed within Oligocene-Early Miocene marine molasse cycle, and lignite phases formed within Middle Miocene-Pliocene intermountain freshwater basins (Fig. 1).

### Oligocene-Early Miocene marine cycles and paralic lignite phases

The regional distribution of the lignite phases in ATHB is controlled by the marine transgression and regression cycles. From Middle Eocene to Middle Miocene (Langhian) time the ATHB have been part of a vast epicontinental marine basin, Tethys. In the present days, ATHB is a narrow elongated intermountain marine piggy-back basin, trending NW-SE, from southeastern Albania to the Northwestern Greece. Its sedimentary evolution was conditioned by tectonic, palaeogeographic and palaeoclimatic conditions and their changes over time. The basin filling is represented by marine transgressive and regressive sedimentary sequences with paralic lignites. The first lignite phases are developed on Morave above the basal conglomerates (alluvial deltaic formations) at beginning of the Rupelian transgressive marine cycle. After this time the transgression flooded a vast area, from Morave to Gore-Moker, reaching NW part of the ATHB, and basin filled by intercalations of fully shallow-marine siliciclastic deposits with *reefal coralinacean* limestone rich in marine *molluscs*, corals, larger foraminifers and scattered irregular echinoids, (Drenice Formation) of Late Rupelian. Transgression continued also during the accumulation of the Chama Marls (Chattian stage), that represents the moderately deep fully marine conditions, and also the top of the marine transgressive phase. The upper sequence, represented mostly by sandstones with leaf flora, *Clypea* scales of Plase Formation, laterally passes in lignite formations, which have been formed during



the Chattian regressive phase of the Oligocene marine cycle. Drenova lignite Formation, about 86 m thick, consists of intercalations of grey marls, 0.2-0.3 m thick dolomite layers, with seven lignite or coal-clay layers rich in eurihaline brackish-shallow marine fossil faunas. The lignite seams are continuous for 7 to 9 km in strike, and only four of them are of economic interest. Coal-bearing migrates gradually from SE towards NW where are encountered the uppermost level layers. The plant fossils and *molluscs* assemblages, mostly *gastropods*, with fluvial influence includes eurihaline marine and brackish-lagoonal species, indicate a coastal brackish-lagoonal facies, affected by gradually marine transgression mostly in lower part of sequence. The Chattian lignite phase consists of Zemblak-Dishnice lignites and Gore lignite Formation, that covers the Gore-Mokerr area and developed from southern centroclinal in Lozhan (Krosnisht) to the both sides of the syncline. Lignite sequence has a big lateral extension, but variable thickness and quality. Its largest development is in the western side from Krosnisht centroclinal to Mesmal, Guri i Nikes, Llenge and northern parts at Velcani i Mokres. Lignite sequence, is generally represented by two lignite complexes, the lower one, which is the most important, about 500 m thick, and composed of 8 layers, of which the layer 3, the most important one, has an average thickness about 1 m, and is traced in strike for ca 15 km, whereas the fourth group of layers 5 and 6, are partially of economic interest. Usually between coal layers and sandy cover are encountered "ichnofauna" 0.05-0.45 m thick, probable burrowing *mollusc Kuphus*, which are indicators of lagoonal-mangrove environment rich in organic matter. The upper complex about 150 m thick have only 2 lignite layers, and only in Mesmal, they are partially of economic interest. The siliciclastic layers that are intercalated with lignite layers are eurihaline *molluscs*, mostly *gastropods*, and rarely shallow marine ones. Lignite sequence of eastern side of the basin begins with 3 lignite layers of Dishnice-Zemblak in Morave and extends in northwest towards Velcan-Gore, in Pretushe, Leshnice till to Homesh. The Pretushe lignite sediments have 13 layers of which the 2-5 lowermost ones, which extends till Homesh, are of economic interest. The average thickness of three layers is 0.6 m, but the lowermost one is up to 2 m thick. Siliciclastic sediments intercalated with lignite layers of formations are brackish-shallow marine *molluscs*,

mostly eurihaline *gastropods*, that are indices of lagoonal-brackish facies. Aquitanian sediments represent the uppermost part of the Oligocene molassic cycle and in Morave they consists mostly of marls and clays with fine grained sandstone followed mainly by coarse grained sandstones and conglomerates, in the upper part of section, whereas, in northern part, in Gore-Mokerr area, they are represented by Mokerr lignite Formation. The transition from Aquitanian siliciclastic to lignite sediments, is observed in southern centroclinal of Gore-Mokerr, in Dardushe-Qershtize. The lignite sediments of the Mokerr Formation that begins in southern part of Gore-Mokerr region, extends along both sides of the area, and generally contains up to 11 lignite seams, of which 2-5 seams are of economic interest. The western synclinal side is mostly lignitophyle, and lignite horizon extends from Osnat and Qafe Panje to Cezme. In eastern side from Dardhas mine the lignite series extend to Verdove and more in north. Mokerr lignite Formation. passes up in Aquitanian siliciclastic sequence, represented mostly of shallow-marine coarse grained sandstone and conglomerate (Guri i Kamies), accompanied by an erosional phase. The fully marine Burdigalian-Langhian molassic cycle consists of typical shallow marine lithothamnium facies, followed by deep marine marls (Langhian) and are known only in the southern part of the basin, from Morave to western side of Korce depression, transgressively on the Aquitanian sediments.

#### **Lignite phases of continental intermountain basins**

At the end of Langhian time, the extensional regime, that affected the ATHB, resulted in the rapid uplift, marine regression and termination of marine sedimentation, and the new small, mostly NNW-SSE trending, gradual subsiding intermountain basins were formed. In its sedimentary filling, represented mostly by lacustrine and lacustrine-fluvial sediments, the different lignite phases are formed. The *molluscs*, flora and microflora, ostracoda and vertebrates are the fossils found related to them.

During the Middle Miocene the adjacent coastal plain with extensive deposition of highly clastic, reddish deposits of Librazhd area, was occupied by the western Serravalian marine transgression, followed by fluvial-lacustrine lignite deposits with *Melanopsis impressa*. The lignite horizon represented by three layers, two of which averagely 0.45-0.7 m thick, passes up

to the marine sedimentary sequence of the Golik Formation. At the Late Miocene time, a wide, long life intermountain freshwater basin is developed east of the Morave Mountain, in Devolli plain, and extending towards Florina-Servia and Macedonia basins. The sedimentary sequence of the basin characterized by the continuous succession of lacustrine-fluvial sediments: claystone, marls, diatomaceous marls with intercalated lignite layers from Late Miocene to the Pleistocene, reaches up to 850 m thickness. This basin is a half-graben, fragmented of unique basin during subsequent Pleistocene tectonic episodes. The Pontian sedimentary filling consists of the intercalation of about 300 m thickness, predominantly lacustrine diatomaceous marls, sands and claystone and lignite layers (Menkulas Formation) that developed in SW part of the plain. The lignite horizon consists of 5 lignite seams, of which, a lower combined coal layer reaches 2.6 m thickness, mainly in eastern parts. The calcareous silt (molluscas debris) and the unsculptured *Viviparus cf. brussinae* occur in the topmost part of the coal strata package. The 220-230 m thick Pliocene lacustrine deposits dominated by intercalations of the gray to blue claystone, light siliceous sands lignite layers (Kuc-Dobranji Formation.) with *molluscas Bithynia tentaculata*, *Planorbis corneus*, *P. planorbis*, *Dreissena polymorpha*, ostracods, and *microfloristic* association start with basal Zicishti sands (70-80 m thick) with *Anancus arvernensis* and "Mammut" *cf. praetypicum* of Early Pliocene (Ruscinian) age and developed in NE of Menkulas. Kuc-Dobranji Formation contains 3 lignite layers, of which, the lower layer 1, is averagely 1,70 m thick and varies from 0.4 m to 3.0 m thick. The Late Miocene Alarup coal layers are formed within about 50 m thick grey and green claystones with some lignite layers on the 100-200 m thick basal conglomerates and followed by 250-300 m thick highly coarse-grained, yellow-brown poorly sorted gravels and conglomerates of the metamorphic rocks. *Hipparion gracile*, scarce *Viviparus* sp., *Psilunio* sp., and ca. 50 m thick grey and pollinomorphs association *Quercus pseudocastanea*, *Betula* sp., *Stratitotis* etc., are found. The Alarup lignites horizon consists of only 2 layers, that are averagely 1.21-2.12 m thick. In the southern part of the Korce-Kolonje graben, the Pliocene lignite of Bezhani Formation occurs and it consists of 2 lignite seams respectively 0.6-5.8 m, and 0.6-1.3 m thick within a succession, up to 160 m thick, of lacustrine sediments claystone,

predominantly diatomaceous marls, with two lignite layers from 0.6 to 5.8 m thick and plant fossils, *mollusc Valenciennius* sp., and Vertebrates (Bezhani Formation), whereas northerwards, in Korca Plain, the 500-600 m thick gray claystone with many thin coal and clay-coal layers, 0.4-0.7 m thick (Pojani Formation.) are extended in N and NW part of the basin and they contain ostracods.

### **Lignite accumulation, marine cycles, palaeogeography and climate**

Times of accumulation of the lignite phases and clastic sediments were related to the tectonic evolution of the basin and climate events. Generally, the fine sediments, clay-marls with lignite layers are accumulated during the warm climate phase, while during the cooler phases the coarser-grained sediments were deposited. In the ATHB, after the highest temperature during the Middle Eocene (molluscs and flora, leaf Palms of subtropical climate), the temperature tends gradually decreasing until the Pleistocene, but warming and humid phases documented by the fossil flora and fauna from the beginning to the end of Oligocene, and during the accumulation of Aquitanian Moker lignite Formation. The Late Miocene-Pleistocene times characterized by the alternations of clay and occasional lignite layers that correspond to cyclic oscillations of climate and tectonic activity. Individual coal seams vary in thickness from a few centimeters up to 3-4 meters and are in general widespread in the area, but like lenses interrupted by siliciclastic sediments. The studies confirm, that the different marine cycles, lignite accumulation, climate, and its biostratigraphic correlations are dated mostly by mollusks faunas. The data on the flora, microflora and fossil vertebrata are limited. The palaeogeographic evolution of ATHB is the most dominant factor for the lignite accumulation. In relation to marine cycles, the main extensive lignite deposits occur during the Chattian-Aquitania regression, particularly in northwestern part of the basin, whereas, during Rupelian transgressive cycle, lignite accumulations of minor importance are only known in the Morave area. The lignite seams are intercalated into brackish-shallow marine sediments with eurihaline fossil faunas, mostly molluscs. The Drenove lignite formation is rich in marine eurihaline-brackish molluscs, such as bivalvia *Barbatia albanica*, *Ostreacyathula*, *Cyrena sirena strangulatam*, gastropods *Tympanotonos margaritaceus*, *Granulolabium plicatum galeotti*,

*Ampullina crassatina*, *Globulosa gibberosa* and freshwater *Melanopsis impressa*, that reported to have lived in lagoonal brackish conditions in fluvial-estuaries or mangrove swamps facies of tropical-subtropical areas. In addition the large *A. crassatina*, was a eurihaline species occurring in lagoonal environment of Tethys Oligocene. The molluscs assemblages of Chattian Gore Formation comprise *B. albanica*, *T. margaritaceus*, *Gr.plicatum galeotti*, *Terebralia bidentata*, *A. crassatina* etc., which also are inhabitants of brackish shallow marine environments and are interpreted also as indices of tropical-subtropical environments. The burrowing molluscs *Kuphus*, that are found in Chattian sediments of Plase and Gore Formation, is a inhabitant of shallow marine, mainly lagoonal-mangrove environments. The Early Aquitanian basal sediments of Moker Formation, include shallow-marine molluscs, and passes up to lignite sequence with *Terebralia bidentata*, *Tympanotonos margaritaceus* and benthos foraminifera. This gastropod species living near and within the coastal swamps and mangrove forests are indicators of the brackish-shallow marine, lagoonal swamps environments. The biostratigraphic and sedimentologic data of intermountain basins indicate the close relations between tectonic evolutions, climate and lignite accumulation. All of the Neogene intermountain basins are its sedimentary sequence, poor or relatively rich in lignite layers. Its lignite phases indicates a humid and warm climate phase, particularly during the accumulation of lignite horizon with fine grained sediments, while the coarser-grained layers are accumulated during the cooler phases. In general the high repetitive alternations of lignite seams and clastic layers are product of cyclic changes in climate associated by tectonic activity, mostly during the formation of Gore and Mokerr lignites in ATHB basin. The global cooling during the Neogene in intermountain basins has conditioned the poor and occasional lignite formation and the coal facies mainly are controlled by lateral fluvial migrations.

## Conclusions

During the Oligocene-Early Miocene marine molasses cycle are accumulated Rupelian Drenove, Chattian Gore and Aquitanian Mokerr paralic lignite phases, whereas in intermountain freshwater basins the Middle Miocene Golik, Late Miocene Menkulas and Alarup, and Pliocene Kuc-Dobranj, Bezhan and Korce freshwater lignite phases. The lignite seams are in general relative extensive in area, but combined and lenticular in form, interrupted by clastic sediments.

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## SEDIMENTARY COVER ON THE OPHIOLITES IN THE MIRDITA ZONE (ALBANIA)

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### Abstract

The Mirdita Zone is found in the eastern part of the Albanian territory. It consists of Permian, Triassic-Middle Jurassic limestones and dolomites, radiolarites, volcano-sedimentary formation, Middle Jurassic ophiolites and Upper Jurassic-Cretaceous -early Palaeogene sedimentary cover.

The ophiolites of Mirdita Zone are very important geological occurrences that represent the remnants of the Tethyan oceanic crust, uplifted during the Late Liassic and Early Dogger on the sea floor. Their emplacement on the continental margins during Late Dogger and Early Oxfordian along the Mirdita- Subpelagonian-Tauric basins as serpentinite diapir and/or by the mechanism of obduction, points out the end of the development of the ophiolitic volcanism in this belt. This ophiolite belt is of same age and type as the eastern Vardar-Ankara one. The Korab-Pelagonian intermediate massifs divide these two belts.

The study of the Albanian ophiolites and their related sedimentary rocks is a very important matter for the Mediterranean region. The ophiolites section in Albania is complete, very well preserved and exposed, creating the opportunity for detailed observations and correlations among the Albanian ophiolite belts and those from other regions.

In the Mirdita zone, the sedimentary cover of the ophiolites is very well exposed and preserved and has been studied thoroughly from the biostratigraphic point of view. This has allowed the discovery of several sedimentation cycles, interrupted by stratigraphic breaks caused by tectonic movements often accompanied by overthrusts.

In this zone, the previous authors have presented the sedimentary cover of the ophiolites as tectonically very quiet to be intact and without any breaks or gaps in sedimentation. Our studies have established a new concept based on some interruptions that have been found in the sedimentation during the Upper Jurassic and Cretaceous, caused by some tectonic movements,

which have greatly influenced post-ophiolites development of the zone.

Sedimentary cover in the Mirdita Zone consists of several sedimentary cycles, set transgressively over each other and divided by stratigraphic gaps, exposed phases and/or folding deformations. Ophiolites sedimentary cover begins with Kimmeridgian-Neocomian deposits, overlaying the intensively folded Triassic-Middle Jurassic limestones, radiolarite, volcano-sedimentary formation and ophiolites. In the southern Voskop-Polena sector, the transgression happened earlier than in the other parts of the Mirdita Zone and begins with Kimmeridgian-Tithonian of thin alterations of conglomerates, sandstones and thin reddish marly limestones, very rich in yellow ferruginous particles originated from the weathering of the ophiolites. They contain many ammonites, *Calpionella*, *Cadosina*, etc. Other parts of Mirdita Zone's territory have been subsided only during the Berriasian and Valanginian and the deposits formed during this time are of the same facies as those from the southern part. The strong Mirditean Orogeny during the uppermost Valanginian and mainly Hauterivian brought the uplifting and the continental conditions in all territory and in some sectors, very big rock masses are observed to be overthrust westwards over the oldest formations, forming some tectonic nappes.

Later Paleomirdita subsides again and the new cycle of sedimentation begins with the Barremian-Aptian that marks the greatest transgression in all the Mirdita Zone, all the territory being occupied by shallow water environments. The conglomerates at the base and limestones with many rudists, algae, nerinea and other significant fossils are frequently found in these deposits. These conditions continue till the end of the Turonian when the territory of Mirdita uplifted again and turned into a big continent due to the Mediterranean movements.

After the subsidence of the area, the shallow marine Santonian-Lower Campanian cycle of sediments lie with unconformity over the old formations. During the Late Campanian-Early Maastrichtian,



the area of Mirdita Zone was uplifted over the sea level as consequence the Subhercinian phase. A new transgression returned to the region Mirdita Zone during the Upper Maastrichtian and continues up to Middle Eocene (Lutetian), where due to the strong Illyrian orogeny, the territory was turned again into a dry land. This period is marked by the sediments of Upper Maastrichtian-Middle Eocene cycle.

During the latest epochs of the Tertiary and Quaternary in the territory of the Mirdita Zone, the marine conditions continue, but this work is not concerned with this time interval.

## GEOCHEMICAL EVALUATION OF EVAPORITE SECTION CROSSED BY DUMRE-7 WELL

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### Abstract

Diapir of Dumrea lies at the northern extension of the anticline belt of Berati. Evaporite formation of the dome is the upper Triassic age (Vranaj et al. 2002). The present morphology is conditioned by the tectonic phase after Pliocene time. This is confirmed by seismic studies and drilling of the Dumre-7 well. During the drilling of the well had gas shows where the hydrocarbon gas stream going to the top of the drilling tower (file of the well). In these circumstances, the geochemical study of the well during the drilling process, is completed. Geochemical studies were conducted in coaly shale and hydrocarbon gas seep. Geochemical evaluation is based according to (Prifti et al. 1994) the experience in Oil and Gas Geological Institute of in Albania (OGGI) as methane/ethane (C1/C2), methane/methane counterparts (C1/C2 +) and ethane/propane (C2/C3).

**Key words:** Free hydrocarbon gases, thermal vacuum gas, evaporate formation, wetness ratio

### Methods of study

Dumre-7 well intersects evaporate section and in the depth 6101 m came evaporate formation. During drilling there were frequent performances of hydrocarbon gaseous. Drilling process was based on these geochemical studies:

ing drilling there were frequent performances of hydrocarbon gaseous. Drilling process was based on these geochemical studies:

- Pyrolyse studies of coaly shale which is identified on cutting particles.
- Organic petrology studies of coaly shale (maceral composition analysis and vitrinite reflectance).

Geochemical studies of hydrocarbon gases based on gas chromatography (GC) method of free hydrocarbon gases appearing during drilling, hydrocarbon gases in mud, separated by thermal vacuum method (ThVG) and hydrocarbon gases studied by “gas log”. “Rock-Eval” method involves pyrolysis of coaly shale samples under precisely controlled temperature gradual increase from 250 to 500 °C. This procedure was carried out with equipment “Oil Show Analyzer”.

Petrologic study of coaly shale was carried by “Microphotometer MPV3”. Through this method groups of macerals were separated and measurements (Prifti et al. 1996) of vitrinite reflectance (Ro) were performed.

Gas chromatography studies are conducted for free gases, hydrocarbon gases separated by thermal vacuum method (ThVG) and hydrocarbon gases studied by “gas log”. Homologues series

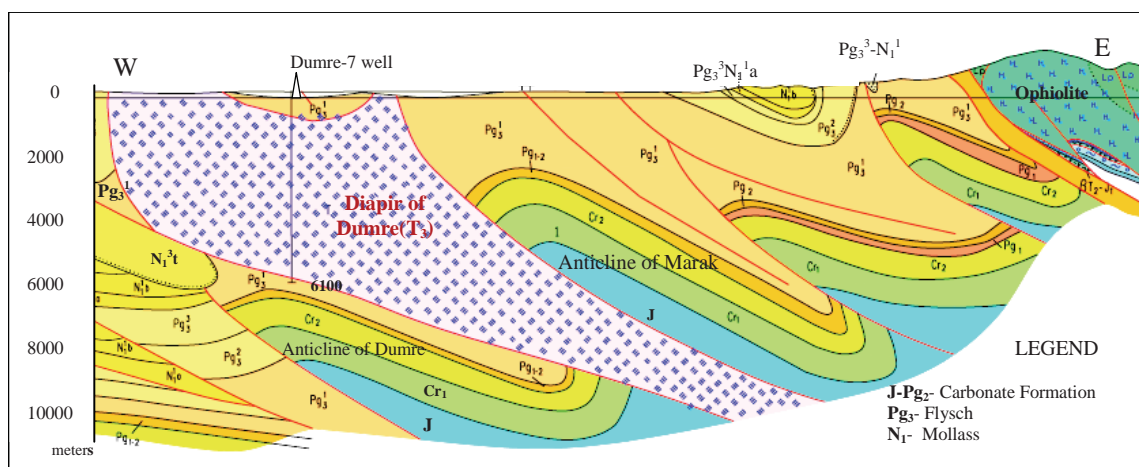


Figure 1. Dumre diapir crossed by Dumre-7 well (Prifti et al. 2013)

of methane up to heptane (C<sub>7</sub>H<sub>16</sub>) are performed (Shkurtaj et al. 2002; Prifti et al. 1994).

## Results and Discussion

### Geochemical properties of organic matter

In the Dumre-7 well are studied three levels in the depths of 4745-4795 m, 4905-4910 m and 5230-5235 m. These levels are represented by coaly shale (Folder of Dumre-7 well). The content of organic carbon ranges from 29.29 % to 38.73 %, which are characteristic for coaly shale and coal. Hydrogen Index has values (130-319) which are characteristic of a type III-II of organic matter. Type III-II confirmed by the petrologic study where gelinite maceral dominate, which are derived from lower plants in lagoon environments.

deposits as very good thermal conductor, affecting the growth of maturity younger sedimentary rocks. When diapir exposed on the surface, starts cooling of the region.

### Geochemical properties of hydrocarbon gaseous

During the drilling of the well Dumre-7 in evaporite formation, gaseous hydrocarbons are met. Geochemical types of hydrocarbon gases are defined by experience of the Oil and Gas Geological Institute, Fier (OGGI) as C<sub>1</sub>/C<sub>2</sub>, C<sub>1</sub>/C<sub>2</sub>+

The geochemical gaseous hydrocarbons indexes of Dumre-7 well are:

A) Free hydrocarbon gases, were obtained during drilling, during maneuvers and during mud circulation in the Dumre-7 well (4524-5290 m). In their composition the full range of gaseous hy-

Type of methods	C <sub>2</sub> +	OGGI geochemical indexes			i-C <sub>4</sub> /n-C <sub>4</sub>	Wh	δC <sub>13</sub> (‰) of methane
		C <sub>1</sub> /C <sub>2</sub>	C <sub>1</sub> /C <sub>2</sub> +	C <sub>2</sub> /C <sub>3</sub>			
ThVG	0.8-19.05	11.48-148	4.25-124	1.01-12.64	0.44-0.92	0.78-18.84	-32 ÷ -35
Free Gas	0.44-10.0	11.46-147.72	8.96-123.6	2.59-12.3	0.53-0.92	0.78-10.04	-
GasLog	0.54-3.22	38.86-396	11.46-67.27	0.68-4.15	0.48-1.14	1.46-8.03	-

The maturity of organic matter is estimated by reflectance of vitrinites (R<sub>o</sub> %). This ratio varies in the range from 0.402 to 0.446 %. Based on this parameter organic matter is immatured and maturity level involved in coal subbituminous stage (stage of mixed gas generation). The low level of maturity is due to the high thermal permeability of evaporite section (Downs 2009) also evaporite formation have a low thermal capacity. Evaporite

drocarbons is included. Based on geochemical indicators (C<sub>1</sub>/C<sub>2</sub>, C<sub>1</sub>/C<sub>2</sub>+) free hydrocarbon gases are primarily very dry gas, dry gas and wet gas types. While free gases of Pekisht wells (Pekisht oil field) are mainly very wet hydrocarbon gases or petroleum associated gas (Fig. 2).

B) Hydrocarbon gases separated by thermal vacuum of mud (ThVG), are dry gas type and wet gas type. One sample (5290 m) is very dry gas type.

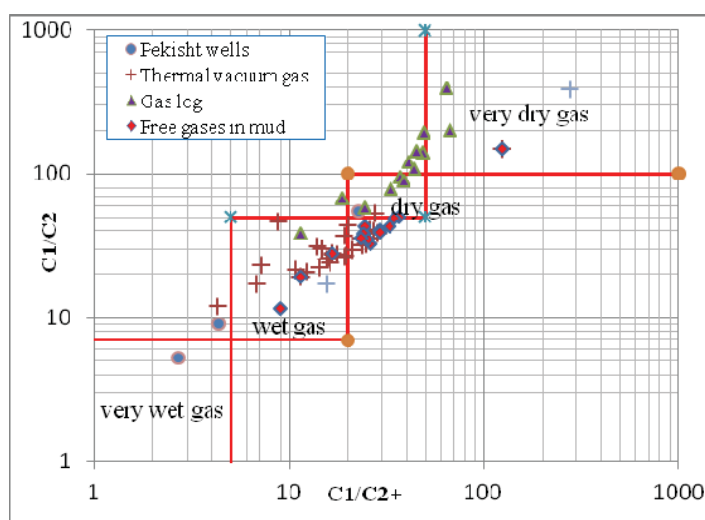


Figure 2. Geochemical type of gaseous hydrocarbons by OGGI indexes.

C) “Gas log” is applied during drilling of Dumre-7 well (5109-6119 m). Well Dumre-7 underwent “gas log” study from 5109 m to 6119 m depth, this depth belonging exit of evaporate deposits. Based on hydrocarbon gases reports  $C1/C2$  (43.07-184.37),  $C1/C2 + (18.36-57.8)$  are dry and very dry types of gases.

### Geochemical gaseous hydrocarbons indexes of Dumre-7 well

#### *The maturity of hydrocarbon gases*

The degree of maturity of hydrocarbon gases is evaluated by two main indicators, the carbon isotopic ratio of methane ( $\delta C13$ ) and izomerization rate ( $i-C4/n-C4$ ). Values of carbon isotopic ratio of methane ( $\delta C13$ ) range from -35 ‰ to -35 ‰ (Durand 2003), indicating that the hydrocarbon gases are very matured (Prifti et al. 1994; Diamanti et al., 1998). Izomerization ratio takes value  $i-C4/n-C4 < 1$ , then gas is mature. Two “gas log” samples are immature and generated by organic matter of evaporate formation (Diamanti et al. 1998).

#### *Accumulation of gaseous hydrocarbons*

Manifestations of hydrocarbon gases have met almost all the evaporate section penetrated by Dumre-7 well. Their origin is related to the old sedimentary section that has passed “oil window” and contacts diapir body. Diapir body included

gaseous hydrocarbon keeping within his measure. These hydrocarbons are stored in tectonic blocks of dolomite, limestone and other rocks which have porosity. The main task of the organic geochemistry science is whether this gas seep represents petroleum hydrocarbons traps. Geochemical indicators accounted by the experience of the Oil and Gas Geological Institute in Albania (OGGI). These indicators are: Wetness Hydrocarbon Ratio (Wh), Hydrocarbon Balance Ratio (Bh), Character hydrocarbon Ratio (Ch), ethane/propane ratio ( $Ep=C2/C3$ ).

According to Wh parameter evaporate section is gas production, in fact accumulations named “imprisoned gases” by the diapirism evaporate formation. This term includes, for the first time in the science of organic geochemistry. Such accumulations have less hydrocarbon and gas reserves are utilized.

This indicator ( $Ep=C2/C3$ ) conducted in studies at the Geological Institute of Oil and Gas in Albania (OGGI) is performed to assess the oil and gas traps. Thus high values are characteristic of hydrocarbon gases traps,  $2 < C2/C3 < 3$  is characteristic of condensate traps, while for smaller values of 2 are characteristic for the petroleum traps (increase of propane).

High values of  $C2/C3$  indicate the presence of hydrocarbons traps at depth (Prifti et al. 2010).

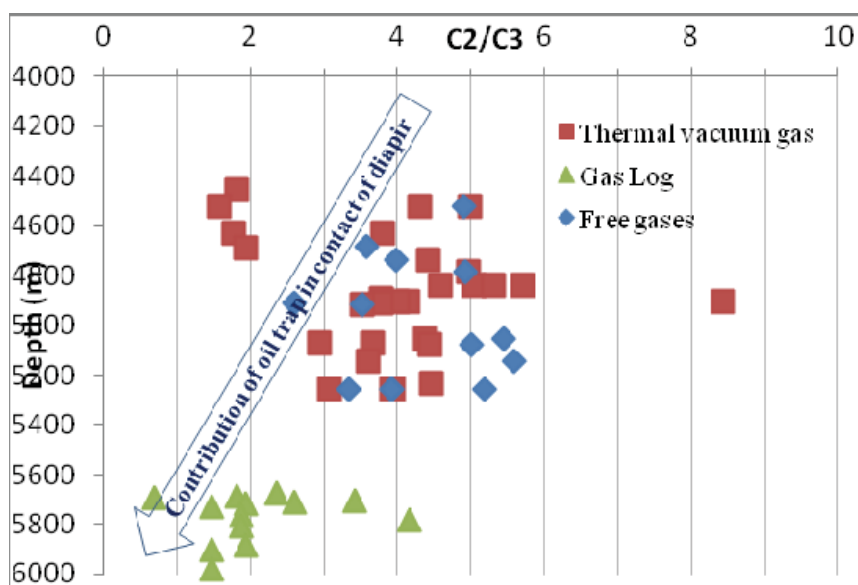


Figure 3. Gas accumulation of Dumre-7 well based on Ethane / Propane Ratio ( $Ep= C2/ C3$ ).



## Conclusions

Dumre-7 well spent Dumrea diapir body in depth of 6101 m. In the evaporate section penetrated by well Dumre-7, three levels of coaly shale at 4745-4795 m, 4905-4910 m and 5230-5235 m depths, are met. Based on petrologic and rock-eval studies, organic matter is of III-II type. While its maturity level is low ( $R_o = 0.4\%$ ).

During the drilling process there were hydrocarbon gases performances which were studied by the Gas chromatography. According geochemical indicators hydrocarbon gases are of dry and wet types. Based on the carbon isotopic ratio of methane ( $\delta C_{13}$ ), hydrocarbon gases are mature, generated by the source rocks that have passed the oil window. While according to the izomerization ratio ( $i-C_4/n-C_4$ ) only two gas samples were generated by organic matter of evaporite formation.

Hydrocarbon gases from evaporite formation do not represent gas traps, but the gases are “imprisoned” by the diapirism phenomena of evaporate formation.

Geochemical indicators tendency towards lower contact to evaporate formation indicates the presence of hydrocarbons traps in depth.

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## REGULATING ASPECTS AND GEOLOGIC SOLUTIONS OF THE NATURAL GAS BUILDING CAPACITIES TO A GAS MARKET MODEL IN ALBANIA

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### Abstract

Natural Gas supply into Balkans underdeveloped through Caspian regions over medium to long term became case on June 2013 when TAP route has been selected. After Albanian National Territory Council approved on March 2014 the Compound Development Permit of TAPAG, the project should officially start activities for the construction phase (called as Phase 1). Connection of existing gas pipelines of Albania within the European network via TAP and new others projected to build in order to meet seasonal fluctuations for local gas consumption, as well as needs of Kosovo and FYROM for gas supply, it's compulsory to think about some of most important points over this period: determination on the capacity building of gas sector for a due Albanian Gas Market Model, supply options for the future gasification of the country, alternatives of opening underground gas storages in the salt domes of Dumre region and extending gas pipelines to these neighboring countries. Albpetrol will participate at the Booking Capacity considered as the Phase 2 of TAP and the Albanian Government has signed Gas Purchasing Agreements with E.ON Ruhrgas AG at a quantity of 0.5 bcm/year and with AXPO at a quantity of 0.25 bcm/year; eventual local new significant gas discoveries due to the successful result of recently drilled well Shpiragu 2 (up to 50,000 mc per day) and 4 year project funded by Swiss Government for the capacity building of gas sector starting within 2014, pledge secure supply on initial demand gas natural stock. With the assistance of the Secretariat of Energy Community, the MEI has started the drafting the new gas law, by transposing the Third Energy Package aimed to finish within 2014. Assistance is required for the drafting of secondary legislation.

A Gas Market Model is needed for the development of the market (i.e. unbundling of production, transmission and distribution). MEI has just applied on February 2014 to WBIF for funding around 1.1 million euro Gas Master Plan of Albania. One combined cycle power generation plant of 97 MW convertible to NG in Vlora may need 0.15 up to 0.2 bcm/year, for more this TPP is expandable up to 300 MW. Natural Gas demand assessment in Albania is total 0.6 bcm up to 1.85 bcm from 2015 to 2030. Supply options for the Gasification of Albania: Trans Adriatic Pipeline project, Ionian Adriatic Pipeline project, Albania Kosovo Pipeline, construction of an LNG plant on the Albanian coast that can contribute on the diversification of gas supply of the country, including the proposal projects for constructing and operation of LNG regasification terminals. Underground Gas Storage (UGS) potentials in Albania is a geologic solution considering the Upper Miocene depleted sandstone gas fields of Divjaka and Povelça, as well as the Dumre evaporitic deposits diapir of the Upper Triassic age. The later results as best target alternative for the very underground gas storage.

**Keywords:** *natural gas, supply, demand, capacity build, storage*

## SEM-DATA FOR PLACER GOLD RELATED WITH SOME VALLEY AROUND BOROV DOL PORPHYRY COPPER DEPOSIT, FYR OF MACEDONIA

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### Abstract

This work presents SEM data from research of gold aggregates discovered were during schlich prospection performed along the creek Meckin Dol, around the Borov Dol Cu-Au porphyry deposit. The size of the tested gold aggregates ranges from 30 µm to about 600 µm. The form of gold aggregates was isometric – irregular. The chemical composition of gold aggregates shows 74.15-99.32 wt.% Au, 0.3-24.68 wt.% Ag and 0.04-11.06 wt.% Cu. Fe, Bi, Se, and Te are represented with a content less than 1%. In general, by their chemical composition, the examined gold aggregates are characterized by high purity, ranging from 750 to 996.

**Key words:** *placer, gold, chemical composition, gold morphology, porphyry deposit*

### Introduction

In FYR of Macedonia are known many of metal and non-metal minerals, including gold. Studies of gold in Macedonia have a long history. A large number of gold occurrences, about thirty, are more or less studied and provide impetus for further serious research (Bogoevski 1998; Percival et al. 1994; Serafimovski et al. 1999; Kovacev et al. 2007; Stefanova et al. 2007, 2012; Volkov et al. 2008). Most of these have no economic value but genetically, they are very interesting.

Our main goal is the study of the gold aggregates found in stream sediments along the creek Meckin Dol. Tests were made in order to examine the range of physical characteristics such the size and shape of the gold aggregates and mineral content. Primary source of this placer gold should be very close upstream where occur primary porphyry mineralization of copper and gold within the Borov Dol deposit. Downstream along the creek, the gold occurs even further up to Kriva Lakavica River, which is backed up by the historical data.

### Materials and methods

In this research, schlich prospection was applied. There were taken about 10-15 kg from each sampling location. After panning off, magnetic separation of the magnetic fraction was manually performed. Both fractions obtained were observed under binocular and the identified gold aggregates were separated manually and subjected to further study.

To determine the morphological features of gold, primarily, the roundness, flatness and serrations of grains, the scanning electron microscopy (SEM) was used. This type of analysis allowed to determine the length of transport and nature of the environment in which the schlich material was deposited. The SEM study was performed in the Laboratory of Electron microscopy at the Faculty of Natural and Technical Sciences “Goce Delcev” University, Stip, Macedonia. Analyses were performed on a VEGA3 LMU. Etalons are from TESCAN. Specific operating conditions: Tension 20 keV; Test Method: EDS; Type of analysis: Quantitative X-act: 10 mm<sup>2</sup> (Silicon Drift detector); -Max resolution 125 eV; Resolution of MnK $\alpha$ , FK $\alpha$ , CK $\alpha$  according to ISO 15632:2012.

### Results and discussion

The studies were performed along Meckin Dol in the length of about 0.6 km. From the total of 13 schlichs, 5 were taken for more detailed processing. We found a total of 56 gold grains of different shapes and sizes. The other minerals are represented by chalcopyrite, which is the bearer of copper mineralization in this locality, followed by pyrite and galena. Less prevalent are sphalerite, malachite, azurite, hematite. As nonmetallic minerals, zircon, mica and epidote occur.

The most important mineral of this prospection is the gold which is found in elongated, dendritic irregular shapes and less frequently in spherical-round shape. In order to precisely define and determine the size and shape of gold aggregates, detailed scanning electronic microscope investigations were performed (Fig. 1). From these

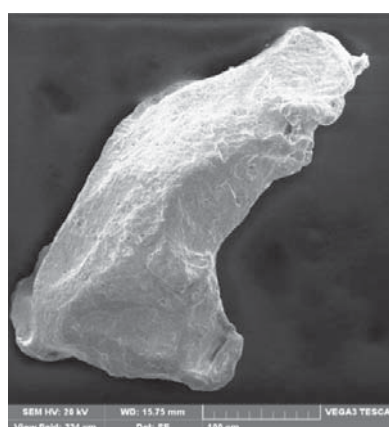
examinations it can be said that isometric form prevails (Fig. 1f) while elongated gold aggregates (Fig. 1a,b), round-spherical shape (Fig. 1b,c) and platiness form were also found (Fig. 1e).

The physical characteristics of gold such as the size of the grains depend on the type of primary mineralization, type and length of transport and erosion of land terrain (Mudaliar et al. 2007).

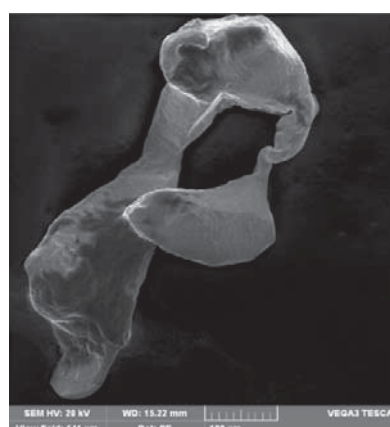
Studies of gold aggregate forms from the above mentioned locality display that irregular isometric shapes prevail in the vicinity of primary source, while downstream of the creek as a result of

transport, these forms are lost, i.e. the grains are elongated and rounded off. At a distance up to 50 m from the primary mineralization, almost identical shapes as well as primary gold, prevail. At a distance of 50 to 300 m, secondary grains became elongated and even get triangular shapes with the appearance of small voids on the grain surface. At a distance greater than 300 m, primary shapes of grains were lost (Townley et al. 2003; Nakagawa et al. 2005).

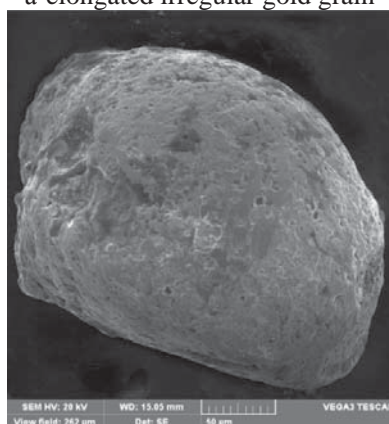
This morphological forms suggests that studied gold s probably has similar characteristics as the



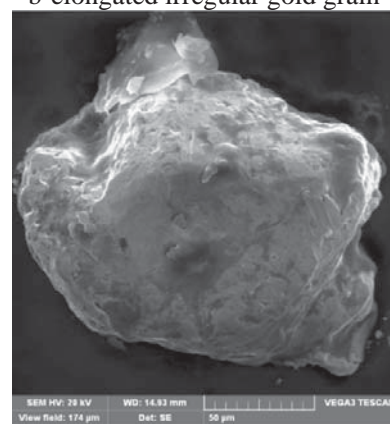
a-elongated irregular gold grain



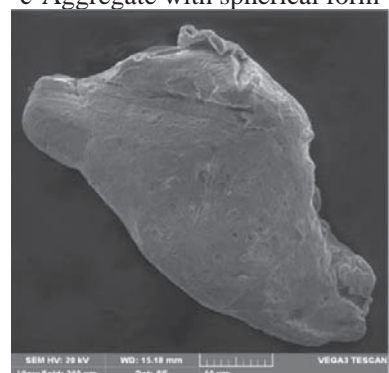
b-elongated irregular gold grain



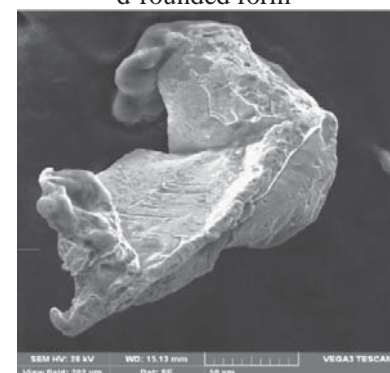
c-Aggregate with spherical form



d-rounded form



e- Aggregate with platy form



f-isometric gold grain

**Figure 1.** Morphological forms of matching gold aggregates of Meckin Dol creek, Borov Dol locality.



primary gold and has not suffered long transport. Squamate or flat shape as well as elongated shape identified in the study locality are a features of primary gold that typically occurs in such shapes, although sometimes it may occur in square to rectangular but very irregular shape with expressed sharp contours and edges on grains (Mudaliar et al, 2007; Townley et al, 2003; McClenaghan, 2005; Nakagawa et al, 2005).

Beside the shape, analyses of the chemical composition of gold aggregates were performed

Based on this data it can be concluded that gold aggregates in general have a homogeneous composition which leads to the assumption that gold aggregates derive from one source (Florescia et al. 2004).

## Conclusion

The results of investigations of the morphology of gold aggregates from the Meckin Dol Valley suggests that there is a primary deposit in the immediate vicinity from where the material was

**Table 1.** Average chemical composition of gold aggregates – Meckin Dol, Borov Dol locality (wt.%).

sample	Fe	Cu	Ag	Au	Bi	Se	Te
MD-1 grain-1	0.39	0.06	0.315	99.32	0.07	0	0
MD-1 grain-2	0.12	0.17	7.6	91.09	0.74	0.16	0.47
MD-1 grain-3	0.05	0.39	0.74	99.26	0.5	0.07	0
MD-3 grain-1	0.15	0.48	7.67	91.43	0.2	0	0.30
MD-3 grain-2	1.23	0.52	3.8	94.5	0.29	0	0
MD-3 grain-3	0.21	0.22	12.58	86.97	0.41	0.01	0.2
MD-4 grain-1	0.11	0.14	24.68	74.15	0.42	0	0.72
MD-4 grain-2	0.54	11.06	3.31	90.24	0	0	0
MD-4 grain-3	0.14	0.59	1.7	98.06	0	0	0
MD-5 grain-1	0.025	0.12	14.83	84.67	0.63	0.17	0.14
MD-5 grain-2	0.38	0.32	8.99	90.07	0.22	0	0.22
MD-5 grain-3	0.35	0.57	18.35	80.57	0.4	0	2.65
MD-7 grain-1	0.1	0.23	20.14	79.02	0.22	0	0.31
MD-7 grain-2	0.78	0.22	24.31	74.34	0	0.06	0.30
MD-7 grain-3	0.18	0.19	12.35	87.13	0	0	0.22

which showed that it was native gold characterized by high purity. Most of the tested gold (Table 1) aggregates belong to the group of high purity gold (900-950) where the average gold is 88.05 %.

Studies of the relationship between the composition of gold and the transport length showed that there is no change in microchemical record of alluvial gold during transport (Chapman et al. 2005).

As for other ingredients, the presence of Fe, Cu, Bi, Se, Te is determined. Average iron content is 0.32%, and average copper content is 1.02 %. Other impurities such as Bi, Se, Te are underrepresented and in some aggregates they are even not present.

disintegrated. The size of the found gold aggregates ranges from 30 to about 600  $\mu\text{m}$ . Based on tests it was determined that gold aggregates commonly occur in irregular isometric form, in a round-spherical shape and in the shape of plates. The irregular shape is the most common.

Studies of the chemical composition showed that gold is characterized by high purity ranging from 750 to 996. Of all impurities, the silver content is the greatest ranging from <1 to 26.91 wt.%. As for other ingredients Fe, Cu, Bi, Se, Te have low content.

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## AIRBORNE ELECTROMAGNETIC SURVEYS OVER THE ARTANA ORE DEPOSITS IN KOSOVO

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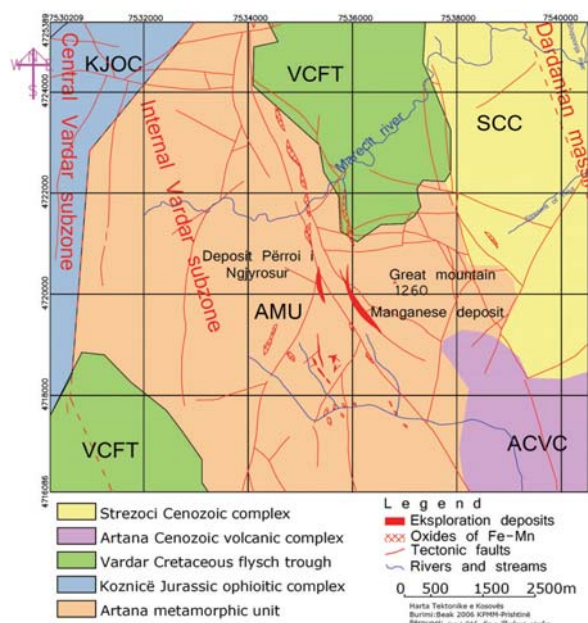
### Abstract

The Airborne electromagnetic methods (AEM) are used in Kosovo to locate conductors (i.e., sulfide ore deposits). The recording data of the second field electromagnetic waves using a four-frequency system (0.9 kHz, 3 kHz, 12 kHz and 25 kHz) and the calculation of the apparent resistivity  $\rho_a$  ( $\Omega m$ ) applied in the region of the Artane ore deposit, Kosovo, indicates that on the known deposits and in some other areas around, their apparent resistivity decreases. This decrease in apparent resistivity is explained by the presence of sulfide ore bodies which were treated as electromagnetic AE anomalies. This study reveals the existence of very consistent aerial geophysical anomalies in the known ore deposits, as well as to identify other anomalies in the studied region, which should be treated as possible potential in searching for new deposits of sulphides mineralization.

**Key words:** Aero Electro Magnetism (AEM), geophysical anomalies, Artane ore deposits, Kosovo

### The geological background of Artane region

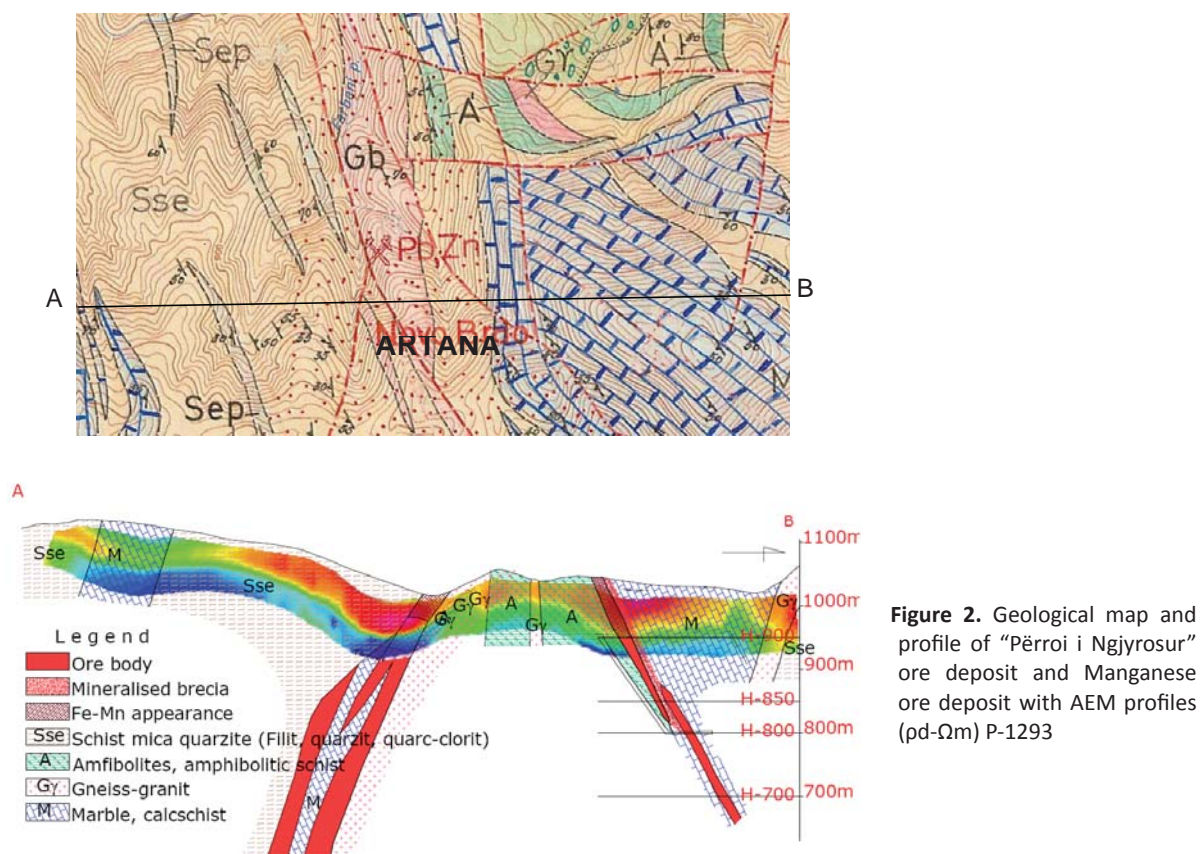
In the area of Artane, four ore deposits were known: “Vendburimi i Manganit”, “Përroi i Ngjyrosur”, “Kaltrina”, “Përroi i Thartë”. From geological point of view, the Artana ore deposits belong to the eastern part of Vardar tectonic zone which consists of Paleozoic metamorphic rocks (quartz schists, green schists, amphibolites, marbles and gneiss). Close to the ore deposits are found andesites and andesitic breccia of Tertiary age. In the area west of Artana, in the tectonic boundary, the metamorphic rocks are in contact with the Jurassic ultramafic rocks belonging to Vardar zone. In the north and south of Artana, in the tectonic contact, are lying Cretaceous deposits containing conglomerates, sandstones, marls, etc. The eastern part of Artana is built by Cenozoic deposits representing the Tertiary volcanism and lacustrine deposits, (Fetahaj and Shabani 2010)(Shabani 2010).



**Figure 1.** The tectonic map of Kosovo and the location of Artana ore deposits.

### Aerial electromagnetic surveys on the Artana ore deposits

The Aerial Geophysical survey of this region was carried out during 2006 including 47 flights with a length of 480 km. During the survey, the distance between the flights was 200 m. The data were collected during a flight with an aircraft having integrated digital devices for magnetic, electromagnetic and radiometric studies, through a flight at low altitude, at a nominal height of 30 m over the ground and with a speed of 60 m/s (Lahti 2006; Lahti et al. 2006; Airo et al. 2007). The purpose of this paper is the interpretation of some of the data extracted from aerial data and treatment of anomalies shown on deposits sulphite ores “Përroi i Ngjyrosur” and “Manganese old mine”. The electromagnetic data were performed by electromagnetic waves emitted by four types of frequencies (0.9 kHz, 3 kHz, 12 kHz and 25 kHz) and recorded the components data (component in phase and quadrature component) in the secondary aerelectromagnetic field. On the basis of this data collection was possible the calculation of



**Figure 2.** Geological map and profile of “Përroi i Ngjyrosur” ore deposit and Manganese ore deposit with AEM profiles (pd-Ωm) P-1293

the apparent resistivity  $pd$  ( $\Omega m$ ). The application of AEM waves with different frequencies was made to study the Earth on its depths (Huang et al. 1996; Suppala et al. 2005). The application of these types of frequencies made possible to study a depth of from approximately 30 m to 120 m. During the data treatment was noted that on the known ore deposits and in some areas around them, the apparent resistivity falls as a result of the presence of sulfur mineralization ore bodies, this decrease of the apparent resistivity was treated as electromagnetic anomalies AEM (A5 and A6).

### ANOMALY A5.

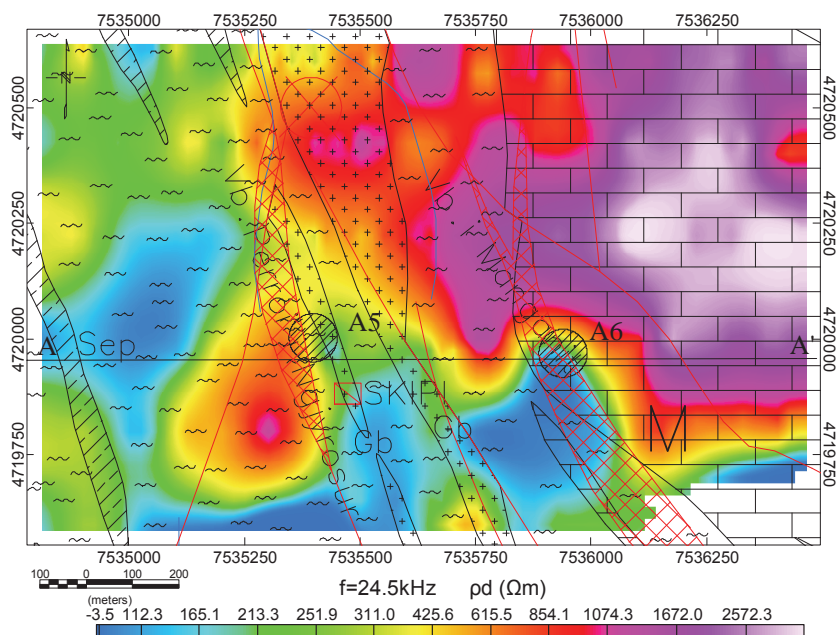
The A5 anomaly, “Përroi i Ngjyrosur” of Artana which is an sulphide ore deposit of Pb, Zn, Ag, Au, hydrothermal and metasomatic types, which is going to be exploited. The ore deposit is located between gneiss (Gb), on the floor and the argillaceous schists, phyllites (Sse), on the ceiling. Using electromagnetic waves (AEM) appears an anomaly ranging with the frequency of 3 kHz and strengths at 912 Hz. This ore deposit is covered at the flight lines taken from L- 1293 and L- 1294. The ore bodies of “Përroi i Ngjyrosur” are exposed to the surface in the form of oxides of Fe and Mn and they have a South –West dip angle, initially from

35°-45° and deeper over 65°. This is clear from the maps of the apparent resistivity and conductivity, as well as from the electromagnetic profiles of the apparent resistivity with four frequencies. During the application of the electromagnetic waves with frequencies of 12 kHz and 25 kHz, the resistivity varies from 77  $\Omega m$  to 211  $\Omega m$ , while the waves AEM with frequencies of 3 kHz and 912 kHz show that the apparent resistivity falls to 9  $\Omega m$ , indicating that the AEM waves are yet penetrating in the oxidized zone about 120 m depth. We have to mention that the intensity of the anomaly is higher in the western part (about 240 m) than in “Përroi i Ngjyrosur” ore deposit.

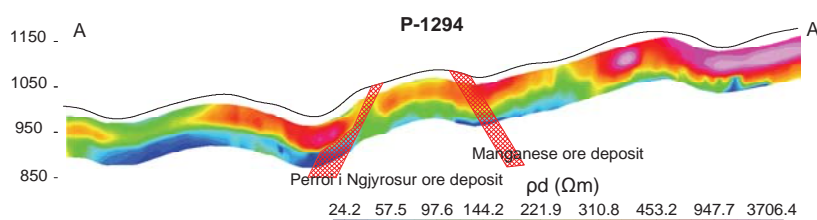
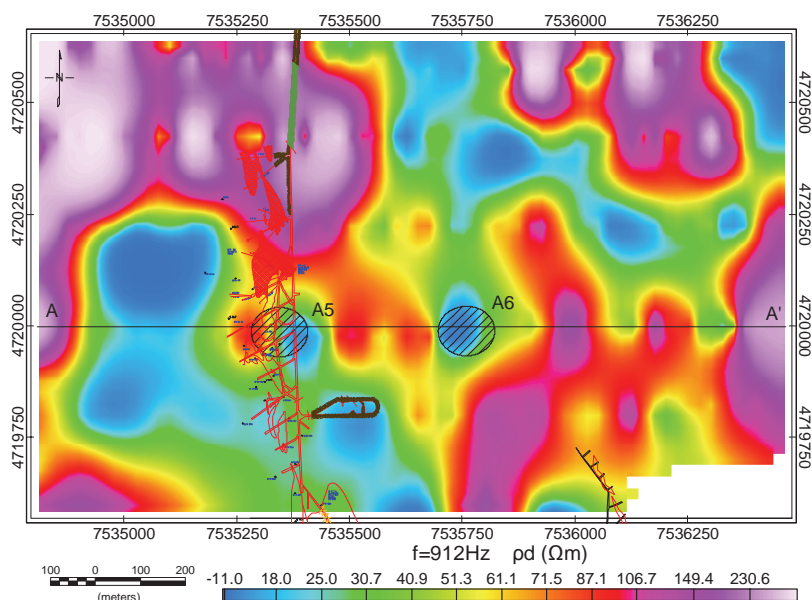
### Anomaly A6

The manganese ore deposit (the old mine) it is located at about 500 meters to the east of “Përroi i Ngjyrosur” ore deposit. The ore bodies are located between the amphibolites (A), on the floor and marble (M), on the ceiling and have a north- east dip angle around 60°. According to the aerial electromagnetic measurements AEM, this ore deposit shows clear anomalies at the frequencies of 3 kHz and 912 Hz. Also the northern part of the ore deposit shows a large size anomaly with very low apparent resistivity. The NNW-SSE





**Figure 3.** Map of  $pd$  ( $\Omega m$ ) and the geology of Artana ore deposits ( $f = 24.5kHz$ ).



**Figure 4.** Map and profile P1294 of apparent resistivity  $pd$  ( $\Omega m$ ) over the Artana ore deposits ( $f = 912Hz$ ).

extent of the anomaly is very consistent with the ore deposit extension. Using 25 kHz frequency, The A6 anomaly it is not visible, shows very high resistivity values, which means that the oxidized zone is a barrier to the passage of electricity. Meanwhile in 12 kHz frequency the penetration of electromagnetic waves is up to 60 m, the values of resistivities fall from 17  $\Omega m$  to 11  $\Omega m$ . In greater

depth, using 912 Hz frequency the values of the resistivity drops almost to 0  $\Omega m$ . Mentioning that the manganese oxides are in abundance >20 %, we think that on and close of the surface the ore bodies are in the form of oxides of Fe and Mn.

## Conclusions

AEM measurements can resolve conductivity variation at near surface over large area. The electric and magnetic susceptibility distributions can be used to interpret soil thickness, rock types, water systems and most important (show in this study) to interpret different kinds of conductive ore deposits. We have demonstrated that the decrease in apparent resistivity in the region of the Artane ore deposit, Kosovo is explained by the presence of sulfide ore bodies. This study show a very consistent aero-geophysical anomalies in the known ore bodies and we suggest to use other terrestrial (more precise) methods to check the others identified anomalies in the studied region, which should be treated as possible potential of new ore sulfide deposits.

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## AKÇATAŞ (HACİBEKTAŞ-NEVŞEHİR) LOW SULFIDATION TYPE EPITHERMAL SYSTEM: AU-Sb AND U MINERALIZATION IN CENTRAL ANATOLIA

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### Abstract

Granitoid hosted Akçataş epithermal system is located at 6 km SW of Hacibektaş and geologically at the southern part of Kırşehir Massif. Structurally controlled epithermal system is also located near the NW-SE trending and approximately 60 km long Salanda Fault. Host rock granitoid intrudes the metamorphic basement rocks and is overlain by sediments and basaltic flows at the top.

Au-Sb mineralization lies in brecciated zones and stockwork type quartz veins. U mineralization occurs as coatings in the outcrop of a breccia zone. The main ore minerals are stibnite, marcasite, pyrite, arsenopyrite, goethite, electrum, uraninite, zeunerite and torbernite. The hydrothermal solutions that originated the mineralization have also caused kaolinization, sericitization and silicification.

The study on fluid inclusions in barite and quartz minerals suggests that the homogenization temperature ranges of 88-352 °C and the salinities are 3.4-5.7 wt.% NaCl equivalent.

Akçataş is the first known Sb mineralization with Au and U in the same vein system in Central Anatolia. The data on the alteration types, metal content, mineralizations and fluid inclusions show that the Au-Sb mineralizations are the product of a low sulfidation type epithermal system occurred in an extensional regime. Secondary uranium mineralization, low Au content (max. 170 ppb) and antimony ochres found at the surface, are the products of a secondary oxidizing hydrothermal activity.

## THE ROLE OF LARGE-TONNAGE DEPOSITS IN THE INNOVATIVE DEVELOPMENT OF EXPLORATION

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### Abstract

The fast growth of global gold prices over the past two decades has boosted interest in the development of large-tonnage deposits with low metal contents. The rapid growth of gold mining in China, Australia, United States, Russia, Peru, Chile, Argentina, Ghana, Indonesia and Papua NewGuinea is largely related to the development of large-tonnage deposits. The world's gold-mining practices classify operating and operation-ready large-tonnage deposits into lateritic weathering crusts; gold-silver epithermal (HS-type) ores in volcanics; gold-(arsenic)-sulfide disseminated refractory ores with invisible gold in carbonate-terrigenous strata; impregnated and stockwork ores of gold-porphyry and gold-bearing copper-porphyry types; gold-sulfide-quartz ores in terrigenous strata and in green-stone belts and auriferous conglomerates. The scale of gold reserves in these deposit groups is such that we may speak about a new and previously unknown phenomenon in gold geology - a stable level of metal concentration (two orders of magnitude higher than its Clarke level) in various geological formations. Another important global trend is the quickest to develop large-tonnage gold deposits, which may conventionally be called "100 tonners." They helped China to increase its gold mining quickly and take the first place in the world. Largely due to such assets, gold mining is currently developing in Nevada and Utah (United States), West and East Africa, Russia, the Middle East, South Australia, and Brazil. Thus, in China, the commissioning period of a 100-ts deposit is two years on average. This happens especially quickly if heap leaching is used. Large-tonnage fields in Russia are primarily Sukhoi Log, Vernenskoe, and Golets Vysochaishi in Irkutsk area; Natalka in Magadan area; Olimpiada and Blagodatnoe in Krasnoyarsk area; Nezhdaninskoe in the Republic of Sakha (Yakutia) and Pioneer, Malomyr, Abyl in Amur area.

The development of large-tonnage deposits stimulated the innovative development of exploration in the world, largely increasing its efficiency. Innovative methods have helped and are helping to discover many new ore bodies. In regional scale prospecting for large-tonnage ore deposits of same types the ASTER space observing system (the result of NASA's cooperation with the Japanese Ministry of Economy, Trade, and Industry), has been used successfully since 2001 to survey remote and desert regions of West Africa, South and Central America, East Africa, Canada, Australia, Northeast Russia and Central Asia. Thus, the ASTER maps together with other geological, geophysical, and geochemical instruments are widely used at the stage of selecting an exploration area. At the prospecting and exploration stages, exploration drilling has started to play the main role. The special type of large-tonnage deposits stimulated the design of highly productive reverse circulation (RC) rigs. The new rigs, such as Explorac 220RC, can drill 750 m deep wells (the usual depth is up to 350 m). At present, RC drilling is widely used in world exploration practice, because it is fast, efficient and cheap compared to diamond core drilling. Field express analytics has been used widely during prospecting for large-tonnage deposits. The well reputed portable metal, soil and ore analyzers Delta Standard and Delta Premium can rapidly test for 60 elements, including precious, rare and rare earth metals. The involvement of many large-tonnage deposits in operation stimulated the creation and development of computer geoinformation systems and computer simulation. At present the world knows many such programs, like MapInfo, ArcView, Datamine, Micromine, Techbase, Geoblok, Autocad Map, and Surfer. They allow us to solve a wide complex of exploration and design problems that arise during the formation of mining enterprises.



## HYDROCARBON POTENTIAL FORMATIONS FROM BULGARIAN PART OF THRACE BASIN

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### Abstract

Thrace basin is one of the largest and the most productive hydrocarbon basins in Turkey. Major reservoir intervals are of Eocene, Oligocene or Miocene age and the hydrocarbons in these rocks are associated with both stratigraphic and structural traps. The geological and structural conditions in the SE part of Bulgaria are similar. It is supposed that the area under study is a NW "tail" of the Thrace basin.

The sediment complex in the central part of the basin is more than 9000 m thick while in most of the north-western part, behind Bulgarian border, the thickness of whole complex is around 2500 m. Nevertheless the sediments are thick enough to follow the same lithological units as in the deeper part of the basin. The last are very well correlated with ones behind Bulgarian border, where they exist with different names but with the same lithological and stratigraphic characteristics. In the Bulgarian part, these rocks express similar reservoir properties as in the hydrocarbon fields and along the areal of their distributions. The sandstone intervals of Clay-marl Formation which is analogue of one of the major reservoir units Oligocene Muchachir group, is characterised by a porosity between 9-25 % and a permeability of 2-6 mD.

The most hopeful seals could be the shaley intervals of the Terrigenous-limestone-shale Formation in Eocene sequence and shales and mudstones of Mezardere and Danismen formations analogue in Oligocene sequence. These intervals are characterised by good generation potential as well. Shaley intervals of Ceylan Formation possess source potential in Turkey. In the same intervals in the Bulgarian part of the basin, TOC attains 1.88 %. Oligocene Clay-marl Formation could be considered as an analogue of Mezardere Formation in the lower intervals and to Osmanchik and Danismen formations, in the upper interval.

Mezardere is characterised by TOC in the range of 0.5-1.6 %. The last TOC data for Clay-marl formation in Bulgarian part are 1.20-2.3 %.

**Key words:** Thrace basin, Bulgaria, formations, correlation

### Introduction

Thrace basin covers European part of Turkey, most NE part of Greece and SE part of Bulgaria. It is one of the largest hydrocarbon basins in Turkey (Huvas et al. 2007), where more than 11 gas and 3 oil fields were discovered. These hydrocarbon accumulations are associated with structural and stratigraphic traps in the clastic and carbonate reservoir rocks of the basin with Oligocene and Eocene ages. Since the year of the first discovery to nowadays, numerous studies on the rocks of the sedimentary complex in the Turkish part of the basin were performed. These results had been the reason for launching in 80's of the last century of oil and gas prospecting and exploration activities in the Bulgarian part of the basin. In this study we evaluate and analyse the potential hydrocarbon formations from the Bulgarian part of the basin and compare them with those from the Turkish part, based on the previous and actual data.

### Tectonic framework of Bulgarian part of the basin

In tectonic aspect, the studied area is situated in Madjarovo foreland depression (Fig. 1A) considered as Early-Palaeogene and formed on the intensively faulted eastern part of Rhodope massif (Yovchev 1971). The depression passes into large Thrace basin of NW Turkey to SSE and should be treated as a NW flank of this basin, which is indented deep in Rhodope massif. North the depression is bounded by the southern slopes of Sakar-Strandzha anticlinorium built of metamorphosed sedimentary rocks. To the WNW, the depression is limited by Harmanli monocline,

built of Precambrian metamorphic rocks. SW from the basin, the high-amplitude Imbredjecs anticline spreads on and is composed by of Upper-Eocene rock and complicated by intrusions. These tectonic units are complicated with elongated “channels” which probably performed the connection pathways for both big depressions: (i) East Thrace depression (basin) in Turkey where the Tertiary sedimentary section is up to 8-9 km thick; (ii) and, West Thrace depression in Bulgaria, where Paleogene-Neogene sequence is 1.5-2 km thick.

The most significant faulting in this foreland depression is Maritsa fault (suture, shear zone) – a tectonic element still disputable by dozen of authors (Yovchev 1971; Kozhuharov et al. 1995; Turgut and Eseller 2000; Radulov et al. 2007). Some of them (Yovchev 1971; Kozhuharov et al. 1995) treat it as three fault bundles – southern, along the northern slope of Imbredjec anticline, middle, along the southern slope of Sakar, and northern the Chirpan-Elhovo line and eastward. It is considered (Turgut and Eseller 2000) that the faults within the studied area should be connected to the Maritsa shear zone and its continuation as Terzili zone in Turkey.

### Lithostratigraphy of Bulgarian part of the Thrace basin

On the surface of the studied area rocks of different age and composition are outcrop. The fulfilled well investigations are in limited quantities and the deepest well reaches 1754 m total depth. The defined age of the basement is relative. In the

applied lithostratigraphic schemes, the following units for the region are defined (Kozhuharov et al. 1995) (Fig. 1B).

The basement rocks are represented by intensively metamorphosed rocks of high crystalline series. These are mainly Archean gneisses and schists, more than 800 m thick, outcropping in both mountains SW and N of the basin – East Rhodope and Sakar. Their presence in the foreland depression is presumed at depths below 3000 m. Paleozoic granite-porphyrries and granites outcrop in Harmanli monocline and southern slope of Sakar.

The low crystalline series are represented by slightly metamorphosed rocks of Triassic and Jurassic age, with preserved initial view or insignificantly altered. Lower Triassic series are represented by conglomerates and variously grained sandstones, often metamorphosed in quartzites and quartzitised sandstones with a thickness of about 300 m. The Middle Triassic series is built up by grey poorly marbled limestones and dolomitic marbles split by a number of calcite veinlets, the average thickness ranging from 80 to 150 m. The Lower-Middle Jurassic series outcrops are mapped NE and are represented by grey-green phillites with marble interbeds. The Upper Jurassic series were reached in the R-1 Svilengrad (Generalovo)

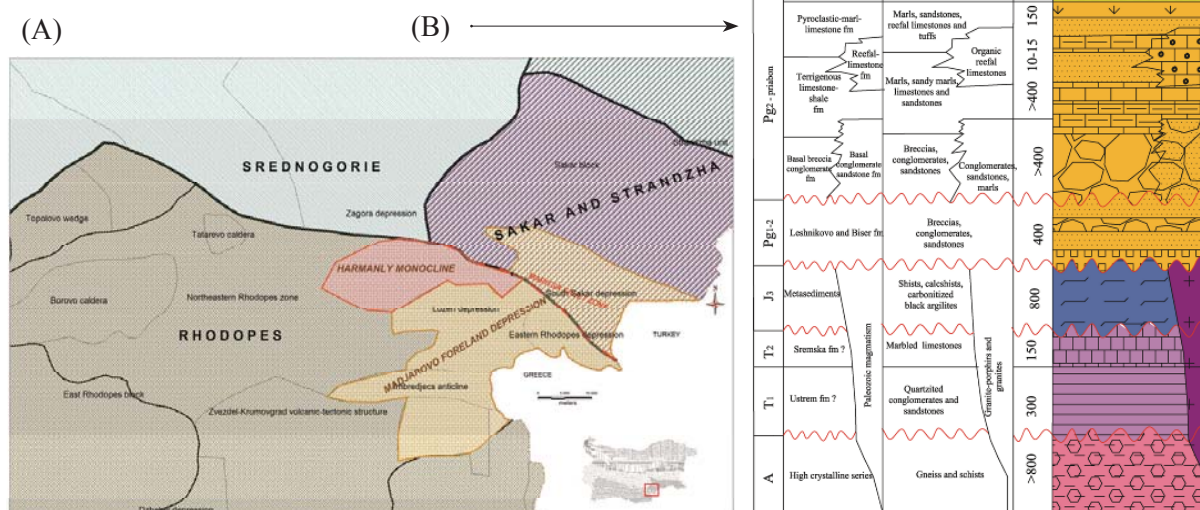


Figure 1. Tectonic scheme (A) and lithostratigraphy (B) of the area under study.

well where at TD were penetrated marbles, creystalline limestones, thin-bedded and shales – shaley schists and argillites. Towards the top of the Upper Jurassic series are subcropped grey to dark grey and variegated calcareous phillites, argillites, phillitized schists and calcschists (Tithonian). It is presumed that the thickness exceeds 800 m.

Paleocene-Eocene series outcrops in the western part of the depression and includes two formations – Biser and Leshnikovo. Biser formation overlies transgressively and discordantly the older rocks. It is built up by breccias, breccia-conglomerates and coarse sandstones on the top. The Biser Formation is covered by Leshnikovo Formation which is built up by alternation of thick-bedded sandstones, polygenetic conglomerates and shaley sandstones. Eocene sedimentary sequence unconformably overlies rocks of various lithology and age, and is split by tectonic disruptions. The Upper Eocene (Priabonian) rocks age are represented by informal lithostratigraphic units as follows: Basal breccia-conglomerate Formation; Basal conglomerate-sandstone Formation; Terrigenous-limestone-shale Formation; Reefal limestone Formation; Pyroclastic-marl-limestone Formation. The Oligocene series is represented by Clayey-marl Formation, subcropping in the region of R-1 Svilengrad well and to the east where it is represented by fresh water facies – alternation of shales, limy shales, marls, marly limestones, siltstones and sandstones. Westward of Svilengrad region, the Oligocene series is deposited in marine environment, with volcanics, represented by a thick tufaceous sequence at the base (alternations of calcareous sandstones, tufaceous sandstones, marls and limestones, calcareous marls, clayey tuffs and organogenic limestones), molasse sequence upward (sandstones, locally conglomerates) and rhyolitic tuffs and tuff-breccias locally distributed. In R-1 Svilengrad well are recognized Mezardere, Osmancik and Danismen formations of Muhacir Group. Neogene is represented by the Ahmatovo Formation covering almost all the area and consisting of coarse sandstones to conglomerates getting finer upward, with marls and limestones on the top. The Quaternary is represented by alluvial, proluvial and alluvial-talus sediments deposited in Maritsa river valley.

### Reservoir systems

From the above described lithostratigraphic units question of interest for oil and gas exploration is

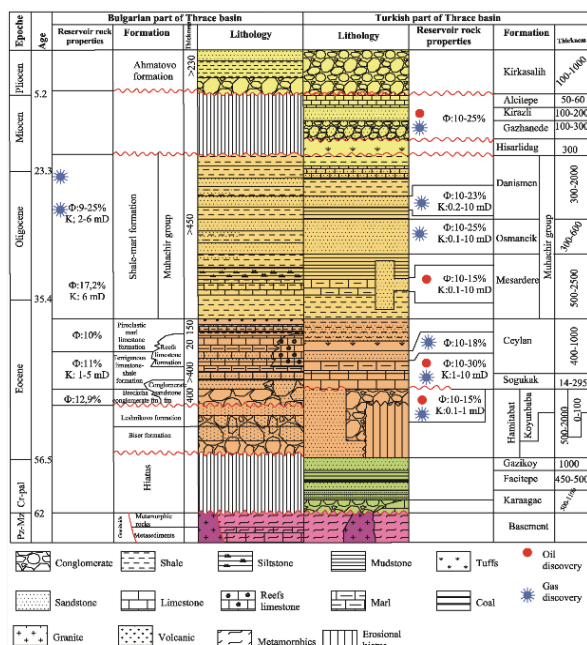
the sediment sequence with Tertiary age. In the Upper Eocene and in the Oligocene intervals (Fig. 2) two reservoir systems could be distinguished. In the Turkish part of the basin these intervals are the major reservoir systems for the hydrocarbon accumulations.

The lower part of Upper Eocene section is represented by the Basal breccia-conglomerate Formation caught in R-1 Svilengrad well. There, the open porosity reaches up to 12.9 %. The Basal breccia-conglomerate Formation is correlated to Koyunbaba Formation from the Turkish part of Thrace basin with 17 % porosity (Huvaz 2007). The Upper Eocene sequence continues upward with Terrigenous-limestone-shale Formation laterally passing to the north into the Basal conglomerate-sandstone Formation. Both formations are correlated to Ceylan Formation of Thrace basin. The sandstone from the base of Ceylan formation caught in R-1 Svilengrad well is characterized with porosity 11 % and 1.5 mD permeability. The Reefal limestone Formation is outcrops in the north of Svilengrad R-1 well but have not been caught in the well. It is correlated to Sogucak formation in Turkey, where it is characterized with porosity of 10-13 %. Such bioclastic limestones are shown at two levels – below Ceylan formation and at Mezardere/Osmancik boundary. In Svilengrad R-1 well and other shallow wells in Kapitan Andreevo area all lithostratigraphic units of Oligocene Muhacir Group – Mezardere, Osmancik and Danismen formations were identified. The sandstone reservoir in Bulgarian part correlating to Mezardere formation is characterized by good reservoir properties, namely porosity up to 17.2 % and permeability from 2.48 close to 6 mD. However, the main sandstone reservoirs here are in correlation with Osmancik Formation with porosity and permeability characteristics of 9–27.8 % and 1–6 mD, respectively. The upper Osmancik sandstone flowed gas 1270 m<sup>3</sup>/d at test in the case of Kapitan Andreevo C-3 well. The sandstone reservoir of Danismen Formation (Oligocene–Miocene) in the same well was tested in casing and flowed gas at rate of 870 m<sup>3</sup>/d. Porosity of Danismen sandstones in Turkey varies in the range of 15–25 %.

The most hopeful seals from the described reservoir systems could be shaley intervals of Terrigenous-limestone-shale formation in Eocene sequence and shales and mudstones of Mezardere and Danismen formations analogues in Oligocene



sequence. These intervals are characterised by good generation potential as well. Shaley intervals



**Figure 2.** Correlation of hydrocarbon potential formations from the both parts of Thrace basin.

of Ceylan formation possess source potential in Turkey. In the same intervals in the Bulgarian part of the basin TOC attains 1.88 %. Oligocene Clay-marl formation could be considered as an analogue of Mezardere formation in the lower intervals and of Osmanchik and Danismen formations in the upper interval. Mezardere is characterised by TOC in the range of 0.5 – 1.6 % (Huvas et al. 2007). The last RockEval TOC data measured for Clay-marl formation are in the range of 1.20 – 2.31 %.

## Conclusions

On the base of the present data it could be stated that in tectonic and lithological aspect it is easy to correlate sediment sections of the Thrace basin in Turkish and Bulgarian territories. Petro-physical parameters of the reservoirs and seals of the rocks in formations give us ground to assume that the main reservoirs could be in the upper Eocene or Oligocene clastic horizons. Good reservoir properties are expressed by the rocks of Terrigenous-limestone-shale formation, analogue of Ceylan, as well as sandy intervals of Clay-marl formation, which is analogue to formations of Muchachir group. The greatest seals development, as the main criteria for reservoir system formation, was observed in the shaley layers of Oligocene, and to a less extent, in the sequence of Upper Eocene. Shaley horizons from all sediment sequence demonstrate good potential for oil/gas generation as well.

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## GEOTHERMAL RESOURCES ON KOSOVO AND THEIR USE, IN THE FRAMEWORK OF THE COUNTRY ENERGETIC BALANCE

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### Introduction

Kosovo has the geothermal resources of a low enthalpy and mineral waters, new technologies of the direct use, which represent the base for a successfully application of modern integral and cascade use technologies, to achieve the economic effectiveness.

At the present, geothermal, hydrogeological, hydrochemical, biological and medical investigations and studies on thermal and mineral water resources are started in Kosovo. The aims of the new studies are to examine, demonstrate and disseminate the positive technical and financial aspects of transfer and utilization of innovative geothermal energy technologies in Kosovo. According to their results, will be selected the perspective level of the best geothermal areas in country, and will be start the investments.

### Geothermal regime

The geothermal regime of the Kosovo geological structures is conditioned by tectonics of the region, lithology of geological section, local thermal properties of the rocks and geological location. The geothermal field is characterized by a relatively low value of temperature in the Rrafshi Dukagjinit region. The temperature at 1000 meters depth varies from 25 to almost 30 °C. The temperature is 70-75 °C at the depth of 3000 meters. Going towards Prishtina, the temperature at 1000m depth vary from 30 to 40 °C, and 140 °C at 5000 m depth. Regional pattern of heat flow density in Kosova territory has two particularities: Firstly, minimal value of the heat flow is equal to 45-50 mW/m<sup>2</sup> in the Rrafshi Dukagjinit region. Secondly, toward north-east the heat flow density is increased to 90 mW/m<sup>2</sup>. The granites of the

crystalline basement, with the radiogenic heat generation, represent the heat source. Geothermal energy of low enthalpy resources is located in different areas of Kosova. Thermal waters, with temperatures that 50 °C, are of sulfate, sulfide, calcium, magnesium, hydrogen carbonate sodium methane type. Kosovo geothermal areas have different geologic and thermo-hydrogeological features.

### Directions for the direct use of geothermal energy of low enthalpy in Kosovo

The geothermal situation of low enthalpy in Kosova offers three possibilities for the direct use of geothermal waters energy.

Firstly, the Ground Heat can be used for space heating and cooling by Borehole Heat Exchanger-Geothermal Heat Pumps modern systems.

Secondly, thermal sources of low enthalpy and of maximal temperature up to 50 °C. Thermal waters of springs may be used in several ways, for a complex and cascade exploitation of this environmental friendly renewable energy, achieving an economic effectiveness:

1. Modern Hotel-SPA clinics for recreation, treatment of different diseases and hotels and tourism;
2. The hot water can be used also for heating of hotels, SPA and tourist centers, as well as for the preparation of sanitary hot water used there;
3. From thermal mineral waters it is possible to extract very useful chemical microelements.

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## INVENTORIZING TECTONIC ELEMENTS IN GEOLOGICAL MAPS AND 3D MODELS – PROBLEMS, CONCEPTS, SOLUTIONS

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### Abstract

The database structure of a structural framework system in a geological modeling project often works with dozens of faults and other types of tectonic elements. The database background in such projects has to deal with not only the unique identification and the spatial positioning of these objects, but many other aspects as well. The method to store geodynamic parameters or the order of magnitude of the objects is one of these aspects, and of course the naming system has to be worked out.

In 2012 a general xml-based database structure was worked out for storing field observations (Albert et al. 2012). This database aim to assist geologists who work with either the digital geological mapping systems or with traditional paper-map based mapping methods. The database can be realized as a kml-file which can be directly visualized on Google Earth/Map. The data collecting app called Geonucleus can be accessed freely with full functionalities for desktop users. This project showed that the flexible structure of an xml-file is very handy if the many aspects of a structural element are needed to be documented in details.

If we want to work with hundreds of faults, we should bear it in mind that either in a modeling environment or on a simple map we will have to recognize these elements. The recognition process for machines is based on a unique identifier, but for humans this key is rather useless. For a structural geologist the geodynamic parameters and the orientation tell the most about a geological structure. Compiling a tectonic map, cartographers usually use line symbols for these parameters, but in a 3D modeling environment we have to rely mostly on colors and names of entities. To provide a useful parameter for structural geologist a naming system was worked out years ago (Albert 2004), which was simplified and refined in recent studies.

Based on this system, and on the previous

experiences with xml-files, a geodatabase was built from the active fracture tectonics of the Carpathian Basin (Albert et al. 2014). In this project the names of the processed structural elements contain five different attributes: the type (i.e. fracture/ductile), the order of magnitude, the sureness, the geodynamic properties (e.g. compressional/extensional types) and the general orientation. For example the FT1u\_NS\_E name refers to an unsure first-order normal fault with sinistral component dipping towards the East.

This descriptive name system was handy to work with in large geodatabases and in 3D models, where the name attribute was easily displayed but the graphical line-symbols were not usable. This uniformed system was used to apply automatic work processes in geological modeling projects as well.

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## PROPOSAL FOR A TECTONIC DATABASE IN THE LIGHT OF THE EXISTING SOLUTIONS

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### Abstract

The tectonic features and movements are well-known phenomena in the field of geology since the beginning of the “scientifically aided” mining and architectural construction. They help us to recognize and determine the spatial and temporal distribution of the lithological formations. Despite these facts, the tectonic is somehow poorly documented content on the general purpose geological maps. Some fields of tectonics, such as the active faults or some distinguished geographical areas have their specialized and adequate techniques and computerized databases to describe the significant characteristics of a given fault.

So far, there have not been either a tectonic database of general purposes or a standardized registration procedure, with the help of which we would be able to describe all of the observed tectonic faults *internationally*. A tectonic database of general purposes would help us to identify all features uniquely and on this basis to cite each of them in the literature unambiguously. Empirical geological research would be more exact if the tectonic features that could be displayed on

maps and the sections were incorporated into a uniform database, ruled by a uniform system of criteria. It is quite common that the descriptions of the fractures contain some omissions that are so serious that the reader cannot “recreate” the thoughts and the decisions of the describer. In this case we lose important facts.

To avoid this deficiency we sketched up and present a simple model and a spatial database (geodatabase) scheme.

All databases have a crucial prerequisite: we should be able to identify all objects—all tectonic features—uniquely. This “unique identifier” could be derived from the coordinates of the primary observation point of a fault. This could be the basis of the above mentioned unambiguous citation of tectonic features. All tectonic phenomena could be treated like a “point” as an observation point, like a line as a strike and like a surface as three-dimensional surface caused by the given fault.

In this database it is *obligatory* to record the all the reasons behind the decisions with the help of a minimal system of criteria.

## Problems of integrating data of a complex fault zone into a database

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### Abstract

Recently several proposals (Albert 2005, Halmai & Konrád 2013, Maros 2014) have stressed the importance of creating tectonic databases, which should be built following a uniform system of criteria, including the format of storing fault data and the required attributes. Before implementing such databases, the proposals should be tested on existing fault systems, the problems identified and the proposed plans improved.

The Mecsek Dislocation Zone (MDZ) in the SW Pannonian Basin is a major strike-slip-dominated fault zone within the Tisza Tectonic Unit. It is one of the most complex and best-exposed dislocation zones in the basin. Studied for decades, it offers a valuable testing site for a pilot database.

The MDZ bounds the Mecsek Mts. in the south and extends further for long distances both towards the NE and the W. In the basement it separates and/or dissects Paleozoic granitoid vs. gneiss and micaschist dominated units, overlain by various thicknesses of Permian to Cretaceous strata. The zone itself is built up of heavily tectonised tracks of basement rocks. Most of the basement in the zone is covered by Cenozoic sediments with thicknesses approaching even 1 km, thus the exact location of individual faults is usually only known in a narrow zone along the mountain front. The MDZ experienced multi-phase deformation, with strike-slip movement being dominant during the Paleozoic, transpressional, strike-slip or transtensional kinematics in the Cretaceous to (Middle) Miocene and compression in the Late Neogene to Quaternary.

In this case study observations of faults are considered on the outcrop (metre) scale and higher, from the aspect of including them into a tectonic database. The examination of fault data was carried out at two scales, with emphasis on the field mapping scale. In the first case the study area was a few kilometres long, covering the best-

exposed segment of the MDZ within the city of Pécs, where rocks of highly varied lithologies and ages are juxtaposed. Here we have a detailed knowledge about the structure of the dislocation zone, therefore faults are best mapped and displayed at scales of 1:5000 to 1:10000. In the second case we considered the known part of the MDZ west of the Danube, which is nearly 100 km long, fitting to map scales 1:100000 or lower.

Data on fault geometries were derived from outcrops, boreholes and geophysical profiles and also indirectly, from cross-sections constructed across the fault zone. The main challenges of entering fault data into a database concerned the definition of the boundaries of the fault zone, the definition of the geometric entities, e.g. the fault arrays to be grouped as one database entity or the fault segments, and the handling of the multi-phase reactivation of the fault system, especially in the case of the master faults. A future, more complex database must address and tackle these problems.

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## FAULT VS DATABASE CONSIDERATIONS AT DIFFERENT SCALES, CASE STUDIES FROM HUNGARY

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### Abstract

The future elaboration of a brittle tectonic database will be proposed for the Alpine-Carpathian-Dinaric realm. Because of the difficulties in correlation of the tectonic planes and their changing behaviour in time, there are some key questions to be answered in connection with tectonic planes and databases. (1) The unique identification methods and algorithms of the planes; (2) the correlation possibilities and methods of tectonic planes, namely what structural networks can be considered as a single database element on different scales; (3) the handling of the varying spatial properties of the planes in the database; (4) the handling of the rejuvenation events that change spatial properties and relative movements.

Based on case studies from the tectonic research connected to the disposal of medium and low level radioactive waste in the Mórág region in SW Hungary (National Repository of Radioactive Waste, Bataapáti) we propose answers and solutions for these problems. In the frame of the exploration of the case study area detailed tectonic mapping in outcrops, core logging of more than 5000 m drillhole cores, nearly 5500 m underground tunnel and another several thousand m borehole exploration, starting from the tunnels, took place. The structural data were collected on different scales, from core scale (dm) to open pit mine scale (10 metres). The sampling of the planes were oriented at all scales. With borehole cores a core scanning method (ImaGeo Corescanner) had been developed. With the help of this equipment, a very detailed geological evaluation was produced on the cores and the data were oriented based on geophysical borehole measurements (BHTV). Nearly 100,000 individual, oriented fracture planes, infillings and slickensides have been described (Maros et al. 2004). For the underground research a unique documentation equipment (ImaGeo Robot) had been developed. With the help of this equipment, the geological mapping of all tunnel faces (2546) and associated mantles along the entire 5362 m length of the tunnels was executed. As part of the in situ drawing and tabular documentation the 3D photomontage of the face and the associated mantle section was composed.

On the top of the brittle structural hierarchy there are fault zones (Maros et al. 2009). They are generally

steep (60–90°), their main strikes are NE–SW, E–W, (N)NW–(S)SE and more rarely N–S. The most significant (thicker than 5 m, clay-gouge-bearing fault zones), mostly NE–SW and approximately E–W striking fault zones appear about 500 m from one another according to the most reliable data source, the tunnel mapping, while the distance of the less important zones from one another is about 50–100 m. The evolution of the zones was basically determined by the fluids that got in and flew in the granite body. The architecture of the fault zones, individual fractures and slickenlines could be described by a succession of oblique dextral and sinistral shear zone events combined with rotations deduced from paleomagnetic measurements. The time sequence of the events begins in the lower Carboniferous (magmatic and ductile stress fields), there were events in the Triassic, Jurassic and Cretaceous (K/Ar measurements from fault gouges), probably in the Paleogene and surely in the Neogene till recent times.

Based on the consequences of the case study results, (1) we agree with Halmai & Konrád (2013) about a coordinate-based identification method; we propose (2) different database levels on different scales, connected loosely to each other; (3) we propose building a 3D model database, because of the unambiguous identification of tectonic surfaces having different dip properties and different cuttings on different topographic levels. The most difficult problem to solve is the (4) handling of the rejuvenation events in the database. In the case of different sense of movements on the same fault plane, they can be recorded as versions or aliases of the same database record. A partly new plane originated during rejuvenation should be considered as a new record, affiliated from a previous fault plane.

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## ACOMPILATION OF TECTONIC UNITS OF THE ALPINE COLLISION ZONE BETWEEN ALPS AND WESTERN TURKEY

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Correlating tectonic units between the Alps and Western Turkey allows discussing along-strike similarities and differences of the Eastern Alpine-Mediterranean orogen. To this goal we decided to remove post-tectonic basin fills, covering large parts of the Eastern Alpine-Mediterranean orogen, and in the case of the Rhodopes, large volumes presently occupied by post-tectonic plutons. This results in the disadvantage that the location of tectonic boundaries occasionally remains speculative. On the other hand our approach has two major advantages: (1) it allows for superimposing additional information, such as e.g., post-tectonic basins, manifestations of magmatic activity, location of ore deposits, onto a coherent tectonic framework and (2) for outlining the following major features of the Eastern Alpine-Mediterranean orogen:

1. Dinarides-Hellenides, Anatolides and Taurides are orogens of opposite subduction polarity with respect to Alps and Carpathians. The polarity switches across the Mid-Hungarian fault zone, a suspected former trench-trench transform fault.

2. The Dinarides-Hellenides-Taurides consist of nappes detached from the Adriatic-Tauride continental margin, separated from Africa by the southern branch of Neotethys, during Cretaceous and Cenozoic orogeny. Internal units (e.g., Jadar-Kopaonik, Drina-Ivanjica, Pelagonia, Tavsanli and Ören-Afyon zones, Lycian nappes) form composite nappes rather than continental terranes, passively carrying ophiolites obducted in the latest Jurassic–earliest Cretaceous (in the case of the Dinarides-Hellenides) and during Late Cretaceous times (in the case of W- Turkey) on top of the Adriatic-Tauride margin successions.

4. Ophiolites on top of composite nappes are not oceanic sutures. They root in the northern branch

of the Neotethys ocean that started closing during obduction. Suturing between Adria-Taurides and Europe-Pontides occurred in the latest Cretaceous along the more internal Sava-Izmir-Ankara suture Zone.

5. Obducted ophiolites are confined to between the Dinarides and Western Turkey. By contrast, in the Alps and Carpathians oceanic units occur invariably within accretionary prisms and suture zones.

6. Important lateral changes also concern the present-day lithospheric configuration. In the Dinarides, the Adriatic lithospheric slab can only be traced down to c. 200 km depth. Below the Aegean Sea, >2100 km of coherent slab are present, indicating long-lasting subduction of lithosphere that probably initiated in Mid-Cretaceous times.

7. The enigmatic Rhodopian orogen is interpreted as a giant core complex that became exhumed in Late Eocene and Miocene below the Carpatho-Balkan orogen, the Serbomacedonian "Massif" and the Circum-Rhodope Unit. Its tectonic position is similar to, but not identical, with that of the Sakarya Zone of the Pontides. The latter preserves the westernmost relics of the Paleotethys suture.

This yet unpublished map extends an earlier compilation by Schmid et al. (2008) into the southern Balkan Peninsula, the Aegean and Western Turkey. The current draft of this map is freely available from the first author and comments are welcome.

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## X-RAY MICROSCOPY WITH SMALL/WIDE X-RAY SCATTERING (SAXS-WAXS) CONTRAST.

Altamura D<sup>1</sup>

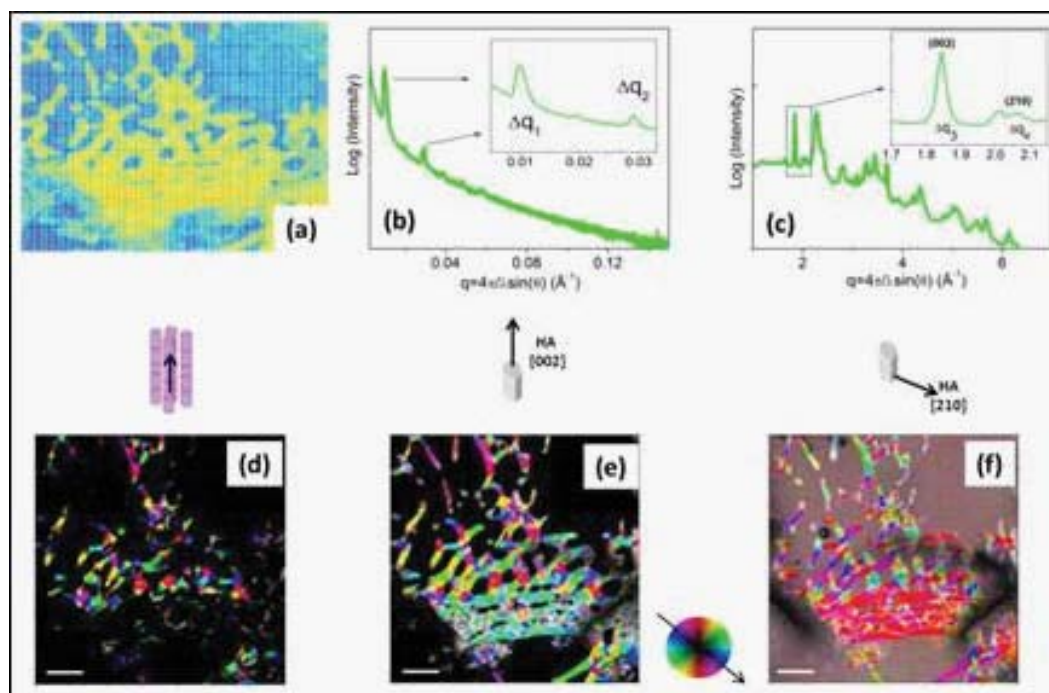
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The emergence of ultra-brilliant synchrotron photon sources and efficient x-ray focusing optics (mainly Kirkpatrick-Baez, mirrors, zone plates, and compound refractive optics) have opened unprecedented opportunities in microscopy techniques, based on hard X-rays, to analyze solid, soft and liquid matter. Although synchrotron light sources are unique for brilliance and available beam spot to investigate the structure of matter, the advent of novel superBright laboratory X-ray microsources allowed the development of laboratory facilities, showing relevant potentialities for a detailed material analyses in ex-situ experiments [1,2,3]. Indeed, such micro-sources, used in combination with X-ray scattering techniques (Small and Wide Angle X-ray scattering (SAXS/WAXS)), proved to be efficient in probing matter at different length

scales providing a structural, microstructural and morphological characterization of the specimens in a non-invasive way, with nanometer (SAXS) and atomic (WAXS) resolution.

Here a brief introduction to the scanning diffractive microscopy with SAXS/WAXS contrast will be given along with relevant examples in biomedical science:

- residues of exosomes' drops from healthy epithelial colon cell line and colorectal cancer cells [4]
- collagen/human elastin artificial scaffolds developed for vascular tissue engineering applications [5]
- coxarthrosis-affected bone biopsies taken from patients, aged 62–87 years, during hip prosthesis implant surgery [6]



**Figure 1.** COXARTHROSIS- AFFECTED BONE BIOPSY: (a) Two- dimensional scanning SAXS data, with each pixel containing a two- dimensional SAXS frame. (b) An azimuthally integrated SAXS profile, with a zoom on the first meridional reflection of collagen in the inset. (c) An azimuthally integrated WAXS profile, with a zoom of the 002 and 210 reflections of HA in the inset. (d) Two-dimensional SAXS microscopy mapping the first meridional reflection of. (e) Two-dimensional WAXS microscopy mapping the 002 peak of the HA component; ( f ) Two-dimensional WAXS microscopy mapping the 210 peak of the HA component. The scale bar length in the microscopy images is 1 mm. The color wheel designates the SAXS orientation for each pixel of the maps in (d), (e) and ( f ). Reprinted from C. Giannini et al, J. Appl. Cryst. 47 110-17 (2014)

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## POWDER X-RAY DIFFRACTION: THEORY AND APPLICATIONS

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The interpretation of powder diffraction pattern is not straightforward: peaks corresponding to different diffraction effects systematically and/or casually overlap; the background is often difficult to be evaluated; the non-random distribution of crystallites can produce preferred orientation effect. As a consequence, the experimental diffraction intensity cannot be accurately estimated. This problem limits all the steps of the structure solution process [1].

Up to twenty-five years ago, the role of powder diffraction was relegated to studies of qualitative and quantitative analysis. Nowadays powder technique is widely adopted for the characterization of new materials: organic, inorganic, metallorganic, biological, pharmaceutical. Such a progress depends on the advances in computing power and experimental equipment as well as the development of innovative theories, methodologies and computing programs aiming at overcoming the typical problems of powder solution: peak overlap, background estimate, preferred orientation occurrence. The scope of modern research in powder diffraction is to attain structure solution in a way as possible as automatic, efficient and fast. In spite of great improvement, powder solution is still a challenge.

EXPO2013 is a well-known computer program devoted to structure solution of small molecules by powder diffraction data and able to automatically perform [2]:

- a) cell parameters determination;
- b) space group identification;

c) extraction of the integrated diffraction intensities from the experimental profile and structure solution working in the reciprocal space;

Direct Methods are applied for solving the phase problem and providing the electron density map chemically interpreted. Then the optimization of the map, by using procedures combining Fourier transform calculations and weighted least squares, is carried out.

- d) structure solution working in the direct space;

The solution in direct space (effective in case of organic compound) can be alternatively applied to the solution in reciprocal space, in particular when the quality of the experimental data and/or the structure complexity prevent for estimating reliably the integrated intensities extracted from the experimental profile. In this case, a casual structure model (compatible with the expected molecular geometry) is considered and driven towards the correct solution by Simulated Annealing based technique.

- e) crystal structure refinement by the Rietveld method.

The main solution strategies of EXPO2013 and examples of successful structure solutions are reported.

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## ATOMIC RESOLUTION ELECTRON MICROSCOPY METHODS IN THE STUDY OF INORGANIC MATTER

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Transmission electron microscopy (TEM) enables to obtain atomic resolution information on specimen morphology, crystal structure, chemistry, electronic structure and magnetic properties. Furthermore, as the electron probe can be focused on sub-ångström areas, it enables to achieve information from extremely small volume of a specimen.

The features of TEM equipment enable to obtain at the same time images and diffraction patterns of the

specimen, tuning the illumination condition and the experiment geometry to highlight the features to be studied (Fig. 1).

The combination of electron diffraction and atomic resolution electron microscopy, allowing

the measurement of diffracted intensities but also phases, combined with crystallographic oriented methods results in electron crystallography, which represents a powerful and fascinating tool for structure analysis<sup>1</sup>. Here we will show some examples of how electron diffraction obtained in different electron optical geometries can be used to study the crystal structure. Moreover we will show how electron diffraction and atomic resolution phase contrast electron images can be used in synergy to achieve detailed crystallographic information on single nano-particles of inorganic materials shedding light also on the crystallography of disordered, partially disordered or defective material systems.

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 – Oxford, New York (2012)

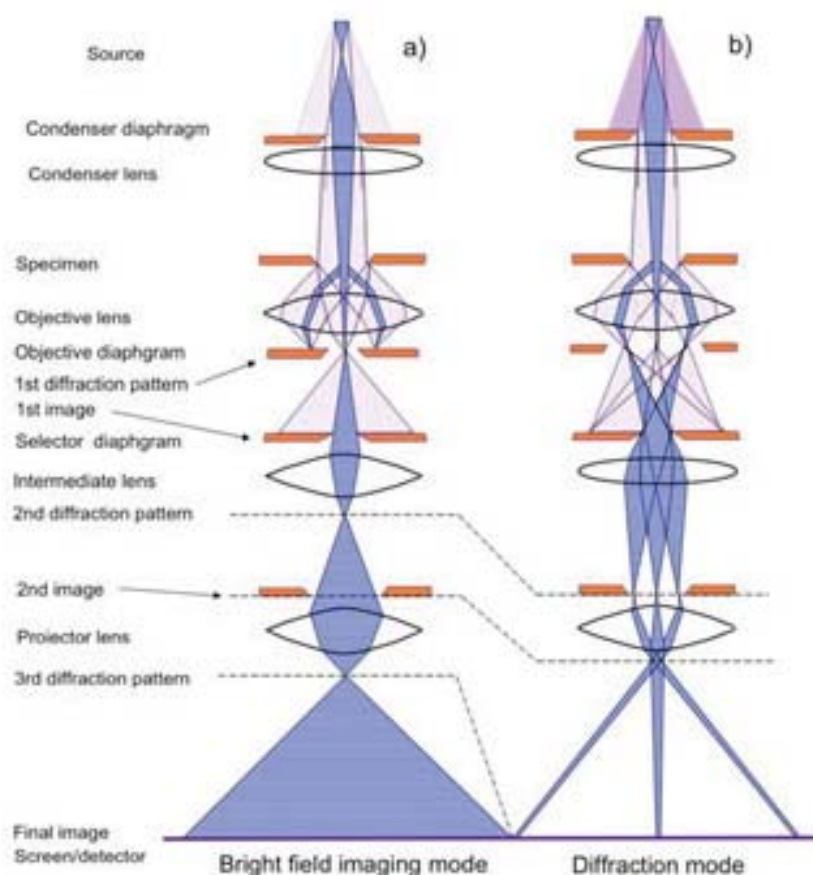


Figure 1: Schematic layout of a TEM operated in imaging (left) and in diffraction (right) mode respectively

## ONE HUNDRED YEARS OF CRYSTALLOGRAPHY

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In April 1912, the physicist Max von Laue, with the collaboration of Walter Friedrich y Paul Knipping, discovered the effect of diffraction of X-rays by a crystal of copper sulphate. The results of this experiment evidenced simultaneously (i) the undulatory characteristics of X-rays - consisting of electromagnetic waves such as visible light but with much shorter wavelengths - and (ii) the periodic nature of crystalline structures

- composed of atoms with inter-atomic distances comparable to the wavelength of X-rays. Two years later, in

1914, William Henry and William Lawrence Bragg (father and son) determined the first structure of a crystalline material (sodium chloride) by means of X-ray diffraction. For these important discoveries, von Laue and the Bragg's received the Nobel Prize in Physics in 1914 and 1915, respectively. Later on the structures of many other crystals and more complex materials were determined by means of the same technique, thus allowing for a better understanding of their properties. Crystallographers have also significantly contributed to the discovery of a number of novel materials with many important applications to industry and medicine.

The first determination of an atomic structure using X-ray diffraction in 1914 is considered to be the initial milestone of Crystallography, which was from then continuously developing until nowadays. Among many important achievements in the research field of Crystallography during the last 100 years, a few of them, listed below, were selected and will be briefly described:

-First use of the small-angle X-ray scattering technique, by André Guinier, in 1939, which explained the observed variations in mechanical properties of aluminium alloys, of paramount importance for aeronautical industry.

-First determination of the structure of globular proteins of great biological importance, by John Kendrew and Max Perutz (1962 Nobel laureates in Chemistry).

-Determination of the structure of the

deoxyribonucleic acid (DNA), a nucleic acid that carries the genetic

information in the cells and is capable of self-replication, by Francis Crick, James Watson and Maurice

Wilkinson (1962 Nobel laureates in Medicine).

-Discovery and physical characterization of graphene, which consists of a two-dimensional graphite single layer, by Andre Geim and Konstantin Novoselov (2010 Nobel laureates in Physics).

-Discovery of the quasi-crystals, novel materials with a totally unexpected structure, by Dan Schettman (2011

Nobel laureate in Chemistry).

This presentation will also describe the main features of the X-ray sources used in X-ray diffraction experiments over the last 100 years: (i) X-ray generators equipped with Coolidge tubes, in operation from

1915 and still been used nowadays in many laboratories of physics, chemistry, biology and geology, among

others, (ii) high intensity synchrotron-based X-ray beam lines, in most cases installed at national laboratories, from 1970 circa, and (iii) X-ray lasers that yield very short photon pulses, only available nowadays in a few laboratories around the world, which allowed for, in 2011, the first determination of a (extremely short) time resolved atomic structure of a protein nanocrystal.

After a century lasted from the first determination of an atomic structure in 1914, 2014 was declared by

UNESCO to be the International Year of Crystallography. In order to commemorate this centennial, the International Union of Crystallography is organizing many activities (workshops, schools, talks, competitions, etc), at different levels and open to scientists, students and other interested people. The whole program of events to be held all around the world is available at the [www.iycr2014.org](http://www.iycr2014.org) webpage.

## BASIC ASPECTS OF CRYSTALLOGRAPHY

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This presentation describes (i) the relevant features of the structures of different types of materials, and (ii) the basic theory of X-ray diffraction and scattering applied to the determination of the structure of materials. The talk will include the following topics:

Structure of perfect crystals and crystal symmetry. Description of crystal structures. Point lattices and atomic basis. Bravais lattices. Unit cells. Crystallographic planes and directions. Miller indexes. Stereographic projection.

X-ray diffraction by single crystals. Bragg equation. General mathematical description of the X-ray diffraction amplitude produced by perfect

crystals. Atomic scattering factor. Structure factor. The phase problem. Reciprocal lattice. Geometrical Ewald construction. Anomalous scattering.

Crystal defects. Nanomaterials. Diffuse X-ray scattering. X-ray diffraction by small crystals. X-ray scattering by imperfect crystals.

Small-angle X-ray scattering produced by nanoparticles embedded in homogeneous matrices. Small-angle scattering at grazing incidence by nano-heterogeneous thin films. X-ray reflectivity of surfaces and thin films.

Experimental instruments: Single crystal and powder X-ray diffractometers, and small-angle scattering and reflectivity setups.



## CRYSTALLOGRAPHY AND THE PHASE PROBLEM: FROM SMALL TO MACROMOLECULES

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The phase problem is notorious in x-ray crystallography. The x-ray detector can only record intensities but not phases of the electromagnetic waves. Each reflection on the diffraction pattern or structure factor corresponds to a wave consisting of an amplitude and a phase. The amplitude is easily calculated by taking the square root of the intensity, but the phase is lost during the data collection. However, the phases contain vital information for the determination of the electron density distribution in the crystal.

Crystal structure determination, especially for macromolecules, via X-ray crystallography is still a complicate multi-step process which involves the availability of different types of data (e.g., diffraction data at atomic resolution, or isomorphous derivative data, or data affected

by anomalous dispersion effects, or a molecular model suitable for molecular replacement), and the combination of different tools (e.g., density modification techniques, efficient crystallographic FFT routines, same probabilistic approaches for substructure determination and for subsequent phase extension, restrained least squares procedures). There is a large ensemble of programs which are in use of the crystallographic community: their combinations into integrated program packages [e.g., AUTO-RICKSHAW (Panjikar et al., 2005; AUTOSHARP (Blanc et al., 2000), BnP (Weeks et al., 2001), CCP4i (Potterton et al., 2003), SOLVE-RESOLVE (Terwilliger, 2000)] have considerably advanced the automation and reduced the human intervention in the structure determination process.

## **CYCLICITY OF THE UPPER CRETACEOUS APULIAN PLATFORM CARBONATES (LLOGARA SECTION, ALBANIA)**

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The Llogara section, situated on the Karaburuni Peninsula in Albania, consists of a complete section of Upper Cretaceous platform carbonates. These carbonates constitute a sedimentary record of the Apulian carbonate platform on its eastern side, and consist of a succession of numerous peritidal to subtidal small-scale sequences. A detailed sedimentological, diagenetic and petrophysical analysis has been carried out on six different intervals, each of them representative of one of six types of shallowing-upwards sequences. Main objective is to unravel the cyclicity of these platform carbonates, expressed in their sedimentological, diagenetic and petrophysical characteristics. Sedimentology, diagenesis and petrophysics have been characterized, mainly based on microscopic observations (Classical Microscopy, Fluorescence Microscopy, Cold Cathodoluminescence and Scanning Electron Microscopy). Mercury Injection Porosimetry (MIP) has been carried out to assess evolution of the porosity. Petrographical observations several phases of diagenesis: (1) early diagenesis evidenced by the presence of rhombohedral molds of small dolomite crystals scattered throughout

the matrix; (2) early to late diagenesis evidenced by pore-lining and -occluding equant to blocky calcite cements recrystallization of micritic matrix; (3) burial diagenesis evidenced by layer-parallel stylolites (LPS); and (4) late diagenesis evidenced by at least two generations of calcite veins. Diagenesis to be closely related to sedimentology: in general facies at the top of each small-scale sequence have been affected more by diagenesis than those at the bottom. This could suggest that diagenesis is related to meteoric influence during emersive phases at the end of each small-scale sequence. MIP results show that predictability of porosity for each lithofacies is good. A general trend of decreasing porosity towards the top of each small-scale sequence is observed. This corresponds with an early diagenetic overprint affecting the top of the sequences, resulting in the destruction of porosity. These observations highlight the cyclicity and interdependence of sedimentology, diagenesis and petrophysics of the studied section.

## **SEDIMENTARY EVOLUTION, FACIES AND GEOMETRY OF THE APULIAN CARBONATE PLATFORM DURING UPPER CRETACEOUS IN SOUTH ALBANIA**

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The sedimentary system including the Apulian carbonate platform and the Ionian Basin in south Albania provide an excellent example of sedimentation transfer system from carbonate platform deposition to gravity slope re-sedimentation. It offers a good analogue to understand processes controlling the basin infill, giving perspectives for hydrocarbon exploration. The Apulian platform crops out on both sides of the Adriatic Sea. Many studies addressed the sedimentary evolution of Apulia during Upper Cretaceous on its western side (the Italian side). However, none have been issued on its easternmost side. In Albania, the Karaburuni peninsula exposes the whole Upper Cretaceous succession up to the Paleocene. Investigations have been carried out in order to describe this section in detail along the Llogara mountain pass. Eleven lithofacies are identified along the 1500 meters of the Upper Cretaceous section. They evidence a wide range of depositional settings. Intertidal to supratidal conditions are highlighted by a broad spectrum of microbial laminae and thin layers with micro-breccia, emphasizing subaerial exposures. Subtidal ramp-like depositional settings are evidenced with both floatstone and in-growth-position rudists-rich intervals. Proximal-slope deposits, documented by large scale slump-like Mass Transport Complex (MTC), are exposed as successive thick (20 to 50 meters) chaotic layers at the top of the succession.

A precise onfield sedimentary study is supported by paleontological stratigraphy and Strontium Isotope Stratigraphy. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the carbonates were converted to numerical ages using the LOWESS look-up table version 4:08/04. These analytical methods are carried out in order to highlight the transitional relations between these lithofacies as well as the timing of deposition. The lithofacies are arranged in short-track sequences, reflecting high-frequency sea-level fluctuations and allowing paleo-environmental reconstitutions. Early and late diagenetic processes affecting carbonates allowed evidencing the boundaries of peritidal to subtidal cycles by characterizing subaerial exposures, showing a rhythmicity within the carbonate deposits. The carbonate succession, exemplified by variations in terms of facies and thickness, document a transitional evolution. From shallow water conditions during Cenomanian, characterized by peritidal lithofacies settings, the system gradually evolves towards a subtidal shelf setting. The latter is evidenced by (mainly) radiolitic floatstones to boundstones during the Senonian. The top of the section is affected by large-scale slump-like MTC, reflecting major destabilizations. The latter clearly record regional tectonic events, also reported for the same period in other peri-adriatic locations. These destabilizations mark a brutal change in the sedimentation processes, from platform sedimentation to proximal-slope re-sedimentation.

## UPPER CRETACEOUS CARBONATE GRAVITY-FLOW DEPOSITS IN SOUTH ALBANIA: LITHOFACIES, SEQUENCES AND MEGA-STRUCTURES, AN INTEGRATED OVERVIEW

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Being part of the NNW-SSE structural Ionian fold-and-thrust belt, the Upper Cretaceous carbonate deposits of the Ionian Basin expose a unique example of a gravity-flow system. Sediment input derived from the Apulian carbonate platform to the west, document a wide range of depositional processes building up the Upper Cretaceous sedimentary architecture. Our data provide a detailed view of the facies diversity. From inversely-graded coarse-grained decimeter-size clasts to finely grained laminated facies, a wide range of facies are documented, reflecting a wide diversity of depositional processes. Based on field observations and published studies on gravity-flow deposits, a number of typical stacking facies

patterns were identified.

They form carbonate sequences and document the composite nature of carbonate gravity-flow deposits. Large-scale slump deformations make up thick packages during the Maastrichtian. These mega-structures document a wide range of geometric features, allowing an assessment of type and degree of the soft-sediment deformation. Integrated in a three-scale classification (facies, sequences, and megastructures), the carbonate gravity system of south Albania can be described accurately regarding the settling of gravity-flow deposits and their synsedimentary deformations.



## NEW DATA ABOUT SINEMURIAN CARBONATE CONSTRUCTIONS OF NZALA (CENTRAL HIGH ATLAS, MOROCCO)

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The cartographic, stratigraphic, anatomic, and biosedimentary integrated study of the carbonate constructions located on the northern part of the Nzala Liassic series allow us to propose a new interpretation these constructions and their geological history.

The cartography of the bioconstructed unit was carried out at an appropriate scale to describe its geometric characteristics. The elaborated map shows a geometric irregularity of the top of the bioconstructed episode. This feature proves a diachronic “slaughter”. The geological timing of the standard section carried out by Chafiki (2004), on the left part of Oued Nzala, allowed the sketching of isochrones, which are continuous and visible within the geographic space. It shows that these monticules are quite evident in the Lower Sinemurian-Upper Sinemurian transition. They locally grow in the Upper Sinemurian and disappear at the bottom of the Lower Carixian.

The anatomic and biosedimentologic study allowed the distinction between three different sets:

- a lower set (25 m) where the carbonate monticules are simple shaped and small sized boundstones with silicate sponges;
- a medium set (35 m) which shows complex

shaped and big sized constructions including sponges and thrombolites.

- an upper set (50 m), massive and less developed. It consists of an arrangement of lense structures of metric width and decametric extension where the thrombolites and sponges are very rare. The sole corals become frequent. The set is surrounded by a surface strengthened rich in ammonite.

The sedimentary and biologic data provided by the Nzala carbonate constructions seen and discussed in the present model, give evidence for deep and open depositional conditions in the sub-photic zone, towards the lower part of the storm waves level. Their development is closely related to a change of the sea bottom morphology resulting from the major platform dislocation step within the Lower Sinemurian-Upper Sinemurian transition period. Their localized persistence in the Upper Sinemurian could be related to the irregular distribution of the surrounding sediments or to the development of localized highs in the underlying substratum.

## INFLUENCE OF FLUIDS IN RESEARCH OF POTENTIAL RESERVOIRS

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This work concerns Albania, and more particularly the diagenetic evolution of the Triassic-Liassic's carbonate reservoirs in the Ionian zone.

The results of thermal modelling GENEX-GenTect and Thrustpack were compared with the microthermometric data in order to clarify if the mineralizing fluid was in thermal equilibrium with the surrounding material (heat transfers remaining essentially conductive), or if the circulation of a deep fluid along fractures was sufficient to maintain a sustainable thermal balance with the host rocks (heat supply by advection of hot fluids).

One of the fundamental problems in the studies of diagenesis is the flow of the event(s) related to the geological phenomena that affected the basin or the foothills in a larger geological scale.

By making calculations with the Thrustpack software, I noticed that the Upper Triassic autochthonous deposits stayed at temperatures between 120°C and 145°C during the later geodynamical stages such as the Plio-Quaternary, assuming a surface temperature = 16°C, flow = 30 mW/m<sup>2</sup>, and replacing the Permo-Triassic anhydrite with clay.

This result shows that high temperature fluids have circulated in the autochthonous and could possibly lead to a late dolomitization of Mesozoic carbonate reservoirs during the later geodynamic stages.

It is basically used to study the thermal evolution of the basin, the transfer of the fluids and their respective roles in the fluid-rock interactions affecting the major carbonate reservoirs.

My results show that there were several stages of dolomitization, with strong control of the paleo-environment. I did not observe any hydrothermal sign or dolomite of high temperature in the unit of Mali i Gjërë, which has indeed never been brought to high temperature due to an early tectonic setting, from the Upper Oligocene (maximum temperature reached by the Triassic is only 80°C).

The results obtained in petrography show the following sequence of events:

- Sedimentation of a carbonate mud in a shallow and open environment with algae and precipitation of evaporites;
- Consolidation of sediments with the dissolution of aragonite and evaporites;
- Brecciation;
- Early dolomitization of the matrix;
- Calcareous-dolomite cementation with silica input (presence of quartz and chalcedony, pseudomorphosis of anhydrite);
- Fracturing and dissolution;
- Cementation of dolomite and calcite in fractures, veins and cavities;
- Karstification and late filling of cavities by the dissolution of a clayey mud.

The results obtained by the study of fluid inclusions and stable isotopes of oxygen and carbon show a paleo-maximum temperature reached by the Triassic reservoirs, presently at the outcrop, which remained low (<80°C), and low salinity of the waters related to the burial diagenesis, which unfortunately could not be measured accurately.

## CAMPANIAN PERITIDAL MICROBIAL – FORAMINIFERAL LAMINITES FROM THE MAKARESHI STRUCTURE, KRUJA ZONE (ALBANIA)

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The Makareshi structure in the Kruja zone in Albania is a part of the Apulian passive margin, which is now placed in the External Albanides. Previous studies by Albanian geologists have already revealed the presence of Late Cretaceous peritidal limestones in this zone. Campanian deposits cropping out along the road, ca. 2 km west of Kruja, close to Gjurma e të Shenjtë Sari Salltik were investigated by means of thin-section analysis. The section consists mainly of bedded peloidal-bioclastic wacke- to packstones and bindstones interlayered with rudist floatstones. Studies were focused on analysis of microfacies and microbiota from the laminated limestones. Lamination is underlined by an alternation of wackestones, packstones, bindstones (mostly foraminiferal) as well as the presence of densely laminated and clotted microbial fabrics. Due to the significant role of encrusting foraminifera and the presence of microbial laminae, some of the analysed limestones can be classified as bindstones. Fenestral structures and dolomite crystals occur locally.

The dominant microfossils are different morphotypes of nubeculariid foraminifera, which are abundant in bindstones or scattered in wackestones and packstones. They are spectacularly well preserved in a few millimeters-thick layers/laminae, where monospecific (?) assemblages are embedded in peloidal microbialites and associated

with possibly syngedimentary sparite cement. In some laminae nubeculariids are ferruginized what enhance lamination. Other associated benthic foraminifera include for example the calcareous form *Rotorbinella scarsellai* Torre. *Thaumatoporella parvovesiculifera* (Raineri) – a microfossil *incertae sedis* – is common in some laminae. Based on microfacies characteristics and microfossil association, the studied limestones can be assigned to the so-called *Decastronema-Thaumatoporella* association widely reported from the Upper Cretaceous peritidal deposits of Apulian, Apenninic and Adriatic carbonate platforms. However, our observations have not revealed the presence of the calcimicrobe *Decastronema kotori* (Radoičić). Instead, we observed *Gahkumella huberi* Zaninetti described from the Cenomanian of southern Italy and tiny *Girvanella*-type tubes. Our findings suggest that some Late Cretaceous records of *Decastronema kotori* may, in fact, represent some of these microfossils or small nubeculariid foraminifera. Apart of limestones from Croatia, nubeculariids have not been mentioned in the literature as an important component of the Upper Cretaceous deposits. Nubeculariid foraminifera might, however, play an important binding role in Late Cretaceous shallow-water carbonate settings.

## **FACIES AND MICROFACIES ANALYSIS OF THE UPPER CRETACEOUS (EARLY CAMPANIAN) DEPOSITS FROM THE BORIZANA SECTION, KRUJA ZONE (ALBANIA): PRELIMINARY APPROACH.**

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### **Abstract**

The paper presents the preliminary data of the facies and microfacies study of the Upper Cretaceous (Early Campanian), outcropping along Droja valley, close to “Titan” Quarry, from Borizana section (Makareshi structure, Kruja Zone, Albania). The Upper Cretaceous Formation, in Makareshi structure consists mainly of limestones, dolomitic limestones and different levels of dolomite intercalations. For the first time in the studied section (from all of scientific studies carried out until now in this area by different authors) the presence of a siliciclastic lithofacies is identified, composed of three main facies: sandstone, calcareous sand and clay. The presence of siliciclastic lithofacies is distinguishable at several levels, overlain hard ground surfaces. Petrographic analysis show that the sandstones facies essentially contain quartz, a small percentage of micas set in a carbonate mud and iron oxides matrix. The quartz composition of this facies holds great interest for further interpretations regarding source area because Kruja zone is delimited to the east by Krasta-

Cukali and to the west by Ionian tectonic zones which during this period have represented basins, respectively. The presence of hard ground surfaces observed in the field is another phenomenon present in this section. These surfaces are often associated with boring organisms (Trypanites ichnofacies?), large mineralized zones with iron oxides and tidal channel carbonate deposits. The hard ground characteristics (morphological, mineralogical, sedimentological) may highlight a sedimentological phenomena like the frequent emersion of the Kruja platform during this period. It indicates also sediments deposition in a platform interior (intertidal to shallow-deep subtidal) environments. Detailed work in the field and in the laboratory revealed that it contains microfacies forming SMF zones and exhibits frequent peloidal and bioclastic packstone/grainstone microfacies that constitute a predominant part in this section. Different types of fauna, observed in the formation, include algae, bivalves, ostracods and benthic foraminifera (miliolidae).



## **DEPOSITION AND DIAGENESIS OF CARBONATE CONGLOMERATES IN THE KREMENARA ANTICLINE, ALBANIA: A PARAGENETIC TIME MARKER IN THE ALBANIAN FORELAND FOLD-AND-THRUST BELT**

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The Poçem polymict transgressive carbonate conglomerate was deposited in a shallow marine environment. These conglomerates are covered by intertidal rhodolitic packstones–grainstones.

The diagenesis of the carbonate conglomerates that are exposed in the Poçem outcrop (Kremenara anticline, central Albania) allow to refine the paragenetic history this part of the Albanian foreland fold-and-thrust belt. Of major interest are stylolites (burial as well as tectonic) which are restricted to conglomerate fragments or which crosscut the conglomerate matrix. Based on the inferred age of stylolite development in relation to burial, uplift and tectonic history, and the Lower to Middle Miocene age of the conglomerates, the succession of diagenetic events was subdivided into several stages. The stable-isotope signature of these packstones–grainstones ( $\delta^{18}\text{O}_{\text{V-PDB}} = -1.0$  to  $+0.7\text{‰}$ ;  $\delta^{18}\text{C} = +1.0$  to  $+1.4\text{‰}$ ) plots

within the range of marine Early and Middle Miocene values. Shortly after deposition of the conglomerates, micritization, geopetal infill and acicular calcite cementation took place. A first calcite vein generation is interpreted as having formed from a Messinian brine during shallow burial. Burial stylolites developed during further burial in the Pliocene. These stylolites serve as an important diagenetic time marker. The post-burial stylolite meteoric calcite vein cement probably precipitated during the following telogenetic stage. Karstification and calcite concretion precipitation pre-date overturning of the western limb of the anticline. Reopening of subvertical fractures and tectonic stylolites in the western limb of the Kremenara anticline, followed by oil migration, represents one of the latest diagenetic events. These fractures and stylolites provide major pathways for hydrocarbon production.

## **PALEO-FLUIDFLOWRECONSTRUCTIONINTHEALBANIANFORELANDFORELANDFOLD-AND-THRUST BELT**

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Within the central and Southern part of the Albanian Foreland foreland fold-and-thrust belt a number of carbonate outcrops were selected to work out a detailed paragenesis, addressing the matrix diagenesis as well as the development of veins. Of particular use was the existence of bed parallel (BPS, i.e. compactional) and bed perpendicular (TS, i.e. tectonic) stylolites. Based on the crosscutting relationship with the veins, the diagenetic history could be split into three main episodes, namely pre-BPS, post-BPS but pre-TS and post-TS. Based on their petrography (including cathodoluminescence) as well as trace element, stable C- and O-isotope as well as Sr-isotope geochemistry the origin of the fluids could be regionally constrained.

The pre-BPS veins often reflect host rock buffering, with circulation of meteoric fluids. They reflect the foreland flexuring and the pre-burial stage. Locally indications of interaction with evaporites that likely occur along the décollement horizons took place. Post-BPS to pre-TS veins often reflect high pressure release as testified by the existence of crack-seal and brecciated veins, while the post-TS veins often reflect involvement of non-host rock buffered fluid circulation. Here processes like dolomitisation and locally sulphate precipitation took place. During telogenesis meteoric fluid flow again affected the rocks and locally caused some dedolomitisation. Based on the nearly ideal exposure conditions the Albanian Foreland foreland fold-and-thrust belt forms one of the best exposed systems to study this paleo-fluid flow system.

## PLATFORM SEQUENCE STRATIGRAPHY BASED ON BIOLOGICAL ASSEMBLAGES: THE URGONIAN OF MIRDITA ZONE

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Carbonate environments are partly created by the organisms that inhabit them. Therefore, a close relationship exists between fossil biota and lithofacies. Identification of depth-related benthic assemblages on marine shelves is based on the biofacies present, the diversity and abundance of the fauna and its taphonomic state. Benthic assemblages are linked to ecological factors such as light, temperature, oxygen, salinity, water turbulence, nature of substrate and sedimentation rate, which are limiting factors controlled by water depth. Estimate of the bathymetric depth of benthic assemblages are related to A) the base of the photic zone, which can be identified by the disappearance of benthic algae, and B) the effective storm wave-base, which is characterized by the disappearance of wave-formed structures and benthic fauna fragments reworked from the photic zone during storm events. Low to high salinity environments can be recognized by the low diversity of fauna, the absence of stenohaline taxa, and by the comparison between marine biota with brackish-water biota. The abundance of nutrients corresponds to the type of environment, ranging from oligotrophic to mesotrophic and eutrophic.

A qualitative, quantitative and statistical analysis of bioclasts describes perfectly paleoenvironments and is one of the best indicators of any paleoenvironmental change linked to sea-level change. Vertical fluctuations of each ecological assemblage's percentage along a section reflect sea-level changes at any given location on the platform and allow acquisition of relative paleobathymetry. Within the Urgonian of Mirdita zone, from deeper to shallow water deposits, the next biological assemblages could be separated:

Assemblage A: Echinoderm fragments

Assemblage B: Fauna living below the photic zone and represented by small sized benthic foraminifers

Assemblage C: fauna living below the photic zone represented by Bryozoa and small and large sized

benthic foraminifers.

Assemblage D: Fauna living above the photic zone as corals, red algae, rudists fragments and rare attached benthic foraminifers.

Assemblage E1: Platform margin, fauna living above the photic zone: coral fragments, large algae, large benthic foraminifers with a thick test and conical form.

Assemblage E2: Lagoon, fauna living above the photic zone. Abundant rudists, miliolids and few dasycladaceans.

When the maximum flooding surface (mfs) is analyzed, then maximum deepening corresponds to the highest abundance of deep water species.

The HST can be divided in two parts: an early HST, which is indicated by a relative abundance of slightly deeper water species and a late HST that shows the maximum abundance of shallow marine organisms, which lived in the photic zone.

Differences between the two sections concerning the HST are as follows:

### Early Highstand:

On the platform margin, carbonate rocks are mainly composed of grainstone/wackestone, with interbedded marly limestone, which corresponds to a relative deepening at the parasequence scale. The micropaleontologic analyses display all details concerning the parasequence evolution and the presence of organisms resistant to a high energy environment.

On the inner platform, the mfs corresponds to the first drowning of a subaerial surface.

### Late Highstand:

-on the platform margin, grainstone attesting to a high energy environment is composed of coral fragments, large algae and large conical forams.

-On the inner platform, wackestone-packstones with rudist fragments become abundant and the first restricted environments and lagoonal environments occur.