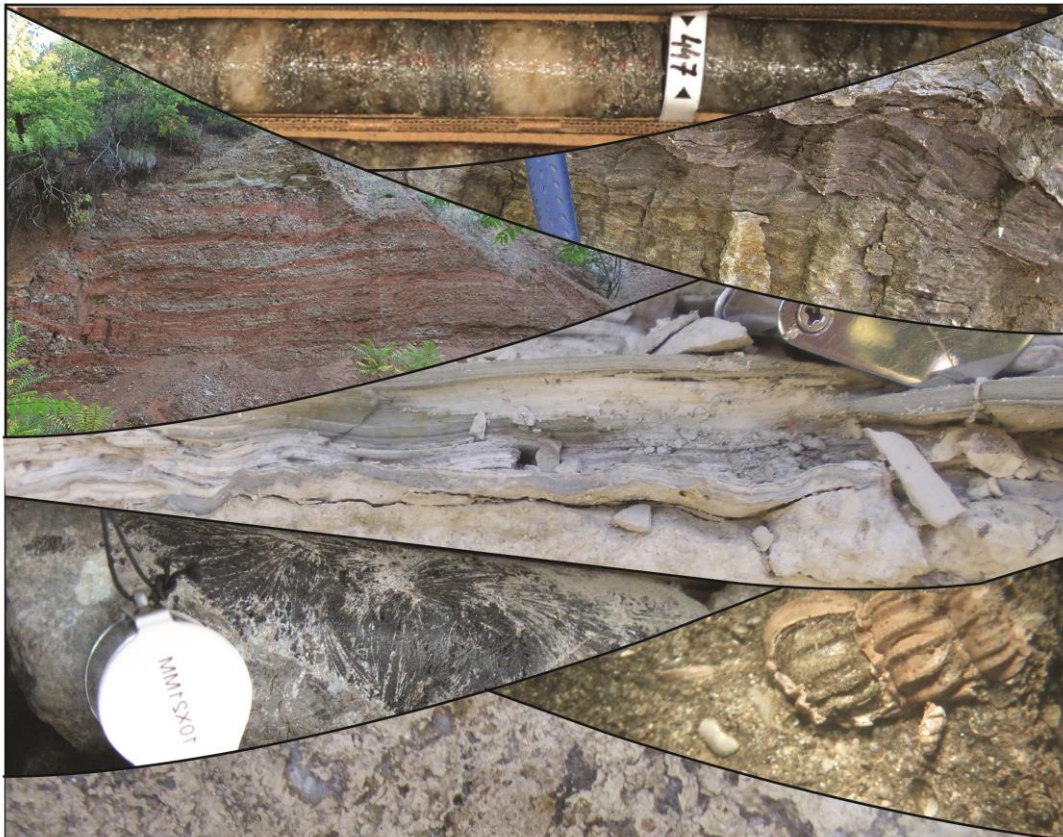


## Evolution of Neogene Intramontane Basins in Serbia

### Field Trip Guide

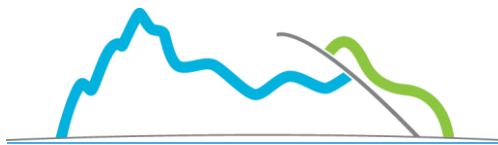


13<sup>th</sup> Workshop on Alpine Geological Studies  
Serbia – Zlatibor, September 2017





## EGU series: Émile Argand Conference



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Vladimir Simić, Dragana Životić, Nevena Andrić, Ljupko Rundić

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## PREFACE

Lakes are important archives recording past climate conditions, vegetation and fauna, but also geodynamic events. Often, they host different mineral and energy resources. These key features of the lakes provided the motivation for dedicating one of the pre-meeting field trips of the 13<sup>th</sup> Apline Workshop to the Miocene Serbian Lake System (SLS). During the excursion, Evolution of Neogene Intramontane Basins in Serbia, we will demonstrate geological evolution and main features of a few intradinaridic Neogene basins (Jadar Basin, Valjevo-Mionica Basin, Pranjani Basin, Kraljevo-Čačak Basin and Ibar Basin).

The late stage evolution of the Dinaridic orogen was characterized by the development of numerous intramontane basins. Often isolated nature of these basins led to development of faunal endemism which prevented reliable correlation with the global time scales.

Typical stratigraphic succession recorded continental alluvial to lacustrine depositional environment (e.g. Valjevo-Mionica, Ibar and Pranjani basins). The expansion of Pannonian basin triggered marine flooding of surrounding lakes and establishment of marine environment in Badenian (e.g. Jadar basin). The depositional geometry in many basins was controlled by the balance between basin subsidence and source area tectonics. The marginal faults influenced the deposition of coarse-grained alluvial fans and fan deltas (e.g. Kraljevo and Ibar basins). The high subsidence rates led to accumulation of thick coal succession and subsequent deep lake sedimentary systems (e.g. Ibar basin). The playa lake deposits reflect the cessation of the fault activity.

Many lacustrine intramontane basins of the SLS host various natural resources such as magnesite, boron and/or lithium mineralisation, zeolite, sepiolite, oil shale and coal.

The organizers and authors of this excursion guide greatly acknowledge the generous help of all colleagues and institutions who contributed to this Guidebook. In particular, we are indebted to the Ministry of Education, Science and Technological Development of the Republic of Serbia, International Association of Sedimentologists, Rio Sava Exploration, Kalisi MC-Plus Ltd., VODAVODA, Mg-Serbien and Balkan Gold for their support and guidance during the excursion.

We wish all the participants pleasant stay during the field trip in Serbia!

*Vladimir Simić, Dragana Životić, Nevena Andrić and Ljupko Rundić*

## 1. INTRODUCTION

During Neogene, series of freshwater lakes were occupying depressions formed in the central regions of the Balkan Peninsula (Fig. 1.1, e.g. Marović et al., 1999, 2007; Krstić et al., 2003, 2007, 2012; Harzhauser and Mandić, 2008, Neubauer et al. 2015a). These depressions were formed in the course of several Neogene geodynamic events affecting the whole Alpine-Carpathian-Dinaride system (e.g., Marović et al., 1999, 2007; Schmid et al., 2008). The deposition in these lakes ended by basin inversion triggered by late Miocene to Quaternary transpressional regime (e.g., Ilić and Neubauer, 2005; Marović et al., 1999, 2007). The following text will be focused on the evolution of the Neogene lacustrine systems in the context of the Dinarides as the basins which are subject of this excursion are formed above palaeorelief which belongs to the Dinarides.

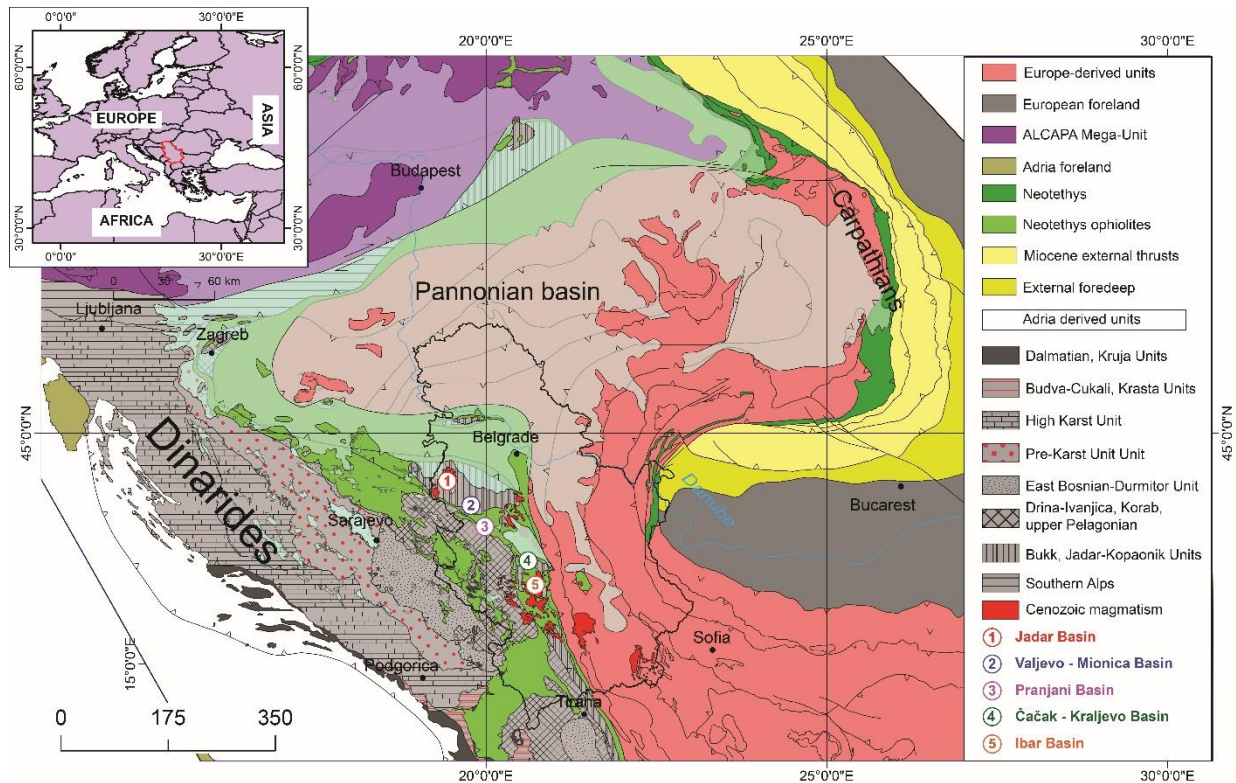


Figure 1.1. Tectonic map of the Alpine-Carpathian-Dinaride system (simplified after Schmid et al., 2008).

### Tectonic evolution of the Dinarides

The Dinarides represent the southern branch of the Alpine-Carpathian-Dinaride system, which resulted from collision of Europe and Adria that followed the closure of the Vardar Ocean during late Jurassic and Cretaceous (Fig. 1.1; e.g., Dimitrijević, 1997; Karamata, 2006; Schmid et al., 2008).

Predating the closure of the Vardar Ocean, intra-oceanic subduction (during late Jurassic – earliest Cretaceous) resulted in emplacement of the ophiolites and associated mélanges over Adriatic passive continental margin (Fig. 1.1; the Western Vardar ophiolites, Schmid et al., 2008).

The following Cretaceous – Eocene orogenic shortening was characterized by the formation of several thrust sheets subdivided into internal and external thrust belt, i.e. Internal and External Dinarides. The Internal Dinarides comprises of composite units including Paleozoic metamorphic basement covered by (pre –) Mesozoic carbonate succession carrying ophiolites in the upper

structural position (i.e. East Bosnian – Durmitor, Drina – Ivanjica and Jadar – Kopaonik, e.g., Đoković, 1985; Dimitrijević and Dimitrijević, 1987; Schmid et al., 2008). The external Dinarides consist of Paleozoic metamorphic basement covered by Mesozoic to Paleogene carbonate and Late Eocene to Oligocene clastic syn-contractonal deposits (e.g., Vlahović et al., 2005; Babić et al., 2007; Korbar, 2009).

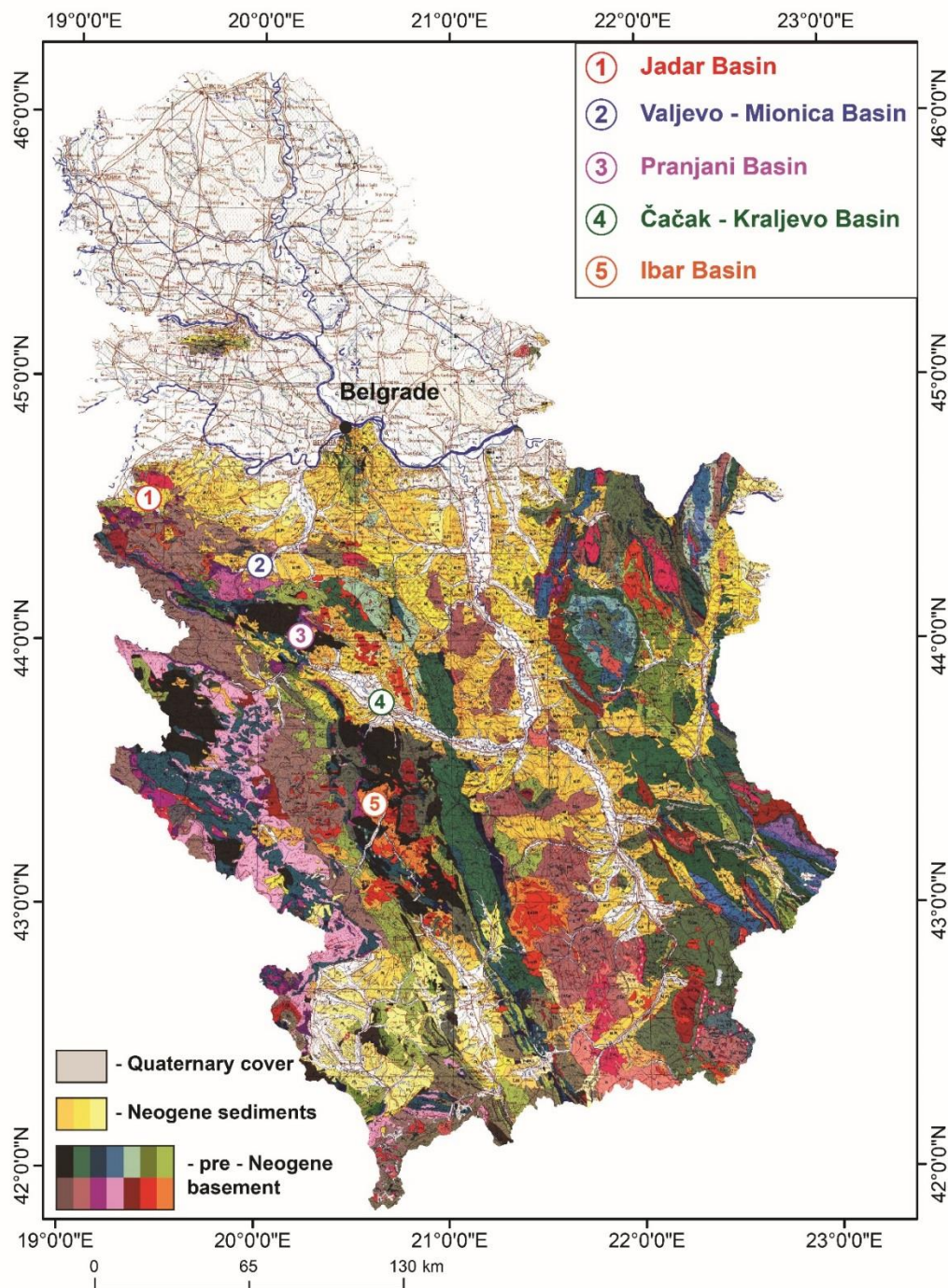


Figure 1.2. Geological map of Serbia with location of basins covered by this excursion (modified after Geological map of Yugoslavia 1: 500000).

During Neogene, the Internal Dinarides were affected by extension which started at low rates during Upper Oligocene-Lower Miocene (e.g., Erak et al., 2017) and accelerated reaching the peak tectonic activity at around ~ 15-14 Ma (e.g., Stojadinović et al., 2013). Andrić et al., (2017)



suggested that extension in the Internal Dinarides migrated towards the foreland (SW-wards) reaching the Sarajevo-Zenica Basin, Bosnia and Herzegovina. Traditionally, this extension was associated with opening of Pannonian Basin (i.e. rollback of the Carpathian slab, ~ 20 Ma, Bálazs et al., 2016 and references therein). The extension led to reactivation of the former suture, trusts and nappe contacts as low – angle normal faults which exhumed parts of tectonic units deeply buried by the previous tectonic events (e.g., Schefer et al., 2011; Matenco and Radivojević, 2012; Toljić et al., 2013). The main transport directions of extensional deformation phases ranges from top to the N to top to the E (e.g., Schefer et al., 2011; Mladenović et al., 2015; Erak et al., 2017).

The final moments of shortening and extension in the Dinarides provided accommodation space for formation of numerous freshwater lakes (e.g., Serbian Lake system-SLS and Dinaridic Lake System-DLS lake systems, in internal and external Dinarides, respectively, e.g., Krstić et al., 2003; Harzhauser and Mandić et al., 2008, Krstić et al., 2012; Neubauer et al., 2015a,b).

### **Neogene lacustrine system in Serbia**

The late stage evolution of the Dinaridic orogen was characterized by formation of numerous freshwater lakes during Neogene (DLS and SLS, Figs. 1.1 and 1.2). These predominantly intramountain lakes were located between Paratethys and Mediterranean sea, but not connected with them, thus leading to development of endemic fauna assemblages (Fig. 1.3 ab, Harzhauser and Mandić, 2008, Krstić et al. 2012, Neubauer et al. 2015a). During Neogene, these lakes have been subjected to several phases of expansion and restriction controlled by combination of climate variability and geodynamic processes. The glacio-eustatic sea level changes additionally controlled the depositional architecture of the basin located along the southern margin of the Pannonian basin and in the Morava corridor which were interrupted by the Badenian marine transgression (e.g., Anđelković et al., 1991; Mandić et al., 2011; Rundić et al., 2013). In the Internal Dinarides, the intense magmatic activity (Cvetković et al., 2013 and references therein) has influenced the lake chemistry and therefore significantly controlled the character of the basin infill.

In the Dinarides of Serbia, combination of all those factors resulted in formation of at least three lacustrine depositional cycles, i.e. Oligocene – Early Miocene, Middle/Late Early Miocene to early Middle Miocene and Late Miocene – Middle Pliocene (e.g. Krstić et al., 2003; Krstić et al., 2007; Obradović and Vasić, 2007; Krstić et al., 2012). The sediments of the third lacustrine depositional cycle are not going to be the subject of this excursion, therefore this cycle will not be further elaborated.

In general, the basins recorded one, two or all three lacustrine depositional cycles. The endemic nature of the fauna makes dating and regional correlations difficult. Therefore, it is still debated, whether all these basins were formed at the same time as a part one big lake or as individual and isolated depocentres, i.e. system of lakes, which may be connected at certain moment of their evolution (e.g., Krstić et al. 2003, 2007, 2012, Neubauer et al. 2015a; Sant et al., 2016).

The first lacustrine depositional cycle corresponds to the Šumadija lake of Krstić et al. (2003; Fig. 1.3c) and was initiated at the end of the Oligocene and ended by the beginning of the Miocene (equivalent to Egerian/Eggenburgian cf. Steininger, 1999). The orogen-perpendicular extension (NE-SW, e.g., Ilić and Neubauer, 2005; Erak et al., 2017) provided depressions which accommodated the sediments of the first lacustrine depositional cycle. Marović et al., (1999) relate this tectonic phase to the collapse of the Dinaridic orogen. The sediments of the first depositional lacustrine cycle are characterized by alluvial, deltaic and lacustrine deposits intercalated with pyroclastites and volcanoclastites (e.g. Anđelković et al., 1991; Obradović and Vasić, 2007).

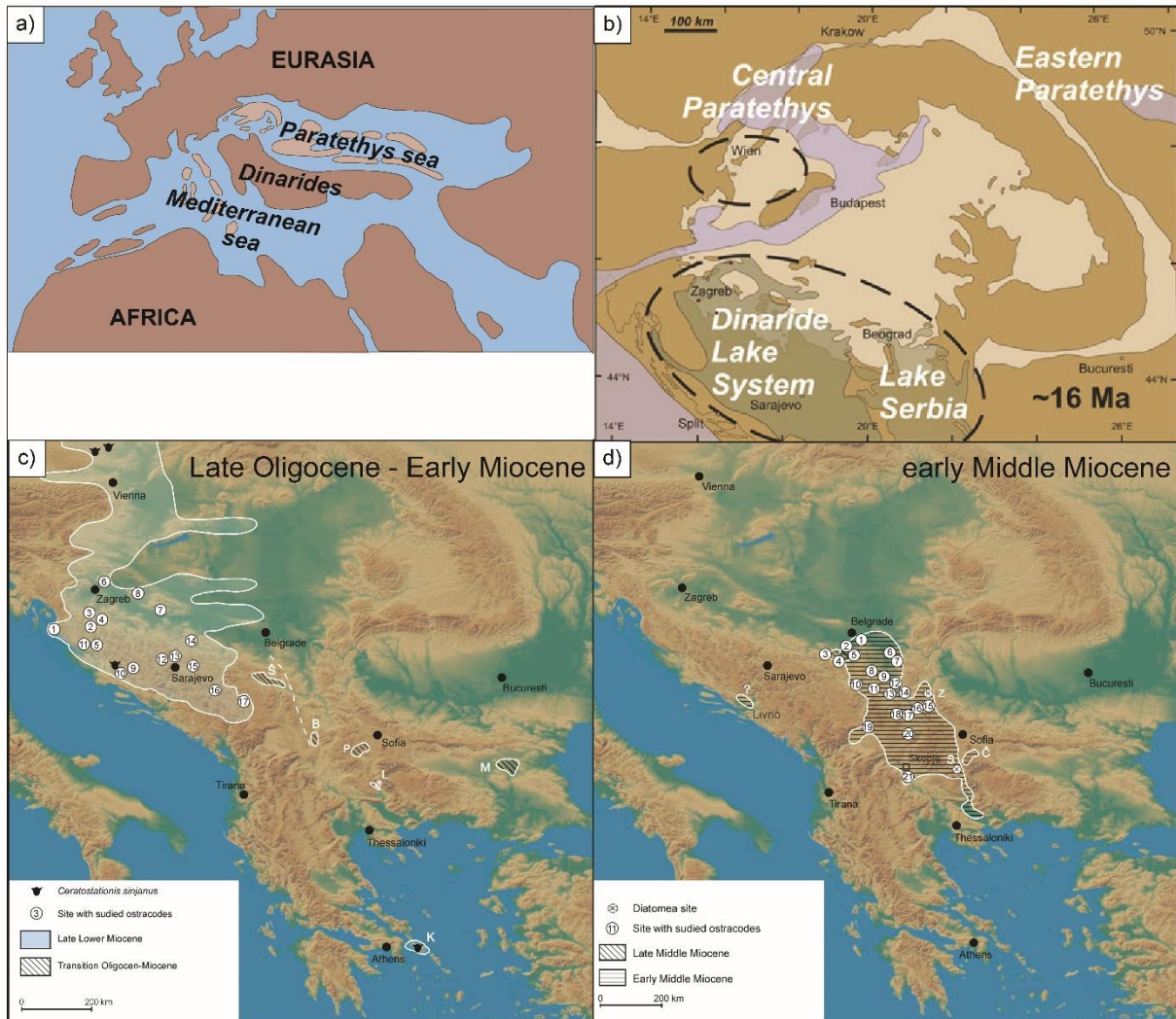


Figure 1.3. a) Paleogeography of the Eurasia – Africa collision zone in the Miocene (modified after Rögl, 1999); b) paleogeographic map showing distribution of DLS and SLS during Middle Miocene (after Mandić et al., 2011); c) distribution of the freshwater lakes in the Balkan Land during Late Oligocene-Early Miocene; b) distribution of the freshwater lakes in the Balkan Land during early Middle Miocene (after Krstić et al., 2012).

The second lacustrine depositional cycle lasted from Middle/Late Early Miocene to early Middle Miocene (Ottangian - Badenian – cf. Steininger, 1999; 18-14 Ma, Sant et al., 2016 and references therein). The lacustrine domain developed during this cycle is called Serbian Lake (Harzhauser and Mandić, 2008, Krstić et al. 2003, 2007, 2012, Neubauer et al. 2015a) or Serbian Lake System (SLS sensu Sant et al., 2016). The SLS co-existed with DLS (settled in the present day Croatia, Bosnia and Herzegovina, NW Montenegro and SW Serbia and lasted from 18-13 Ma, Fig. 1.3b; e.g. Jiménez-Moreno et al., 2008, 2009; Harzhauser and Mandić, 2008; Mandić et al., 2011; De Leeuw et al., 2012). Marović et al (1999) suggest that the initiation of this depositional cycle is driven by the regional extension and subsidence related to the opening of Pannonian basin. This extensional tectonic phase coincides with the Middle Miocene Climatic Optimum which acted as an additional stimulant for the lake formation (Mandić et al., 2011; Neubauer et al., 2015a).

The lower alluvial and swamp successions suggest that the humid periods at the beginning of this depositional cycle provided optimal conditions for deposition of thick layers of brown coal (e.g., Anđelković et al., 1991; Ercegović et al., 1991, 2006). The global temperature rising reaching the

peak between 16.9 Ma to 14.7 Ma (Zachos et al., 2001) caused the change in regional evaporation-precipitation balance and stimulated formation of perennial lakes (e.g. Obradović et al., 1992, 1997; Mandić et al., 2011).

During Badenian, marine transgression flooded lakes situated along the southern margin of the Pannonian basin and Morava corridor (e.g., Rögl, 1998; Harzhauser et al. 2003; Kovač et al. 2007; Mandić et al. 2012). The onset of marine transgression is recorded by the deposition of shallow-water Leitha limestone typical for whole Central Paratethys (e.g., Riegl and Piller, 2000; Rundić et al., 2013; Ali and Wagreich, 2017).

The Neogene lacustrine system of Serbia is characterized by various mineral deposits such as magnesites, Li- and/or B-mineralization, coal, sepiolites, kaolinites (e.g. Fallick et al., 1991; Obradović et al., 1992, 1997; Simić et al., in prep, Ercegovac et al., 2006; Stanley et al., 2007).

## 2. EXCURSION POINTS

Our three-day excursion represents a brief overview on the evolution of freshwater lacustrine environments developed in the intramountain basins of the Internal Dinarides since Oligocene – until Middle Miocene (Fig. 2.1).

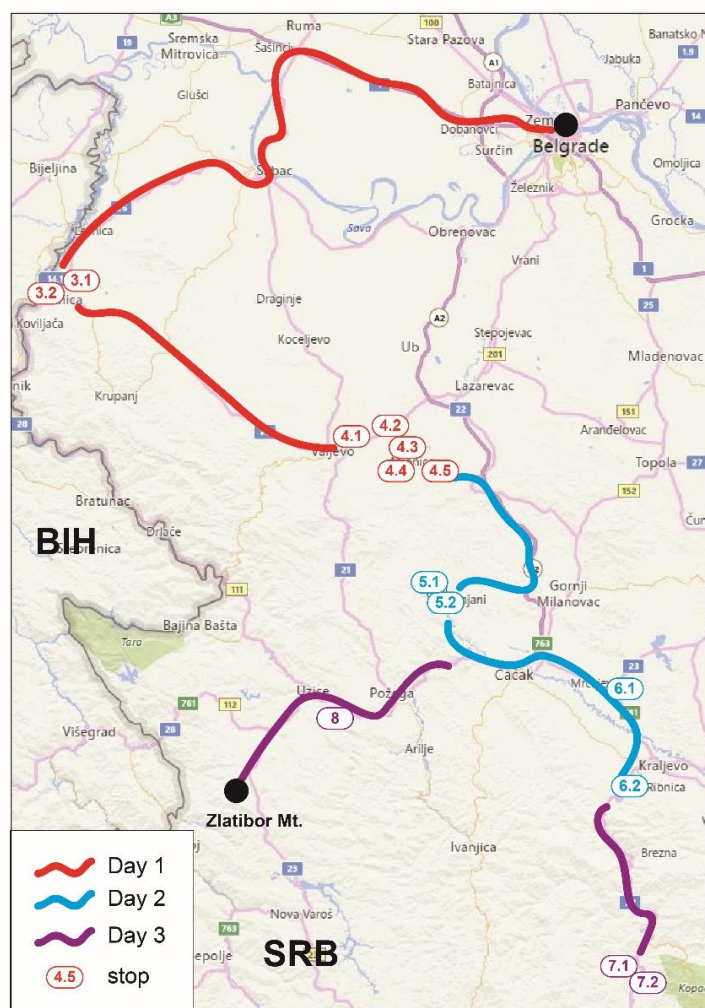


Figure 2.1. Excursion route with marked field stops

The excursion starts with the world-class/unique lithium occurrences (3.1) hosted within lacustrine succession of the Jadar Basin situated on the southern margin of the Pannonian Basin (Figs. 1.1, 1.2 and 1.4). In this basin, we will be able to observe the example of marine transgression which interrupted lacustrine phase during Badenian (3.2). The end of the day will be spent in Valjevo – Mionica Basin dominated by monotonous laminated deep water (organic) lacustrine succession (4.1-4.4).

The second day will be focused on processes developed at the distal alluvial fan and in the profundal lacustrine environment of hydrologically closed Pranjani Basin (5.1 and 5.2). The interplay between climate (evapo-transpiration), available accommodation space, ground-water level and lake chemistry led to deposition of various sedimentary units such as debris, sepiolite and dolomite bearing mudstones (5.1), sedimentary magnesite and laminated oil shales (5.2). The example of continental sediments deposited along the ‘active’ margin (i.e. deposition along the footwall slope) and swamp to lacustrine deposits of the ‘passive’ margin (i.e. deposition along the hanging-wall slope) in this freshwater lacustrine system will be seen in Čačak-Kraljevo (Zapadna Morava) Basin (6.1 and 6.2). The stop 6.1 will include coal succession deposited along the passive margin and its gradual transition to lacustrine succession with fish and freshwater mollusks remains. At the end of the day will be visited red continental alluvial clastics deposited along the active margin (6.2).

The third day will be spent in the Ibar Basin (7.1 and 7.2). There, we will see various sedimentary units clastites, organic rich shales, coals, oil saturated travertines, boron mineralisation, magnesite whose deposition resulted from the interplay between tectonics, climate and nearby volcanic activity. At the end of the day, we will see the Potpeć cave near Zlatibor (8).

### 3. JADAR BASIN

Jadar Basin (JB) is situated in the northwestern Serbia along the banks of Jadar River and between Cer Horst to the northeast and raised Dinaridic morphostructures to the southwest (Fig. 3.1.). It covers area of about 150 square kilometers. JB represents a narrow tectonic trench of E-W direction and has no distinctive Dinaridic orientation. The deep fractured zones are located on the southern edge, while in the north they are covered with delluvial sediments of Iverak Mt. Steep gravity faults in WNW–ESE direction separate the basin from the two blocks (Marović et al., 2007). Along these faults mainly and less along NE-SW faults the blocks were downthrown about 300 m at the most (northeastern basin). JB is genetically related to location and activity of the Jadar fault, an old pre-Alpine structure of WNW-ESE strike and characteristics of sinistral transcurrent shear (Marović et al., 2007). Secondary tension fractures in the left conjugate pattern were, later, active zones of subsidence and consequent formation of the basin. Outline of the basin had formed before the Badenian, but changed eventually during the Badenian through differential downthrows of blocks (Marović et al., 2007). According to some authors, JB represents the last northwestern part of Valjevo-Mionica-basin (Anđelković et al., 1991). Further to the west, Jadar basin is opened towards large Tuzla Basin in western part of Bosnia and Herzegovina. JB was filled by the continental-lacustrine Lower Miocene sediments which are underlying marine Badenian deposits. All together, they cover the Triassic and Upper Cretaceous carbonate rocks and clastites. Marginal parts of JB consist of different Paleozoic rocks (so-called Jadar Paleozoic) and Mesozoic carbonate-clastic deposits (Fig. 3.1.). Recent studies show the total thickness of Miocene deposits is much thicker than previously stated (Mojsilović et al., 1977) and reaches up to 750 m (Kellie, 2009 – Fig. 3.2.).

The first data concerning the geological structure of the basin comes from the end of XIX century (Žujović, 1893). Later, most of authors reported about marine Middle Miocene sediments and its facial diversity (i.e. Obradović & Vasić, 2007 and references therein). For the reason of small distribution on surface, the lacustrine sediments have been less studied.

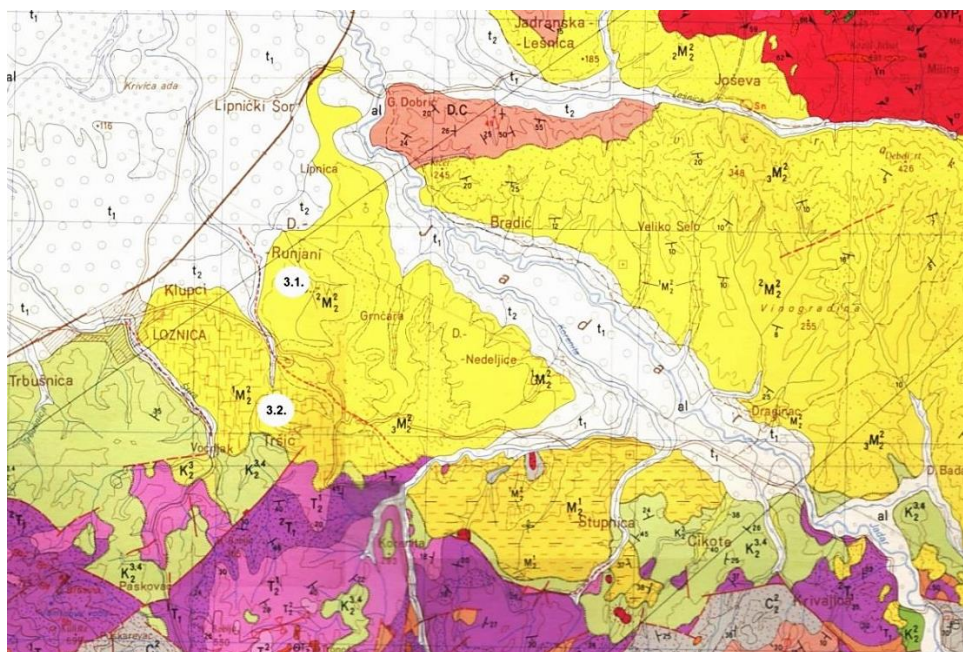


Fig. 3.1. The part of the Basic Geological Map of Yugoslavia, 1: 100,000, sheet Zvornik with position of the observation points (3.1 and 3.2). Jadar Basin infill is marked by yellow color. Key (simplified): D, C – Devonian-Carboniferous, C<sub>2</sub> – Middle Carboniferous, T<sub>1</sub> – Lower Triassic, T<sub>2</sub> – Middle Triassic, K<sub>2</sub> – Upper Cretaceous, <sup>1</sup>M<sub>2</sub> – Lower Miocene, <sup>2</sup>M<sub>2</sub> – Middle Miocene (Badenian), βγ – Miocene granitoids, t<sub>1,2</sub> – Quaternary river terrace.

The basic biostratigraphic study comes from the second half of XX century by Petrović (1967) and author dealt with middle Miocene foraminifers from the Jadar Basin. Based on biostratigraphic analyses, he confirms the existence of the Lower Miocene lacustrine sediments (“Helvetian”) as well as the marine middle Miocene (Badenian) deposits. On the basis of foraminifers, Badenian Stage is divided into three parts: Lower, Middle and Upper Badenian (Petrović, 1967).

As the above-mentioned, from the stratigraphic point of view, lacustrine sediments of JB have not been sufficiently studied (Rundić, 2013). Lake deposits were discovered in the central parts of the basin, while in other parts, especially on the right bank of the Jadar River, they were masked by the Badenian deposits. Some authors like Dolić (1998) think that the oldest part of Lower Miocene so-called the Stupnica Formation (Eggerian-Eggenburgian?) corresponds to the Mionica Formation of VMB. Lithologically, its intrabasinal facies consists of dolomites and dolomitic marls with tuffitic interbeds, oil shale occurrences as well as authigenic minerals (Obradović & Vasić, 2007). Dolomites and dolomitic marl contain fine lamina of kerogen as well as mineralization of searlesite and analcite (Obradović & Vasić, 2007).

It is very important to note that a few levels of tuffs represent the marker-bed in the lacustrine series. For example, within the laminated marl (shale) with fragments of carbonized plants and thin lamina of kerogen, there is up to 0.7 m thick vitroclastic tuff (Obradović & Vasić, 2007). It is a real tool for independent age control and timing of the basin infill (Rundić, 2013). So, they have a great importance for future stratigraphic division of the Miocene of JB. Besides, the marginal lacustrine and swamp facies take part in the basin infill. They contain different rocks such as gravel, sand and striped, fine-laminated marl, silty-clay and clay. Lacustrine series of JB contains very poor record of fossil flora and fauna. Except the mentioned plant remains, sporadic finding of ostracods such as *Candona* sp., *Limnocythere* sp., *Potamocypris* sp., and *Cypridopsis* sp. were reported (Krstić et al. 2012). Interestingly, there are no “Congerian beds” in JB which corresponds to the younger level of lake deposition in the VMB (Dolić, 1998). Author believes that marine Badenian sediments unconformably and transgressively overlie the red clastic series of the Lower Miocene. Similarly, most of researches have more or less similar opinion (i.e. Marović et al., 2007; Rundić et al., 2000, 2005, 2011, 2013, 2015 and references therein).

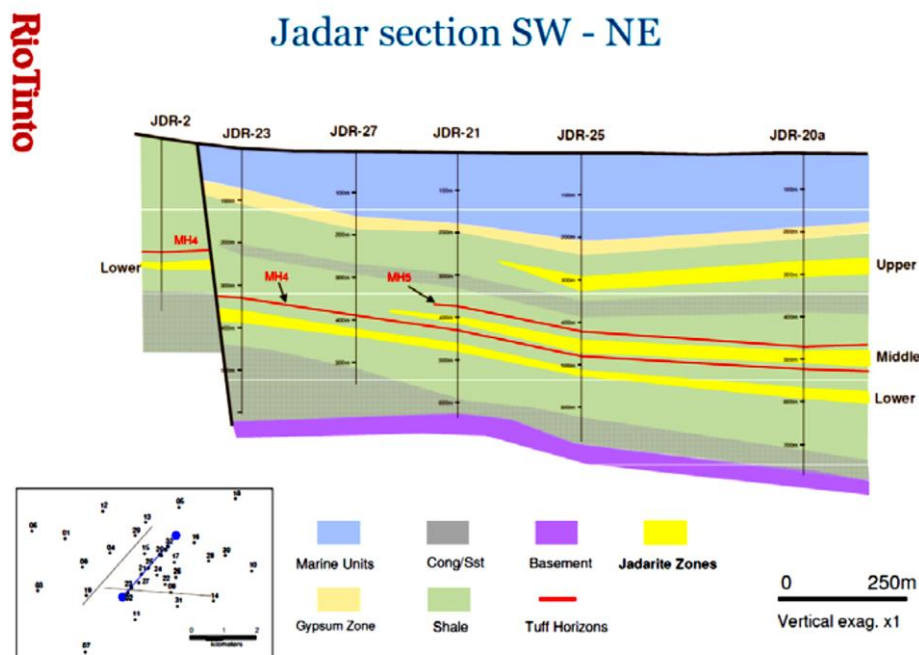


Fig. 3.2. A cross-section through the Jadar Basin and position of marine Badenian deposits (blue color, on top) as well as different continental-lacustrine Lower Miocene units including the Jadarite deposits (yellow). The basement is marked by purple color (Kellie, 2009).

Nevertheless, a recent study of the territory of central Serbia shows that the Serbian Lake System existed in the Middle Miocene as well (Sant et al., 2016). Recent, very detailed investigations of boron minerals from numerous boreholes (Kellie, 2009; Kilpatrick, 2010) have good potential to give precise stratigraphic division of the Miocene of JB. As part of lake sediments, the appearances of organic matter - kerogen are considerably less than in the VMB. According to Ercegovac (1990), kerogen is of a sapropel type. The occurrences of searlesite and analcite bodies as well as gypsum are also less frequent than in the VMB. In addition to the dolomite, they clearly indicate evaporation during the long periods of time and increase of salt in water (increased content of Na and the presence of the above mentioned minerals). This longer period of subtropical arid climate was occasionally interrupted by wet periods (Obradović & Vasić, 2007).

### STOP 3.1. JADAR Li-B DEPOSIT<sup>1</sup>

Locality: East of the Loznica town  
 WGS84: 44°32'10.08"N, 19°16'28.34"E  
 Age: Lower - Middle Miocene

#### Introduction

The Jadar deposit, discovered in 2004 in Western Serbia is a concentration of lithium and borate in a mineral new to science, named Jadarite,  $\text{LiNaSiB}_3\text{O}_7(\text{OH})$ . Deposit is located in a Jadar valley with flat-lying farmland encompassing an area of 3 km by 2.5 km at depths from 100 m to 720 m.

With no outcropping mineralization, all resource data from the deposit comes from drilling. By December 2016 the project drilling database contains 310 drill holes. Of these, 176 holes

<sup>1</sup> Text concerning this point was prepared by N. Petković (Rio Tinto Borates | Rio Sava Exploration)

(100,654 m) were cored and sampled for an aggregated length of 40,923 meters to support the resource estimation, with a total of 25,004 samples in the resource assay database. The remaining drill holes include large diameter holes for process test-work bulk sampling, geotechnical holes in peripheral areas or hydrogeological holes. Other exploration techniques includes geophysical survey (gravimetric, magnetic, magnetotelluric and seismic).

### Regional geology

On a larger scale, the basin represents a relatively narrow tectonic trench where subsidence occurred during deposition. Deep crush lines were identified along the southern edge, while being covered with delluvial clastics of Mt. Iverak along the northern edge. The basin is oriented in the west - east direction, showing a deviation from the direction of the Dinaric mountain range.

The district structural setting consists of roughly E-W trending Eocene-Miocene fault bounded basin on Paleozoic and Mesozoic “basement”. These faults are interpreted to be steeply dipping due to linear pattern on rugged terrain. The Eocene is largely confined to the basin and the Miocene overlaps onto the basement footwall.

The early NE-SW sinistral fault system appears to be cut and displaced by a later system of NW trending extensional faults. The linear trends and breaks in continuity seen on the geological map are broadly repeated in the ground magnetic survey. It is important to realize that the ground magnetic data may enhance minor features near surface at the expense of more important structures.

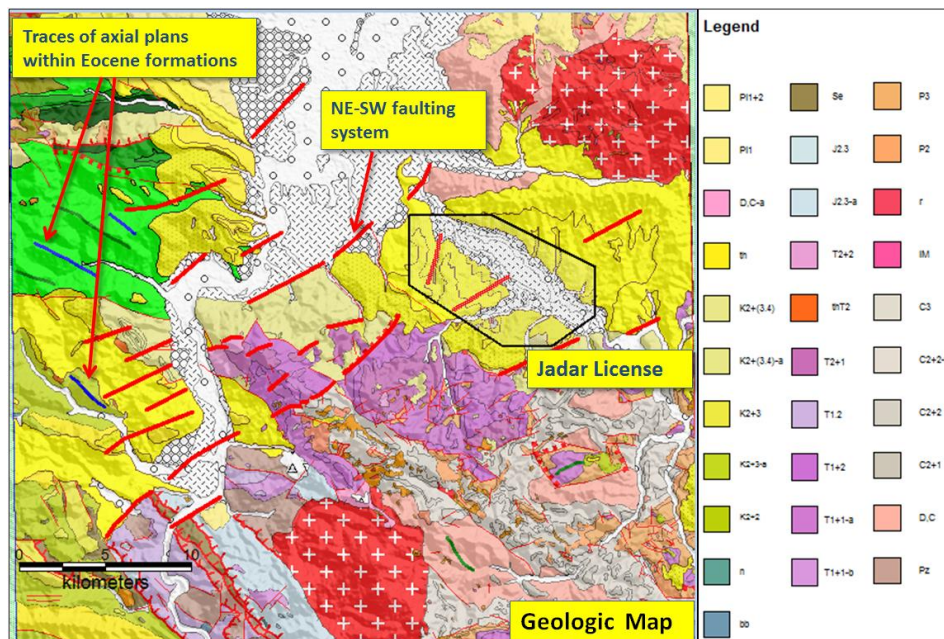


Fig. 3.1.1. Simplified Geological Map of Jadar district. For legend, see also Fig. 3.1. (Pope & Petković, 2014)

A stuck of largely normal faults occurs in several systems, of which two are most persistent in a conjugate relation. Generally, these represent an extensional basin with different fault blocks settling at different rates, but generally with central areas sinking faster than the periphery, so that as sediment came into the basin, a greater thickness was deposited in central areas.

The stratigraphic levels mentioned above incorporate abrupt changes in level due to fault displacements. Other elevation changes are caused by down-warping and possibly folding. Soft-sedimentary deformation or slump structures are frequently seen in core and contribute to the structural complexity. Slumping may have occurred due to movement along the fault planes during deposition while sediments were unconsolidated.

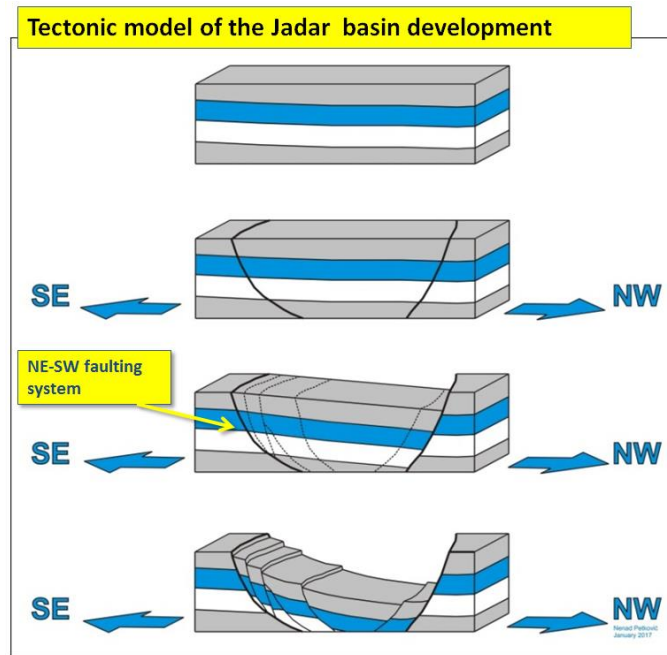


Fig. 3.1.2. Tectonic model of the Jadar basin development (Garcia et al, 2015).

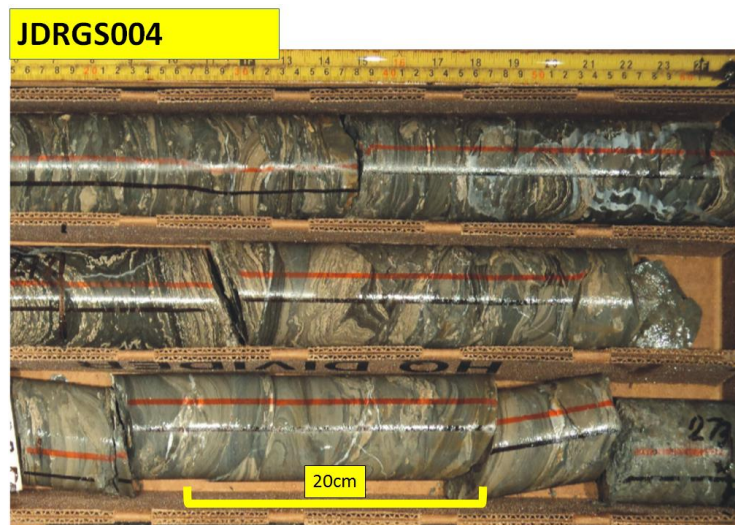


Fig. 3.1.3. Deformation of a laminate sequences as a result of prolonged seismic shock.

### Jadar deposit type

The deposit includes three types of mineralization that are of economic interest. They occur as stratiform lenses of variable thickness hosted in a much thicker gently dipping sequence of mainly fine-grained sediments that is crossed by faults.

Jadarite  $\text{LiNaSiB}_3\text{O}_7(\text{OH})$  mineralization comprises the bulk of the deposit. It is new to science and so far, unique to this deposit. The deposit type is also unusual and Jadarite appears to have formed within the sediments during sedimentation or early diagenesis from lithium and borate-rich fluids. Hydrothermal fluids may have played a role in supplying B and Li to the lake. Jadarite



occurs as clearly visible whitish micro-crystalline grains, nodules or concretions as illustrated next (Fig. 3.1.4).

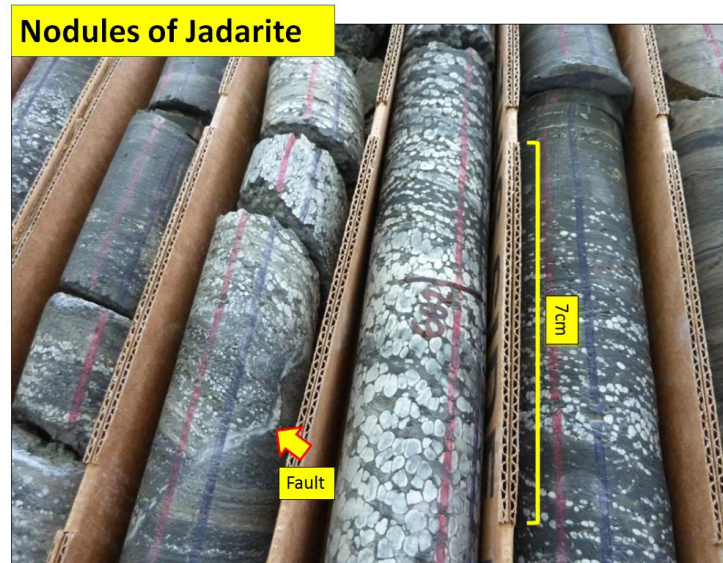


Fig. 3.1.4.: Grains and nodules of low to high-grade Jadarite in core. A fault can also be seen (Interpreter: N. Petković, 2013).

The Jadarite deposit is sub-divided in three gently dipping tabular horizons known as the Upper, Middle and Lower Jadarite Zones (UJZ, MJZ and LJZ), of which the LJZ contributes all the Mineral Resources reported so far (see Fig. 3.1.6.)

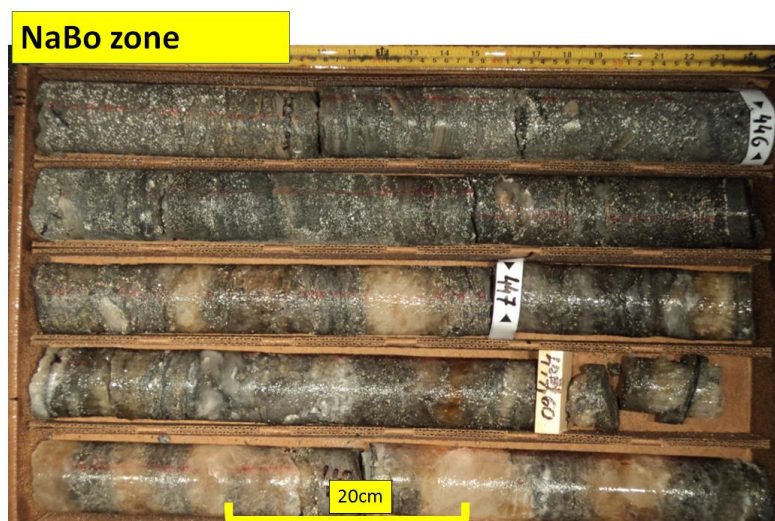


Figure 3.1.5.: NaBo Zone in hole JDR\_68. The hanging wall contact with jadarite mineralization is at 446.7m.

A smaller zone of sodium borates, featuring mainly the mineral ezcurrite ( $\text{Na}_4\text{B}_{10}\text{O}_{17} \cdot 7\text{H}_2\text{O}$ ) but also kernite ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ) and borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), is present enclosed within or adjacent to the LJZ. The zone is known as the NaBo Zone, from 'natrijski borati' the Serbian for sodium borates, and is apparently bounded by structures, in particular to the west.

Mineralization occurs in two or more lenses with reasonably clear upper and lower contacts. These lenses have relatively pure, translucent crystalline borate mineralization and are bounded by a mixed zone of one or two meters thick. An example of mineralized NaBo zone is shown in Fig. 3.1.5.

Gypsum zone lies above the Jadarite-bearing zones (Figs. 3.1.2, 3.1.6)

The mineralization is hosted in a sedimentary sequence of Miocene age dominated by calcareous claystone, siltstone, sandstone and clastic rocks, known as the Lacustrine Unit that is about 400 m to 500 m thick. This lies unconformably on a basement of Cretaceous rocks. It dips to the north at between 0 and 25 degrees or more, but typically between 5 and 10 degrees. It includes several thin tuff beds that provide valuable marker horizons for stratigraphic correlation.

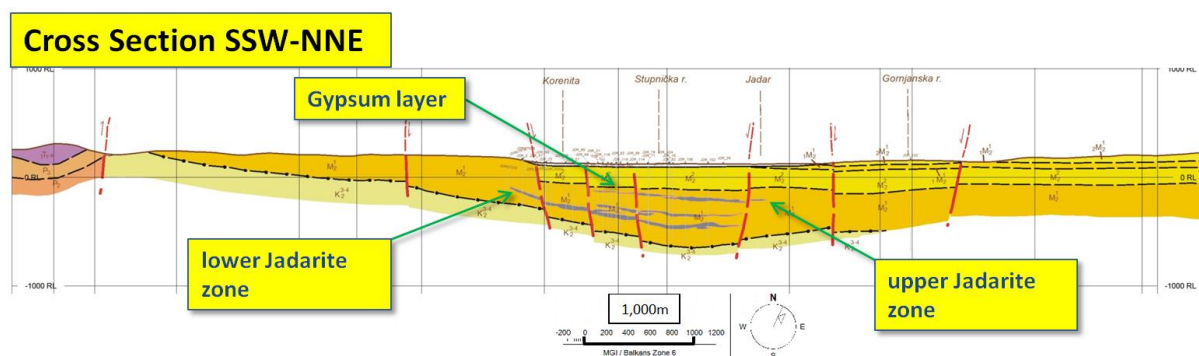


Fig. 3.1.6.: A cross-section parallel to the Formation dipping, and perpendicular to the graben axes (Misailović et al, 2013).

Mineralization is spatially related to the interpreted graben system, and is interpreted to have been introduced along a zone of enhanced structural permeability related to the graben system. As was seen by analyzing the core and other available collected data it is very possible that the ore body horizons follows the shape of asymmetrical synform or half graben structure. The entire settings can be introduced as a system of normal faults oriented to the central parts of deposit, along which the whole series, and therefore the ore bodies were deformed and brought to the recent positions.

The NaBo lenses are located in an area of about 900m x 300m at depths from 450m to 550m. Down-dip there is a second smaller, less defined area of NaBo.

### STOP 3. 2. THE DOBRILUOVIĆ BRDO QUARRY

Locality: 4 km southeast from Loznica

WGS84: 44° 30' 56.92" N, 19° 16' 04.08" E

Age: Middle Miocene – Early Serravallian (Upper Badenian)

The Middle Miocene Badenian transgression is one of the most important geological events which occurred in the Miocene. It left observable marks over the whole Central Paratethys, especially in the Pannonian Basin (Rögl, 1998; Harzhauser et al. 2003; Ćorić & Rögl 2004; Ćorić et al. 2004, 2009; Báldi, 2006; Latal et al. 2006; Kovač et al. 2007; Utescher et al. 2007; Harzhauser & Piller 2007; Piller et al. 2007; Rögl, et al., 2008; Hohenegger et al. 2009, 2014; Mandić et al. 2012). A lot of evidence pointing to a sudden change in the sedimentation regime was described on the southern margin of the Pannonian Basin especially (Krstić et al. 2012; Pezelj et al. 2013). The event was tentatively synchronous and occurred at the beginning of Badenian age but, in fact, it was at different times affecting a large area of Paratethys. Badenian Stage has widespread distribution in JB (Fig. 3.A) and consists of different facies and lithological units. Among them, the Leitha limestone is the most characteristic and widespread shallow-water carbonate unit both in JB and Serbia, as well as other part of Central Paratethys (Riegl & Piller, 2000; Rundić et al., 2013; Wiedl et al., 2012, 2013; Ali & Wagreich, 2017 and references therein). These shallow-water limestones in Central Europe are termed the Leitha limestones (name after the Leitha

Mountains, eastern Austria), a classical name that was already used during the 19th century (e.g. Eduard Suess in 1860, see in Ali & Wagneich, 2017). From that time up to now, the term is used as an informal name because it is not defined formally as stratigraphic unit according to modern stratigraphic codes (Salvador 1994; Steininger & Piller 1999 – In: Ali & Wagneich, 2017). Leitha limestone thus refers to Middle Miocene shallow-water carbonate units composed mainly of coralline algae and subordinate coral-bearing strata. The latter were defined originally as being reefs (Papp et al., 1978 in Ali & Wagneich, 2017), but later studies (i.e. Piller et al., 1996, 1997; Riegl & Piller, 2000 – see in Ali & Wagneich, 2017) confirmed that these carbonates are not reefal deposits *s. str.* but rather coral carpets such as at the type locality in the Leitha Mountains (Ali & Wagneich, 2017). Although a huge amount of palaeontological data is available for these limestones (e.g. Rundić et al., 2013; Ali & Wagneich, 2017 and references therein), the exact chronostratigraphic position of individual units of Leitha limestones remains unconfirmed yet. In fact, a middle to late Badenian (Langhian to early Serravalian) age was determined more recently (e.g., Wiedl et al. 2012, 2013; Hohenegger et al. 2014).

The Dobrilović brdo quarry is located in the area of ethno village Tršić, 4 km to the southeast of Loznica town. This large section represents a part of Badenian carbonate platform which is widespread in the southwest margin of Jadar basin (Fig. 3.1.). Tršić village is a birth place of the reformer of Serbian language Vuk Stefanović Karadžić (1787-1864).

The lithological column is over 25 m high and composed of dominantly redish-brown and creamy-white (when the quarry was active the white color was dominant), coarser grained, porous, pure/impure (limited by  $Al_2O_3$  contents above or below 0.43 wt. % - see Ali & Wagneich, 2017) calcareous sandy limestone made up of coralline algae, bryozoans and foraminifers (the basal part of section) in alternation with a hard, poor-bedded and massive fossiliferous limestone, fractured and partly carstified at the top of section (Fig. 3.2.2.).



Fig. 3.2.1. The Dobrilović Brdo quarry (Photo by Lj. Rundić).

In the creamy/whitish, sandy limestone algal and bryozoans sections dominated. Besides, some parts along the quarry section are deeply weathered and have disintegrated into intensely-colored yellowish to whitish sands. Within the coarse-grained, porous limestone there are blocks of hard fossiliferous limestone and contact between them is clear.

The limestone is determined as biocalcarenite and lithic biocalcarenite, depending on the composition. Fossil detritus is mainly composed of coralline algae, mollusks, echinoids, bryozoans, and large benthic foraminifers (Fig. 3.2.2. b,c,d). Scarce siliciclastic detritus comprises mainly quartz, and clasts of carbonates, quartzites, schists, and cherts, that are well rounded and range from 0.4 to 1 cm in size. Skeletal material is cemented with calcite.  $CaCO_3$  content varies

in range of 83 - 93%,  $\text{Al}_2\text{O}_3$  have wide distribution from 0.98 – 2.87 % and  $\text{Fe}_2\text{O}_3$  reaches from 0.60 to 1.70% (Sekulić et al., 2015).

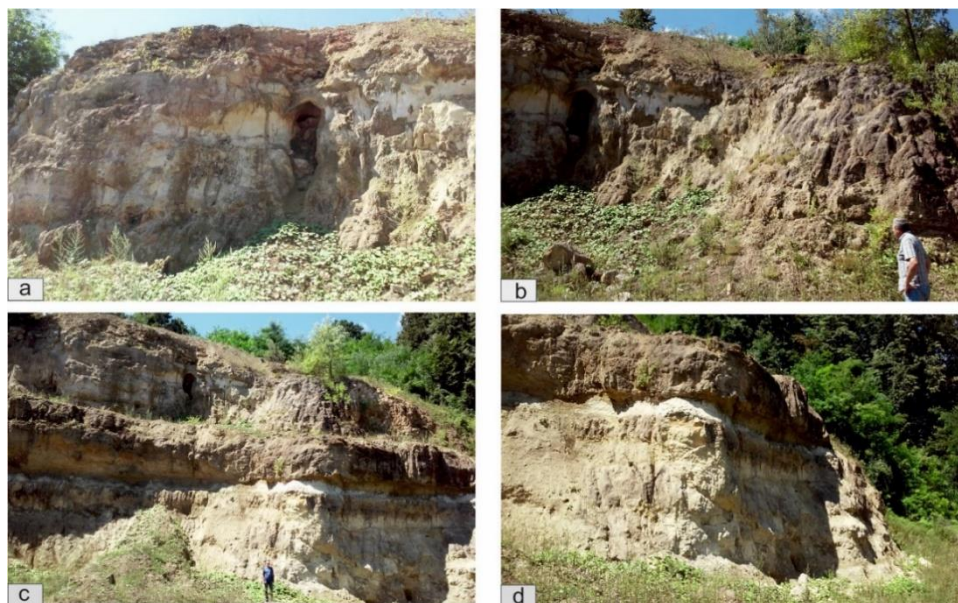


Fig. 3.2.2. Upper part of the section composed of bioclastic, molluscan limestone (a, b), and lower part of the section make more porous, coralline limestone (c, d) (Photo by Lj. Rundić).

The rich macrofauna such as molluscs (*Glycymeris pilosus*, *Flabellipecten besseri*, *Cardiocardita partschi*, and *Ostrea sp.* (cf. *Ostrea lamellosa*), and significantly less gastropods (*Conus sp.*, *Turritella sp.*, *?Hydrobia sp.*, etc.), bryozoans and scarce echinoids (i.e. *Clypeaster sp.*), has been identified. Numerous foraminifers (*Amphistegina sp.*, *Ammonia sp.*, *Borelis sp.*, *Planostegina sp.*, *Lobatula sp.*, *Textularia sp.* and others) have been found, indicating an early Upper Badenian age. Most of the mentioned foraminifers are bad preserved and partly recrystallized (Figs. 3.2.2.c,d). According to dominant fossil remains in the porous, sandy limestone the algal-foraminifer-bryozoan type of bioherm could be proposed (Rundić et al., 2013). In the origin of these deposits, intrabasin factors played a very important role, including huge organic production and high energy water regime (waves and currents). Based on the analyses of thin-sections, the facies comprises packstones and rudstones consisting of angular and subrounded coralline clasts. The corallineans are represented by *Lithothamnion*, *Mesophyllum*, and *?Neogoniolithon*. Sporadically, rhodoliths of coralline red algae are present. Bivalves and gastropods occur in variable quantities (*Ostrea sp.*, *Flabellipecten sp.*, *Aequipecten sp.*), as well as irregular echinoids and bryozoans which are represented by branching forms.

Elsewhere, rotaliid forms, such as *Amphistegina* and *Planostegina* represent the abundant foraminifers. The genus *Amphistegina* has common occurrence and can separate a separate biofacies – *Amphistegina* limestone (Fig. 3.2.3.). Recent *Amphistegina* inhabits the tropical to subtropical belt in shallow waters down to 70 m where it is primarily attached to macrophytes with high densities (Rundić et al., 2013 and references therein). Its presence implies a minimum water temperature of 17°C (Wiedl et al., 2012, 2013). Some living *Planostegina* inhabit commonly water depths between 15 and 45 m, while others have highest abundances below this depth (Hohenegger et al. 2014 and further references therein). In summary, the *Amphistegina* subfacies has been formed in a shallow, sublittoral environment with a depth range of ca. 20–30 (Wiedl et al., 2012). As well, the bryozoan subfacies could be separated within the lower part of section (Fig. 3.2. 3.). It consists of poorly sorted, densely packed rudstones. They are dominated by debris of fruticose and encrusting corallineans (ca. 3–5 mm). Branched or celleporiform bryozoan colonies (~ 1-2 mm) are abundant. The bryozoans often form bryoliths up to 40 mm in diameter, occasionally encrusted by *Acervulina* (Wiedl et al., 2012). Somewhere, *Thalassinoides* burrows are visible. Foraminifers are represented by common biserial textularids, rotaliids (*Amphistegina*).

Molluscs are characterized by represents of pectinids and ostreids. The subfacies is associated with the Amphistegina subfacies. The formation of bryoliths is comparable to that of rhodoliths and similar hydrodynamic conditions can be assumed (Rundić et al., 2013 and references therein). The sphericity in bryoliths is thought to be in part related to the turning frequency interpreted similar sediments as shallow deposits with sufficient water energy for rhodolith movement (Riegl & Piller, 2000; Wiedl et al., 2012, 2013). A depth range from 20-30 m is proposed (Rundić et al., 2013; Wiedl et al., 2013). Modern analogues are found on the Apulian shelf along the shore in range of 10–30 m water depth (Wiedl et al., 2013).

A mollusk subfacies (Fig. 3.2.3.) is identified in the poor-bedded and massive corralinacean limestone (predominantly rudstones) that is characterized by high amounts of different molluscs. Mollusk shells are commonly encrusted and often strongly bioeroded before or after encrustation. Furthermore, foraminifers are represented by rotalids (i.e. Amphistegina), biserial textularids, and sporadic miliolids. Bryozoans are rare. Bivalves are represented by ostreids (e.g. fragments of *Hyotissa hyotis* and *Ostrea*), pectinids (*Flabellipecten besseri*, *Aquipecten* sp.), cardids (*Cardium* sp.), venerids (*Periglypta miocaenica*), glycymeridids (*Glycymeris* cf. *deshayesi*) and lucinids (? *Codakia* sp.). Pectinids are usually disarticulated and randomly distributed. Other small bivalves are commonly articulated and preserved in situ. Gastropods are mainly represented by *Conus* sp., *Cerithium* sp., *Turritella* sp., etc. Irregular echinoids are relatively well preserved (Fig. 3.2.3.d). There are observed similar mollusk associations from the modern Red Sea (i.e. Zuschin & Hohenegger, 1998; Wiedl et al., 2013). Therein, turritellids are widely distributed on soft and hard substrates, muddy sediments, and on the reef slope down to 40 m; cerithiids show distinct habitat preferences and occur in water depths between 1 and 40 m with common occurrences between 5 and 30 m. *Glycymeris* is documented from sands between coral patches in depth of ca. 10 m (Zuschin & Hohenegger, 1998; Zuschin et al., 2009). Aside from subtropic faunal elements, modern analogues are coralline algal deposits in the bays of Naples and Pozzuoli in the Mediterranean area (Wiedl et al., 2012, 2013).

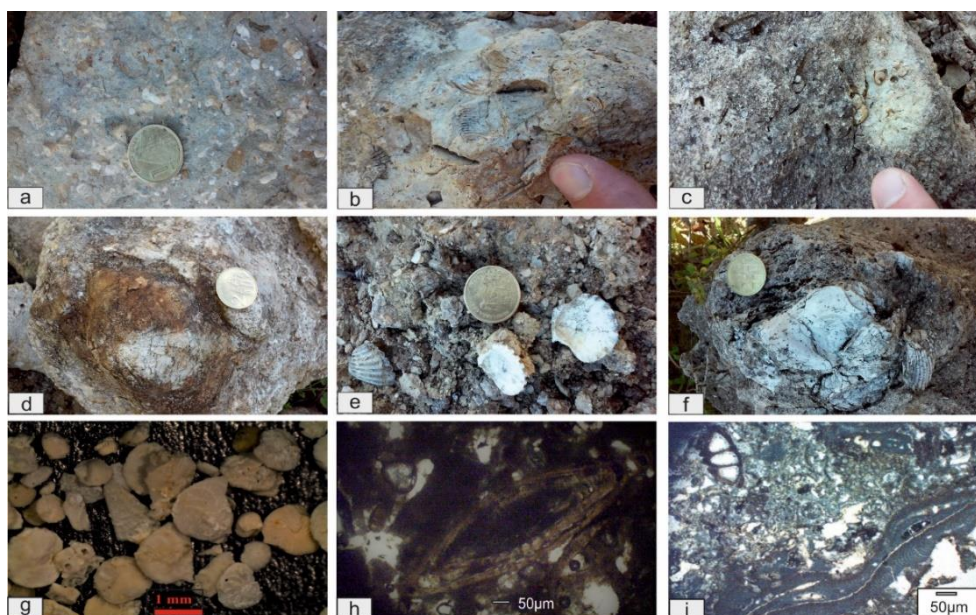


Fig. 3.2.3. (a-i). Rocks, fossils and facies. (a). Coarse-grained fossiliferous limestone with dominant mollusks fragments, (b,c). Different mollusks remains, shell molds and imprints within the rock (*Venus* sp., *Turritella* sp., *Cerithium* sp., (d). partly damaged form of fossil echinoid *Clypeaster* sp., (e). Small disarticulated specimens of pectinids, (f) A large Ostreid shell and other small form of the cardids, (g) A microfaunal assemblage contains rotalid foraminifers (*Amphistegina* sp.), textularids, bryozoan branches, etc., (h). *Amphistegina* sp., (i). Coralline red algal fragments (?*Neogoniolithon* sp.), bryozoan colony, ostracods, and other rotalid foraminifers.

Based on all the mentioned characteristics of the limestone, especially its chemical features, at the beginning of century, the quarry starts to produce the small class and limestone dust to improve the quality of acidic soils (Sekulić et al., 2015).

#### 4. VALJEVO-MIONICA BASIN

A lot of Neogene-age, typically north–northwest and south–southeast oriented basins were formed in Serbia in intramontane (Intra-dinaridic) valleys and grabens between horst blocks, tilted blocks, and half-grabens, which were created as a result of tectonic activity (Fig. 4.1). Such basins can be characterized by alluvial, swamp, lacustrine, or marine-brackish and brackish facies. Typically, the marine basins display a lower rate of sedimentation than do the lacustrine basins. Lacustrine basins are generally shallower and smaller than marine basins, but can also display low sedimentation rates that can give rise to coals and oil shales, or some non-metallic raw material (Kilpatrick, 2010).

Valjevo-Mionica Basin (VMB) is situated in the western part of Serbia, covering an area of 350 km<sup>2</sup> and represents the western part of the Valjevo-Mionica-Belanovica Graben (Fig. 4). The graben was formed during the Otnangian-Karpatian and later was inverted (Marović et al., 2007). Based on geophysical data, Neogene continental- lacustrine and marine-brackish sediments may reach thicknesses of as much as 1000 meters in the center of the basin (e.g. Obradović & Vasić, 2007; Kilpatrick, 2010; Lazarević et al., 2013). Generally, there are different opinions concerning the age of the basin infill. A few authors classified those sediments as the Middle to Upper Miocene sedimentary succession (Filipović et al., 1971, 1978; Stevanović et al., 1977). However, based on the fossil assemblages of freshwater mollusks, ostracods as well as fish and flora remains found within the oldest sediments in the western part of the basin, some authors suggest the Lower Miocene age - Egerian-Egenburgian (Dolić, 1984) or Egenburgian-Otnangian (Anđelković & Anđelković, 1985; Anđelković et al., 1991). Still, there is no other independent age control such as radiometric and magnetostratigraphic data. Following Miocene sedimentation over Paleozoic and Mesozoic basement rocks was primarily lacustrine with occasional flow of salt water during Badenian times (i.e. Anđelković et al., 1991; Jovanović et al., 1994; Obradović & Vasić, 2007) and sporadic deposition of sediments with marine-brackish and brackish-freshwater fauna during Sarmatian and Pannonian times (i.e. Filipović et al., 1971, 1978; Anđelković, 1978; Dolić, 1983, 1984, 1995).

Six different formations have been identified within the range of Lower - Upper Miocene: 1) Mionica Fm. (lacustrine, pyrobituminous), 2) Valjevo Fm. (lacustrine, marly), 3) Tabanović Fm. (lacustrine, clastic), 4) Mađarlija Fm. (marine-brackish, carbonate-clastic), 5) Vračevići Fm. (brackish, marly), and 6) Bogovađa Fm. (terrigenous) (Jovanović et al., 1994; Obradović & Vasić, 2007; Lazarević et al., 2013). There are no gradual transition between the lacustrine and marine sediments and the Sarmatian sediments and tuffites transgressively overlying the older lacustrine deposits (Jovanović & Dolić, 1994; Dolić, 1995; Lazarević et al., 2013). Eastern part of VMB between Toplica and Ljig Rivers (Mionica area) is characterized by brackish deposits of Sarmatian and Pannonian (Middle/Upper Miocene). Western part of VMB in the Valjevo surrounding is filled by lacustrine Lower Miocene sediments with a lateral facial variability from marl with oil shale beds and tuff intercalations, sandstone, mudstone to limestone with gravel. Further to north, there are Pannonian brackish deposits of a coastal sedimentation with evident cross-bedded sediments. Quaternary alluvial and deluvial-proluvial deposits are widely distributed at the surface of the basin area (Fig. 4.1.).

VMB is considered as one of important areas in Serbia in terms of quality and geologic reserves of oil shales (Ercegovac, 1990; Šajnović et al., 2008, 2009). The most important oil shale deposits are located in the central part of the basin (Sušeočka and Radobićka Bela Stena). The kerogen content in oil shales ranged from 8 - 16 % (Ercegovac, 1990). The average oil yield of 6.3 % is of economic value (Šajnović et al., 2009).

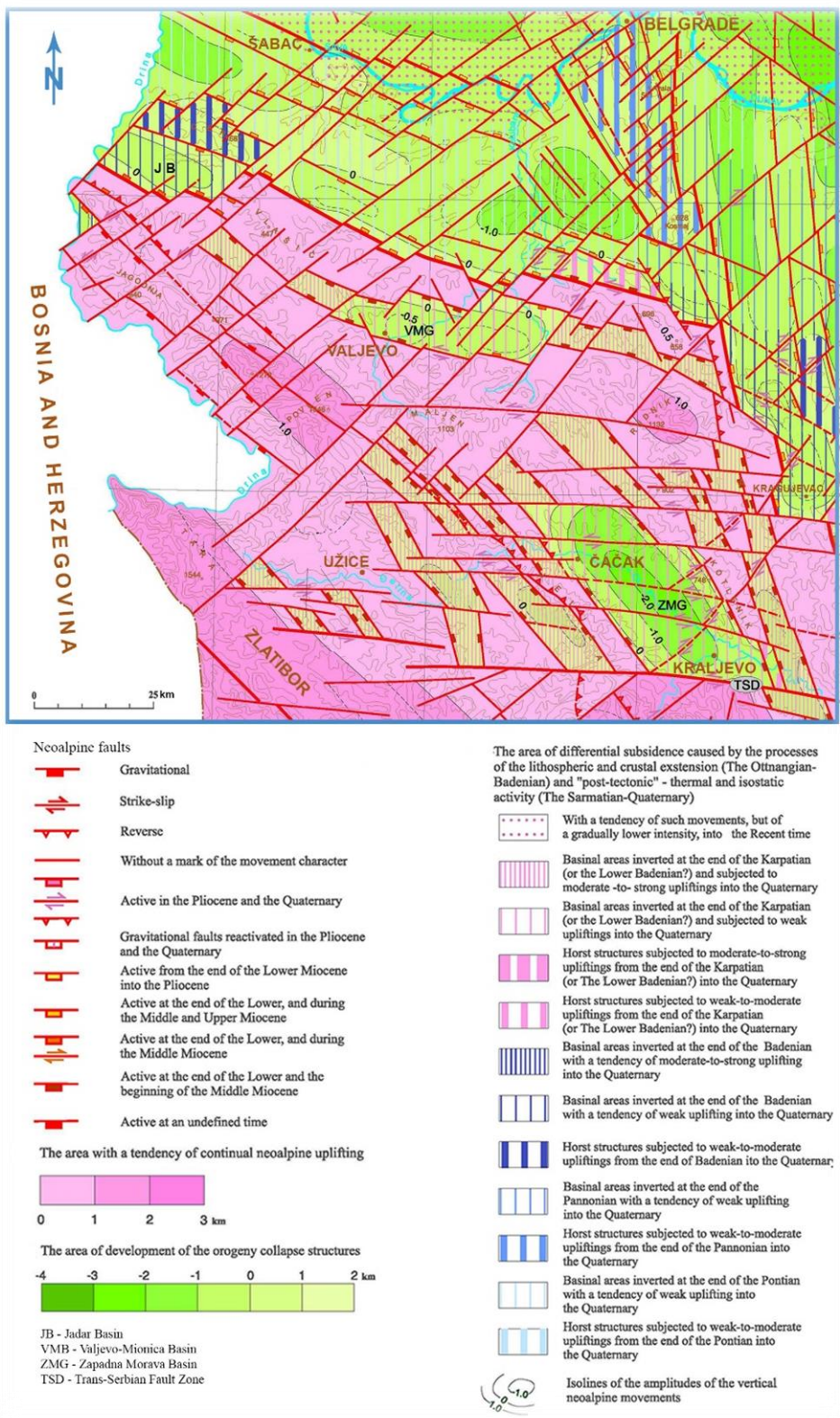


Fig. 4.1. A part of the Neoalpine tectonic map of Serbia and position of the main intramontane basins within the Circum-Pannonian realm (Marović et al., 2007 – slightly modified).

The organic substance is mainly concentrated in lamina of different thickness, which indicates the specific conditions of the sedimentation with very prominent seasonal changes in one lacustrine environment (Šajnović et al., 2008, 2009). According to these authors, there are no crucial differences in the contents of main inorganic components SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and TiO<sub>2</sub> and

contents of macro elements CaO and MgO. The relatively narrow ranges of the values of the mentioned inorganic parameters indicate a calm depositional environment, without prominent turbulences and erosion activities. The most important differences were registered in the content of Na<sub>2</sub>O, in the main elements, and the contents of arsenic and boron, in microelements, which indicate that genesis of the investigated sediments was followed by climate changes and volcanic activity (Šajnović et al, 2008). According to analyses of upper part of the borehole section, it seems that an arid climate was predominant, the result of which was significant increase of the salt content in the basin. This increase in salinity contributed to significantly better preservation of the organic matter and led to the formation of the mineral searlesite due to the interaction of alkaline, sodium-rich saline waters with a source of boron, i.e. volcanic glass. The native organic substance of the sediments which, was preserved to a great extent, originated mainly from algal precursor organisms with no significant contribution of terrestrial higher plants, which provided good quality and high potential for generating liquid hydrocarbons (kerogen type I, mixture of kerogen I/II and kerogen type II). It was deposited under reducing conditions and is at a low level of maturity in the phase of intensive diagenetic processes (Šajnović et al., 2008).

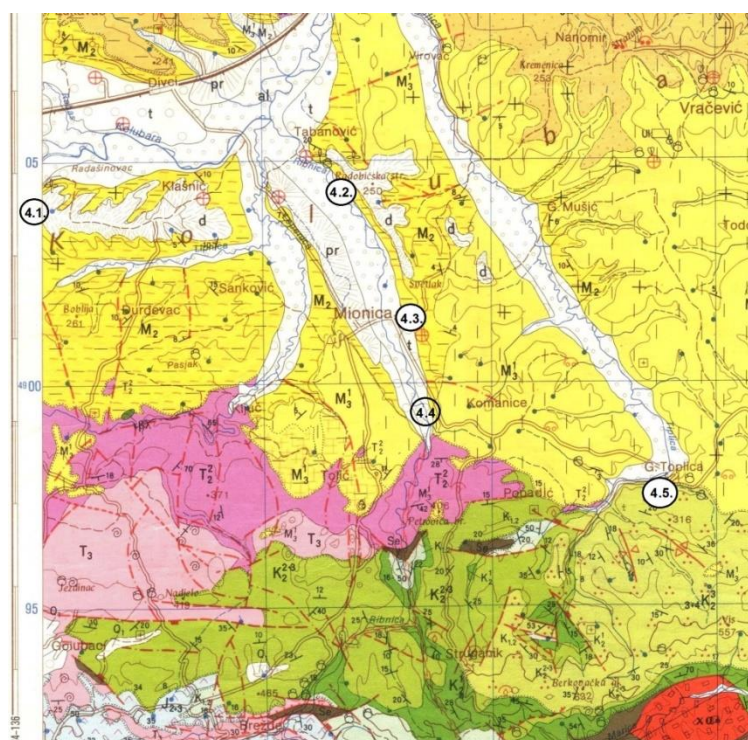


Fig. 4.2. Geological setting of the Valjevo-Mionica basin (VMB) according to Basic geologic map, 1: 100,000, sheet Gornji Milanovac (Filipović et al., 1971) and location of the field stops. For legend, see Fig. 3.1.

## STOP 4.1. ŠUŠEOČKA BELA STENA

Locality: 7 km east of Valjevo

WGS84: 44°16'36.30" N, 19°59'27.71" E

Age: Lower Miocene – Late Aquitanian - Early Burdigalian (Eggenburgian?)

One of the very famous geological points in VMB area is so-called the Šušeoka “white rock” section. This section represents the best exposure of the Mionica pyrobituminous formation, the oldest one in the VMB (Dolić, 1983, 1984, 1995, 1998; Anđelković et al., 1991; Jovanović & Dolić, 1994; Jovanović et al., 1994; Savić & Krstić, 2003; Marović et al., 2007; Obradović & Vasić, 2007; Kilpatrick, 2010; Lazarević et al., 2013 - Figs. 4.1.1, 4.1.2).





Fig. 4.1.1. The Šušeoka “white rock” section. A part of lithological succession with oil shale, tuffs and lenses of searlesite (above), detail of oil shale with organic accumulation (middle) and organic rich lamina and, fossil plant *Glyptostrobus* cf. *europaeus* (Brogniart) Unger (below).

It comprises a mixed succession of sands and silty sands, which progressively increase in clay and calcium carbonate content, and contain laminations of oil shales and searlesite (a sodium borosilicate mineral). Within this 25 m thick section, almost all the rocks contain organic matter (Figs. 4.1.1a,b). Similar lithological succession is observed in nearby borehole Val-1 (Šajnović et al., 2008). Therein, from the surface to the 200 m deep succession, there is transition of oil shale, relatively rare thin beds or lenses of sandy siltstone and laminated shale, marlstone (dolomitic, sandy and clayey as well as tuffaceous), tuff, lenses enriched with searlesite and analcite and limestone with chert concretions. Another sedimentary interval underlying oil shale series is from 200 to 400 m depth. These sediments are represented by marlstone (dolomitic, sandy and clayey as well as tuffaceous), lenses of carbonates, siltstone, tuff and pyrite (Obradović et al., 1994; Šajnović et al., 2008). The thickness of the formation ranges from 150 to almost 300 m, depending on the paleorelief (Dolić, 1984, 1998).

The organic substance is mainly concentrated in lamina of different thickness (Figs. 4.1.1, 4.1.2), which indicates the specific conditions of the sedimentation with very prominent seasonal

changes in one lacustrine environment (Šajnović et al., 2008, 2009). According to these authors, there is no crucial differences in the contents of main inorganic components  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and  $\text{TiO}_2$  and contents of macro elements  $\text{CaO}$  and  $\text{MgO}$ . The relatively narrow ranges of the values of the mentioned inorganic parameters indicate a calm depositional environment, without prominent turbulences and erosion activities. The most important differences were registered in the content of  $\text{Na}_2\text{O}$ , in the main elements, and the contents of arsenic and boron, in microelements, which indicate that genesis of the investigated sediments was followed by climate changes and volcanic activity (Šajnović et al., 2008). According to analyses of upper part of the borehole section, it seems that an arid climate was predominant, the result of which was significant increase of the salt content in the basin. This increase in salinity contributed to significantly better preservation of the organic matter and led to the formation of the mineral searlesite due to the interaction of alkaline, sodium-rich saline waters with a source of boron, i.e. volcanic glass. The native organic substance of the sediments which, was preserved to a great extent, originated mainly from algal precursor organisms with no significant contribution of terrestrial higher plants, which provided good quality and high potential for generating liquid hydrocarbons (kerogen type I, mixture of kerogen I/II and kerogen type II). It was deposited under reducing conditions and is at a low level of maturity in the phase of intensive diagenetic processes (Šajnović et al., 2008). On the other hand, it is proposed that increased salinity was favourable for planktons and algae.



Fig. 4.1.2. A composite lithostratigraphic column at the Šušeočka Bela Stena section. Key: I – marginal facies, II – intra-basinal facies, and III – shallow water facies with opal CT (Obradović et al., 1994 – In: Obradović & Vasić, 2007 – slightly modified).

## THE RIBNICA RIVER SECTIONS

The Ribnica River is cutting the Lower Miocene lake sediments. These deposits belong to the Valjevo Formation, the most distributed Miocene rocks in VMB. Stratigraphically, Valjevo Fm. corresponds to the late Lower Miocene (Ottangian-Karpatian). It overlies different rocks of the Mionica Formation (Dolić, 1995, 1998; Savić & Krstić, 2003, Obradović & Vasić, 2007). Generally, along the Ribnica River stream, three paleoenvironment could be recognized: lentic sublittoral, thermocline belt and profundal laminites (Savić & Krstić, 2003). In the southern part, close to the

Triassic basement, in the Paštrić village area (Stop 4.4), lacustrine sediments are made of massive chalky beds alternating with laminated chalk and marl. Massive chalk contains poor findings of freshwater mollusks (different forms of family Dreissenidae) which were recognized in the earlier references as “Congerian beds” (Filipović et al., 1978; Jovanović et al., 1994; Dolić, 1995, 1998). Also, scarce remains of freshwater gastropods were recorded (*Gyraulus* sp., *Prososthenia* sp, etc.) Besides, relatively numerous ostracod valves (dominant forms of subfamily Candoninae) are bad preserved. Within the laminated marls no fossils were found. In this part of VMB, fine calcium carbonate particles were deposited in calm water under influence of floating plants (massive beds) (Krstić & Popović, in: Savić & Krstić, 2003). Due to the lake level oscillation the environment changes and becoming more deep so the laminated chalk has been deposited during the seasonal variation: grey laminae indicate to spring input of clay and white laminae to restricted wave action during the summer periods (Savić & Krstić, 2003, Obradović & Vasić, 2007).

## STOP 4.2. RADOBIČKA BELA STENA

Locality: Tabanović village, 4 km north from Mionica

WGS84: 44°17'07.68" N, 20°04' 20.09" E

Age: Lower Miocene: Late Aquitanian - Early Burdigalian (Eggenburgian?)



Fig. 4.2.1. The Mionica Fm. Upper part of a cliff section at the southwestern slope of Radobić hill (above, left) and light-greyish thin-bedded and platy marls at the basal part (above, right and in middle). In the basal part (below, left), fish skeleton (courtesy by Katarina Bradić) and fossil leaves (below, right) of *Daphnogene polymorpha*, *Pinus tadaeiformis* and *Glyptostrobus europaeus* have been found (by courtesy of Vladimir Mijatović, from his Diploma work, 2007).

Along the Ribnica River stream, some 2 km downstream of Mionica, there is the large section of profundal laminites (Savić & Krstić, 2003). They are oil rich, with well-preserved fossil algae *Botriococcus* within it. The oil rich laminae alternate with laminae without oil (Ercegovac, 1990, Savić & Krstić, 2003). From the basal part to the top of large outcrop (up to 40 m height), two main type of deposit can be recognized. At the bottom part (the first 4 meters of the section), there are layers of gray thin-bedded marls and sandy, laminated marls in alternation. Within the bottom part, relatively scarce finding of fossil fishes are recorded (Fig. 4.2.1). There are no oil rich laminae in this part of the section. However, in the upper part of outcrop, more oil rich laminates and greyish, thin (somewhere only few mm thick laminites) marls and tuffitic layers were recorded. They contain abundant fossil plants and leaves with dominance of *Glypto-strobus*, *Sequoia*, *Daphnogene*, etc. (Lazarević et al., 2013) - Fig. 4.2.1.

### STOP 4.3. THE MIONICA BRIDGE

Locality: Mionica municipality centre

WGS84: 44°15'16.78" N, 20°05'16.38" E

Age: Lower Miocene - Late Burdigalian (Ottangian-Karpatian?)

A few kilometres more to the south from the previous stop, in the Ribnica river banks below the Mionica Bridge there are relatively small outcrops of the Valjevo Formation (Fig. 4.3.1.). Herein, there is no record about nature of contact to the Mionica formation. However, based on data published by Jovanović et al. (1994), there is a gradual transition between them. More downstream from the bridge, the bedding planes in the thin-bedded silt and marl covered by ostracodes valves. It is supposed that such a feature indicates the position of the thermocline in former lake (Savić & Krstić, 2003).



Fig. 4.3.1. The Valjevo Formation. The three different images of the Ribnica river shoreline with exposed the massive silty clay and silts (bottom part, above) and more laminated chalk and marl (above, right and below).

The sublittoral of subtropic modern lake (e.g. south-eastern shore of the Caspian Lake where the Kara-Kum desert approach it) are subject of evaporation. More dense water body seeps down the sublittoral bottom toward profundal. When seepage stucks the thermocline its speed lessen and ostracode valves and shells fall down in the slow flising mineralized water (Savić & Krstić, 2003). The size of valves and carapaces is nearly equal and deposition position was fixed to the stabile lated by the wave action (Savić & Krstić, 2003). Among ostracods, the characteristic species *Ochridiella? sabantae* Krstić, 1974 with „saddleback“ at the dorsal part of carapace has been found. This feature could be indication of increased mineralization of lake water (Savić & Krstić, 2003). Still, more detailed study of these fossils has not been made (Jovanović & Krstić, 2010; Jovanović, 2012).

#### STOP 4.4. PAŠTRIĆ

Locality: Paštrić village, 3 km south of Mionica

WGS84: 44°14'01.51" N, 20°06'00.19" E

Age: Lower Miocene - Late Burdigalian (Ottangian-Karpatian?)

Only few kilometres upstream of the Ribnica river, close to the basin margin and boundary with Mesozoic basement, numerous small outcrops within the river bottom and its banks can be observed. During the low water level, very fine, silty clay and platy marls at the river bottom are exposed. Laterally, laminated grayish sandy marl with intercalation of chalky marls have been observed in the river banks (Fig. 4.4.1). This whitish chalk contains poor findings of freshwater mollusks (different forms of family Dreissenidae) which in the earlier references were recognized as “Congerian beds” (Filipović et al., 1978; Jovanović et al., 1994; Dolić, 1995, 1998). For example, these freshwater species were determined as *Congeria* ex. gr. *andrussovi* Rzehak, *C.* ex gr. *jadrovi* Brusina, *Prososthenia* cf. *zujovici* Brusina, *Neritodonta* ex. gr. *sinjana* Brusina, *Pisidium* sp., *Lymnaea* sp., etc. (Dolić, 1995). Besides, numerous bad preserved ostracod valves (dominant forms of subfamily Candoninae) have been found. Within the laminated marls there are no fossils records.



Fig. 4.4. The Ribnica river shoreline with exposed silty clay and platy marl (bottom part, left) and a whitish chalk interbed within the marly succession (right).

## STOP 4.5. VODAVODA - WATER PRODUCTION AND BOTTLING

Locality: Vrujci spa, 10 km from Mionica

WGS84: 44°13'28.48" N, 20°09'52.83" E

Artesian aquifer: Upper Cretaceous limestone as main water collector

VODAVODA is one of the newest brands on the Serbian and world market of bottled water. Although the story of VODAVODA begins at the beginning of this millennium, the latest production started just a few months ago. In fact, the bottling of the underground water of VODAVODA started in June in the newly opened Water House. The water comes from the area of Vrujci spa, a real gem of this region thanks to the hot springs, slightly mineral and radioactive, calcium-magnesium water which is used to treat rheumatism, arthritis and infertility. Vrujci spa has earned the epithet of the spa that heals. VODAVODA comes from the depth of 605 m and pass through the different geological formations - Upper Cretaceous carbonates, Upper Cretaceous flysch, Neogene and Quaternary sediments (Brkić, 2015). Upper Cretaceous limestone is intensively karstified and represents hydro-thermal collector of water under pressure. The water, bottled practically directly from the well, keeps authentic purity without any processing and supplements. The VODAVODA is a unique bottling plant, whose modern world production technology allows working in almost perfect conditions, in which there is no pollution of the natural environment.

The latest analyses of VODAVODA water were performed in a biological-chemical laboratory "Labor-Ritter" in Detmold, Germany, and the Institute of Public Health of Serbia "Dr Milan Jovanovic Batut". Studies have shown that the composition of water is optimal, that it possesses an ideal balance of minerals and salts, which is completely similar to the composition of the blood plasma of the human organism. The perfect water characteristics of water enable its unlimited consumption in its original form and everyday use.

In an unusual and original square bottle, you can look for VODAVODA water in PET bottles of 1.5l, 0.5l, as well as glass non-returnable packaging of 0.33l. Except in Serbia and nearby countries, VODAVODA has market in Middle East and Asia.



Fig. 4.5.1. The unusual square shape of the VODAVODA bottles

VODAVODA is natural mineral water, aseptic, without colour, odour and taste, clear, with average temperature of around 30 degrees. VODAVODA belongs to the category of neutral water (pH 7.2), there is very little presence of organic matter. In anionic composition, ions of bicarbonate ( $\text{HCO}_3^-$ ) dominated, with concentrations between 314 and 390 mg/l. In the second place are sulphate ions ( $\text{SO}_4^{2-}$ ) with contents from 5.6 to 12.2 mg/l, followed by chloride ions with contents ranging from 2 to 10 mg/l. Based on this, hydrocarbons give the basic characteristic of water. In the cationic composition, ions of calcium ( $\text{Ca}^{2+}$ ) are dominant with concentrations of 43.6-78.6 mg/l. The average calcium content ( $\text{Mg}^{2+}$ ) ranges from 13.2-18.0 mg/l, and sodium ( $\text{Na}^+$ ) of 10.2-18.8 mg/l.

Among other physical - chemical parameters of groundwater springs of the VODAVODA, there is no observed deviation from the maximum allowable concentration. Content of nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) in the wells is far below the required limits.

Based on all analyses, VODAVODA belongs to the categories of natural mineral waters with a low content of soluble mineral matter, containing 50 mg/l to 500 mg/l of mineral salts, calculated as a dry residue at 180 °C, and according to the predominant ionic composition, water is characterized as hydrocarbonate-calcium-magnesium water (Petrović et al., 2012; Brkić, 2015).

## 5. PRANJANI BASIN

Pranjani Basin is located in the western Serbia and covers an area of 45 km<sup>2</sup> (Fig. 5.1). The basin was developed at the limit between Western Vardar Ophiolite and Jadar – Kopaonik Units (Fig. 1.1, e.g., Dimitrijević, 1997; Karamata, 2006; Schmid et al., 2008). Therefore, the ophiolites and associated ophiolitic mélangé often interrupted by magnezite veins are dominant lithologies in the paleorelief (Brković et al., 1970; Filipović et al., 1971). Only, the north-eastern basin margin is made of Upper Permian terrigenous clastics, Lower to Middle Triassic carbonates, volcanics and volcanoclastics (e.g., Brković et al., 1970; Filipović et al., 1971, Dimitrijević, 1997).

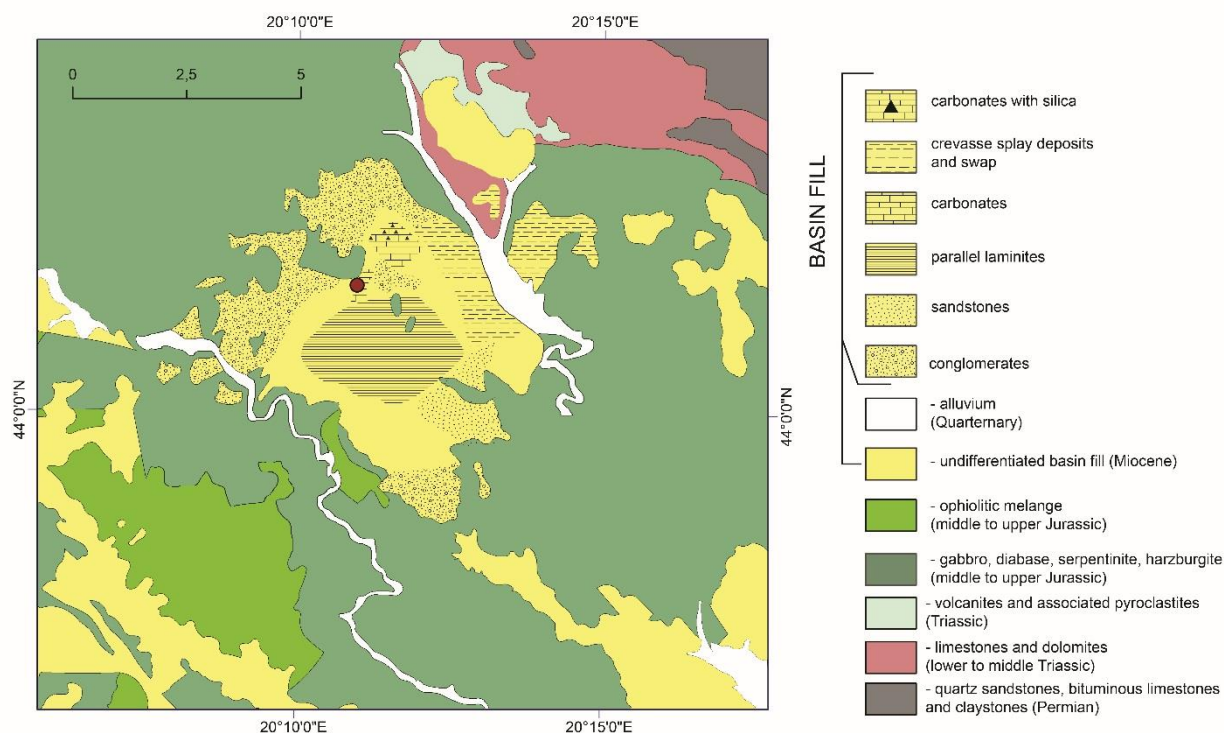


Figure 5.1. Geological map of Pranjani Basin (modified after Brković et al., 1970; Filipović et al., 1971; Đurđević, 1992).

The sedimentary successions in Pranjani Basin comprises two sedimentary cycles. The older sedimentary cycle (i.e. Kamenica series of Anđelković et al., 1991, Fig. 5.2) is of Eggerian age. This cycle is characterized by alluvial clastics, breccia and conglomerate deposited along the active NW basin margin. These sediments laterally grade into sandstone, claystone and bituminous marlstone occasionally intercalated with tuffs. It contain fish remains (*Smerdis minutus Blainville*, Anđelković, 1989). The alteration of volcanic glass and formation of analcime indicated saline and alkaline character of diagenetic fluids developed in arid-semiarid climate (Đurđević, 1992).

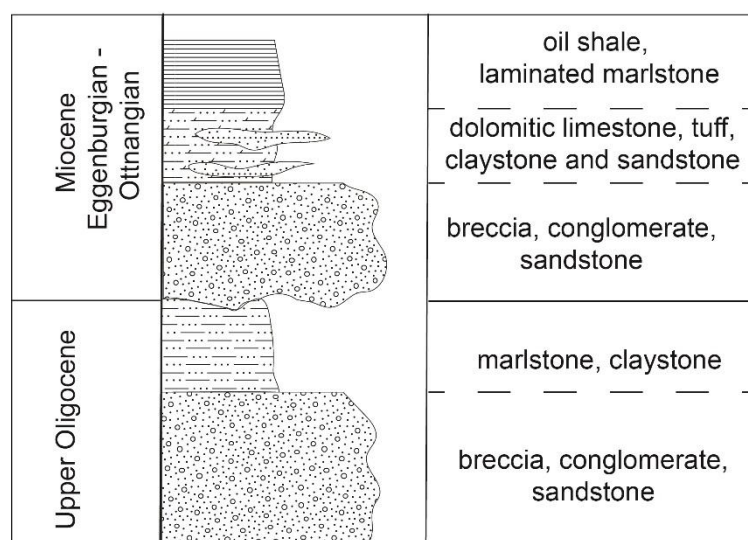


Figure 5.2. Depositional cycles in Pranjani Basin (Anđelković et al., 1991).

The younger sedimentary cycle (i.e. Čačak series of Anđelković et al., 1991) is Eggenburgian-Ottnangian age. This cycle comprises of sediments of alluvial fan, marginal-lacustrine and intrabasinal facies which are distinguished from previous cycle by the presence of sedimentary magnesite, sepiolites and dolomites (Đurđević, 1992; Obradović *et al.*, 1997; Simić et al., 2012; Suarez Barrios et al., 2014). The intrabasinal lacustrine facies often include fish remains: *Clupea humilis* H. V. Meyer; *Aspius elongates* H. V. Meyer; *Alosa aff. normani* Antipa; *Lepidocottus brevis* (Agassi Z.) (Anđelković, 1989).

## STOP 5.1. SEPIOLITE-BEARING SUCCESSION

Locality: Andrići, Plana river, 22 km west of Gornji Milanovac town

WGS84: 44°1'32.82"N, 20°10'39.57"E

Age: Lower Miocene

The outcrops of the sepiolite-bearing succession are exposed in the Plana river in the central part of the Pranjani basin (Fig. 5.1). This succession was deposited during younger sedimentary cycle i.e. Čačak series of Anđelković et al., (1991) in the marginal lacustrine environment with sporadic alluvial influence (Đurđević, 1992).

The base of succession is characterized by matrix-supported, poorly sorted breccia-conglomerates, sandstones and claystones which lay directly on diabases in the basement (Figs. 5.1.1 and 5.1.2a). The nature and angularity of pebbles and isolated cobbles suggest short transport of material derived from ophiolites. The distal alluvial fan deposits are overlain by palustrine to marginal lacustrine deposits which comprise of alternation of dolomitic claystone and claystones interrupted by one layer of sepiolites (Figs. 5.1.1 and 5.1.2b). In the palustrine to marginal lacustrine deposits, sepiolite is the main mineral and it appears from ~50% to 80% with the exception of the sepiolite level in which there are almost no impurities such as dolomite and trioctahedral smectite typical for dolomite, dolomitic claystone and claystones, respectively.



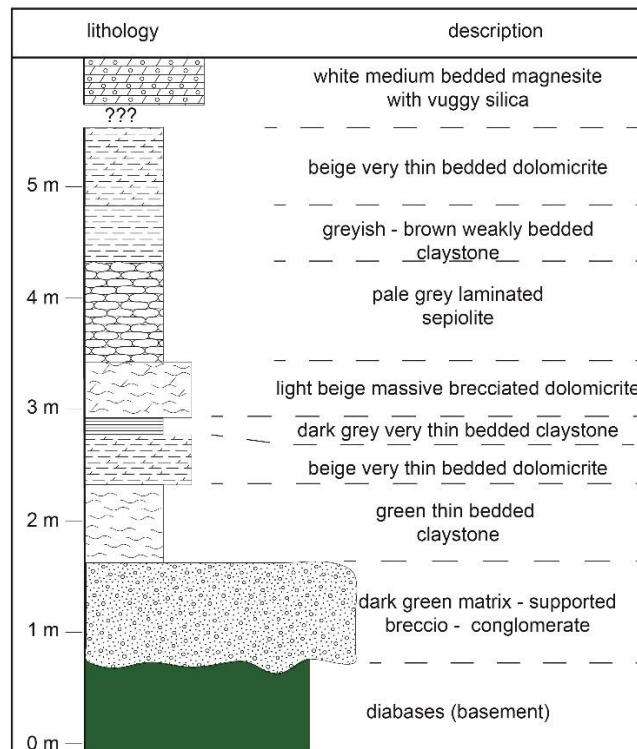


Figure 5.1.1. Sedimentary log of sepiolite-bearing sequence in Pranjeni Basin.



Figure 5.1.2. a) Cobbles to pebbles matrix supported conglomerates at the base of the succession; b) sepiolite bearing succession.

The sepiolite level is made of fibres which are often grouped in bundles which directly crystallized from water column in Si- and Mg-rich ponds or shallow lacustrine environment under arid conditions (Fig. 5.1.3a; Simić et al., in prep). In other levels sepiolites are usually randomly

oriented engulfing dolomites (Fig. 5.1.3b), or intimately coalesced with smectites. The latter may suggest that sepiolite could grow from the smectitic precursor (Suarez Barrios et al., 2014; Simić et al., in prep).

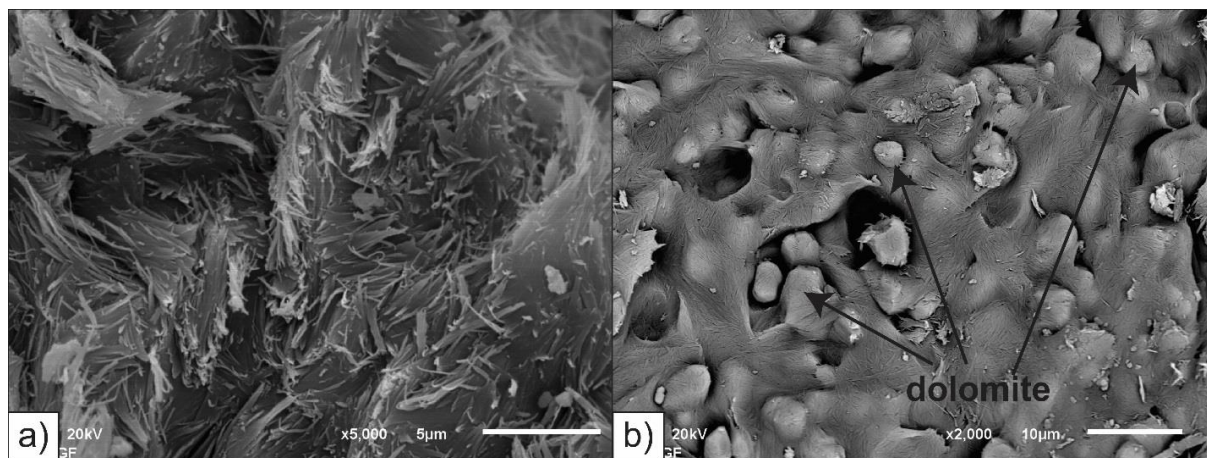


Figure 5.1.3. a) Sepiolite fibre bundles; b) sepiolite fibres enclosing dolomite rhombs.

This stop also includes whitish medium bedded magnesite with vuggy silica (Figs. 5.1.1 and 5.1.4), which is located 130 m to the SW. This magnesite is of sedimentary origin and younger than sepiolite section.



Figure 5.1.4. Sedimentary magnesite.

## STOP 5.2. INTRABASINAL ORGANIC-RICH MARLSTONES

Locality: Andrići, Plana river, 22 km west of Gornji Milanovac town

WGS84: 44°1'9.85"N, 20°10'54.65"E

Age: Lower Miocene

This stop is represented by (a) cyclic alternation of more indurated carbonate rich and less indurated clay rich packages of parallel laminites deposited in profundal lacustrine environment

(Fig. 5.2.1). These parallel laminites are made of alternating kerogen-, dolomite- and clay-rich laminae (Obradović *et al.*, 1997).



Figure 5.2.1. Profundal lacustrine facies.

## 6. ČAČAK-KRALJEVO BASIN

Čačak-Kraljevo Basin (Zapadna Morava Basin) is one of the largest Miocene basins in Serbia, covering an area of 1000 km<sup>2</sup> (Obradović and Vasić, 2007, Fig. 6.1). It is oriented NW-SE and overlies paleorelief which includes thrust sheets of the Adriatic margin of the Dinarides (Drina-Ivanjica and Jadar-Kopaonik) and obducted ophiolites (Fig. 1.1, Schmid *et al.*, 2008).

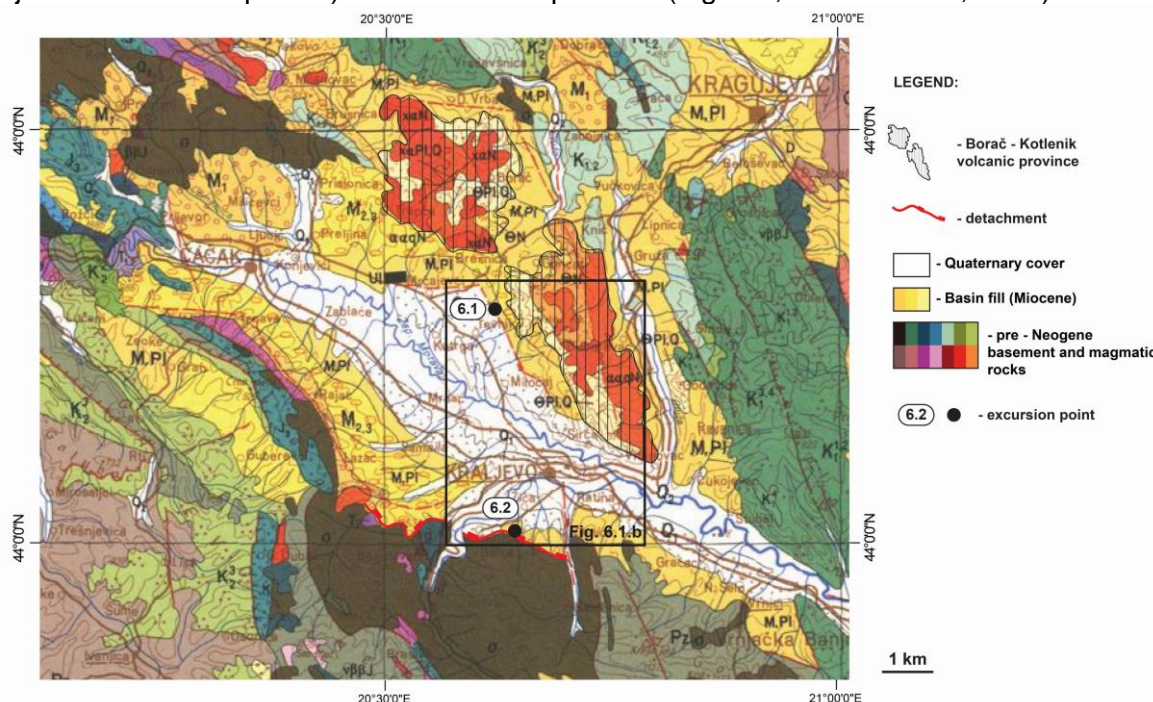


Fig. 6.1. Part of the Geologic map of former Yugoslavia, 1: 500,000, sheet Kraljevo, with position of the field stops 6.1 (Tavnik) and 6.2.

Like the whole internal part of the Dinarides, this area was affected by extension during Oligocene and Miocene (e.g. Marović et al., 2007; Stojadinović et al., 2013; Erak et al., 2017). Čačak-Kraljevo Basin was formed in the hanging-wall of the large top to the N(NE) detachment delineating southwestern margin of the basin (Erak et al., 2017) or at least one stage of its evolution was controlled by the activity of that detachment. During Miocene this area was affected by volcanic activity of the neighbouring Borač-Kotlenik eruptive complex close to the north-eastern basin margin (e.g. Cvetković et al., 2001).

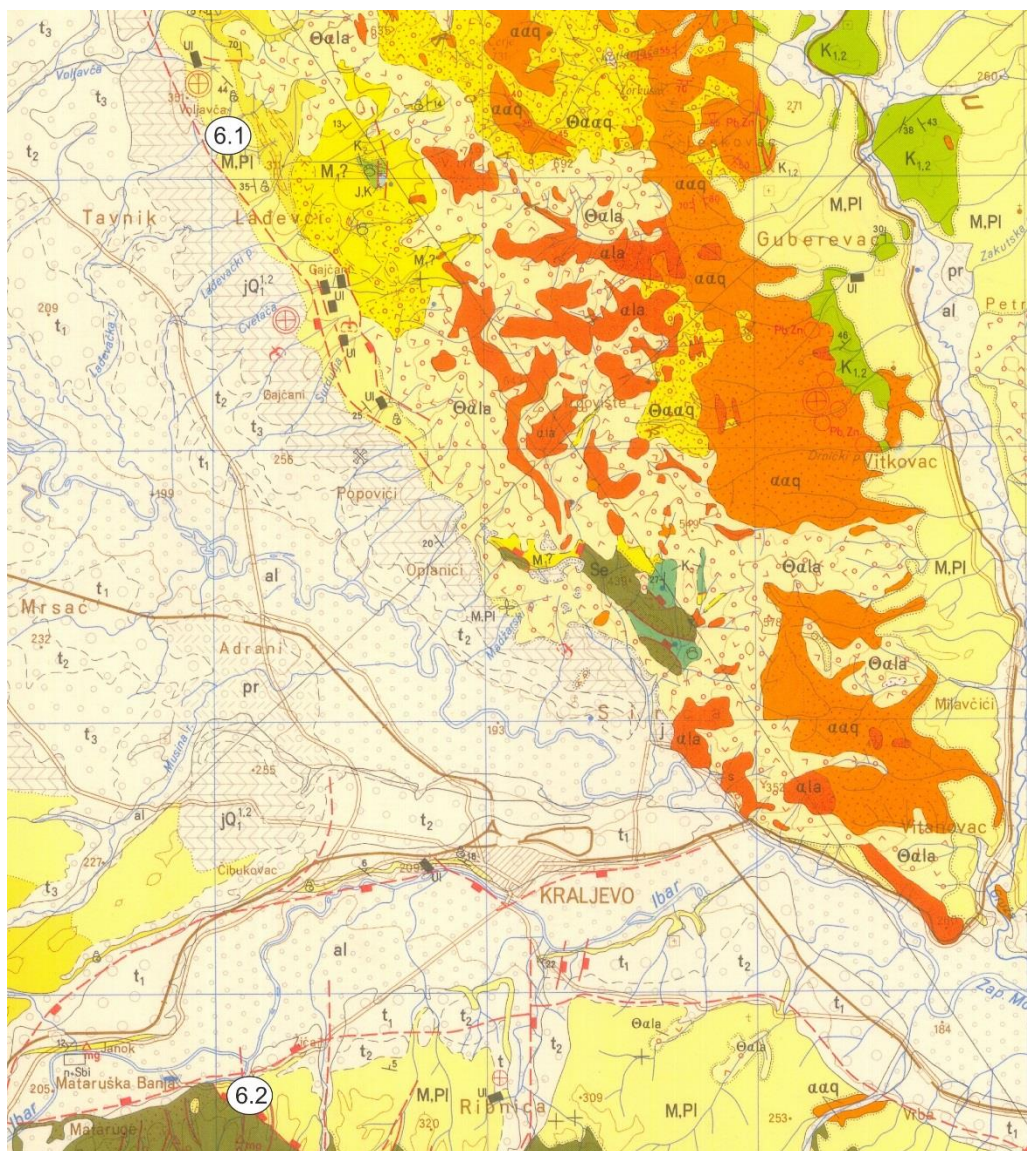


Fig. 6.2. The part of the BGM, 1: 100, 000, sheet Kraljevo, with position of the stops 6.1 (Tavnik) and 6.2 (Mataruška banja). A part of Čačak-Kraljevo basin infill is marked by yellow color. Key (simplified): Se – Serpentinities, K<sub>1</sub> (a few green units) – Lower Cretaceous, M<sub>1?</sub> – Lower Miocene, M<sub>2,3</sub> – Badenian and Sarmatian, M,PI – Upper Miocene to Pliocene, aaq – Hydrothermally altered dacites and andesites, θaaq – Pyroclastites of dacites and andesites, ala – labradorit andesites, θala – Pyroclastites of labradorit andesites, t<sub>1,2,3</sub> – Quaternary river terrace.

The deposition of ~ 2000 m recorded two lacustrine depositional cycles (Anđelković et al., 1991). First depositional cycle was characterized by coarse-grained clastites overlain by marls and clays with fish remains. Second depositional cycle, i.e. Čačak series comprises of alluvial to deltaic coarse-grained clastites aligned predominantly along south-western margin. They laterally grade into silts, marls, claystones intercalated with three coal and two volcanic ash layers which are

characteristic for north-eastern margin (Anđelković et al., 1991). This succession vertically passes into sandstones, siltstones, marlstones and oil shales (Novković, 1975).

The above-mentioned sediments correspond to the lacustrine Lower-Middle Miocene (Gagić, 1972; Stevanović et al., 1977; Anđelković et al., 1991; Knežević, 1996; Krstić & Komarnicki, 1996; Savić & Krstić, 2003; Krstić et al., 2003, 2007, 2012; Jovanović & Krstić, 2010; Jovanovic, 2012). Unfortunately, more precise age determination is missing until present time. Mollusks and ostracod fauna have endemic character and it is difficult to give a valid stratigraphic range (Krstić et al., 2012). Until now, there is no attempt to detail systematic and taxonomic studies of the freshwater gastropods. They could be used as a tool for stratigraphic correlation to the well-dated Dinaridic Lake System (de Leeuw et al., 2010, 2011, 2012; Neubauer et al., 2013, 2015). A good intention based on radioisotope dating and magnetostratigraphic analyses of these sediments remain unfinished yet (Sant K., personal communication).

## STOP 6.1. TAVNIK

Locality: 22 km north from Kraljevo, near the Voljavča monastery

WGS84: 43°51'58.85"N, 20°37'0.17"E

Age: Lower to Middle Miocene – Burdigalian to Langhian (Ottangian – Badenian)

Near the Voljavča monastery (XVII century), in the area of Tavnik village, 22 km north of Kraljevo, at the Voljavča stream and in its banks, there are a few small outcrops with sediments of the Serbian Lake System (SLS) (Fig. 6.2). At the right bank of stream, sedimentological successions starts with the cca 10 m long and up to two meter high outcrop (Figs. 6.1.1, 6.1.2.a). It consists of dark-green and grayish thin-bedded marl, sandy marl and silty clay with thin coal interbeds.

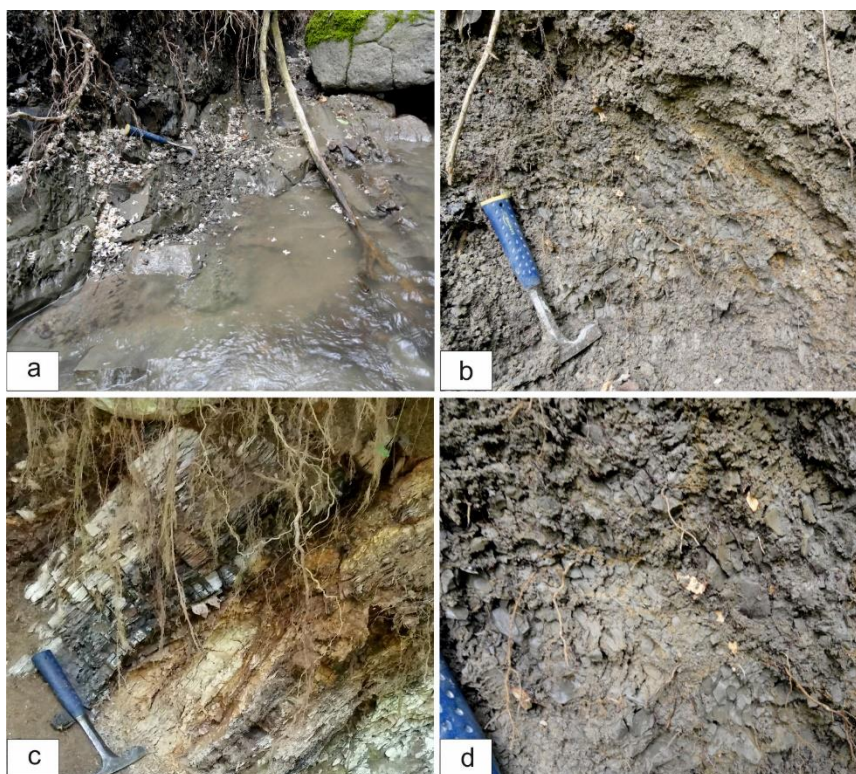


Fig. 6.1.1. The Voljavča stream outcrops. (a) Grayish sandy silt at the stream bottom, (b, d) close-up of the dark-green and grayish thin-bedded sandy marl and silty sand, and (c) silty clay with thin coal interbeds.

Paleontological record from these outcrops is relatively rich. Among the mollusks, there are findings of different „congeria“ bivalves such as *Congeria ornithopsis* Brusina, *Congeria neumayri* Andrusov, *Congeria hoernesii* Brusina, *Congeria neumayri* Andrusov, *Congeria spathulata* Partsch, *Dreissensia cf. turislavica* Jekelius, etc. (Popović & Novković, 1966/67). It is important to note the determination of Lake Pannon species was false. Besides, some authors recognized abundant fossil gastropods: *Brotia (Tinnyea) escheri moravica* Popović, *Brotia (Brotia) spinosa* Popović, *Melanopsis bouei affinis* Handmann, *Neritodonta brankovići* Brusina, *Neritodonta venusta* Brusina, *Neritodonta brusinae rugosa* Pavlović, *Prososthenia žujovici* Brusina, *Prososthenia radicevici* Brusina, etc. Similarly, some of the mentioned species are not correctly identified and indicate to younger stratigraphic level (Upper Miocene).

On the other hand, there are typical lacustrine genera which were recognized as *Lymnaea*, *Theodoxus*, *Prososthenia*, *Melanopsis*, etc, which settled older Serbian lake during the Lower-Middle Miocene (Jovanović & Krstić, 2010; Jovanović, 2012; Krstić et al., 2012). Very abundant association (a few hundred specimens) of the gastropod species *Theodoxus brusinae rugosa* was found (Jovanović, 2012; Krstić et al., 2012). Generally, *Theodoxus* is a genus that gives a lot of information on the reconstruction of the history of these freshwater fauna (Bunje & Lindberg, 2007). *Theodoxus* inhabits a sweet and salty aquatic environment with increased water energy, or a little mobile water with a flood of river.



Fig. 6.1.2. The Voljavča fossiliferous outcrops. (a) Slightly tilted grayish sandy silt and marl at the stream bottom, (b) a detail of the dark-green, compact silty sand with rich small-size fossils of mollusks, ostracods and fishes, (c) a part of dark-green, compact silty sand with fossil gastropods such as *Prososthenia* and *Melanopsis* and fish remains, and (d) close-up of *Prososthenia* sp. and relatively large candonid ostracod (*Candona* sp.)

Representatives of *Theodoxus* today live in Europe, North Africa and the Middle East (Bunje, 2005; Marković, 2014). The systematic identification of modern *Theodoxus* is very difficult, and when it comes to fossil taxa this problem is even greater. The explanation for this can be found in local hybridization (Bandel, 2001). The relatively high diversity of species in Anatolia and the

Balkans indicates that this is a possible center of origin for this branch of snails, from which they later distributed to the west and north. It is also very possible that the historical biogeography of this genus is a mosaic of mechanisms that have led to modern diversity and distribution of *Theodoxus* (Bunje & Lindberg, 2007; Jovanović, 2012). Additionally, representatives of the genus *Tinnyea* (family Pachychilidae), previously incorporated into the genus *Melania* or *Brothia*, were also found among the mollusks in the Voljavča and Surdulija stream, near Tavnik (Fig. 6.3.). However, modern Pachichilidae (the genus *Brothia*) are limited to the tropics. *Tinnyea* is inhabited by freshwater aquatic environment, and unlike modern pahilides, it prefers the waters of slower rivers and can tolerate warmer temperature conditions (Kowalke, 2004).

Similarly, findings of genus *Melanopsis* are recorded, both nodular and smooth morphotypes (Jovanović, 2012; Krstić et al., 2012). Modern *Melanopsis* are known from freshwater rivers and lakes with high oxygen content, but they can tolerate salt water. Some *Melanopsis* that have nodular shells are more frequent in freshwater environments, while smooth morphotypes inhabit more estuarine water (Jovanović, 2012 and references therein). *Melanopsises* from Serbia are very varied in the morphology of shellfish, ranging from those with smooth shells to specimens with very pronounced ribs (Fig. 6.1.2.) (Jovanović, 2012; Krstić et al., 2012).

Rare unionid bivalves are recorded at the Voljavča stream and they indicate the inflow of clean freshwater (Jovanović, 2012; Krstić et al., 2012).

In the wider area of Tavnik, based on the borehole data (drilled up to 134 m) the next freshwater species was recorded: *Mytilopsis* cf. *novica*, *M.* aff. *nitida*, *M.* cf. *sumadica*, *Hydrobia santrici santrici*, *Prososthenia* cf. *serbica*, *Planorbis* cf. *nisseana*, etc. Amongst the ostracods following species were found: *Neglecandona* sp., *Dinarocythere* cf. *trigonula*, *Cypridopsis pannonica* (Krstić et al., 1997). Different thicknesses of mollusks shells and the appearance of tubercles on *Cypridopsis pannonica* caps indicate the increased mineralization of lake water (Jovanović, 2012).



Fig. 6.1.3. *Tinnyea escheri* from the Surdulija stream, near Tavnik (Jovanović, 2012)

Besides mollusks, ostracods are very common and abundant microfauna. From the silty clay close to the coal beds, numerous single valves and carapaces are extracted. Among them, dominant forms are candonids and cypridids (Fig. 6.1.4.). Genera such as *Ilyocypris* and *Candona* s.l. have widespread distribution. Very frequent distribution has an *Ochriedella? sabantae* Krstić, 1974 with a characteristic "saddle" at the anterodorsal margin (Fig. 6.1.4.b). This species was noted in the other SLS areas in Middle Miocene (Krstić et al., 2012). Similarly, sporadic findings of *Reticulocandona? baljkovacensis* Krstić, 1974 and *Mediocypris* sp. indicate the Middle Miocene age of SLS as well (Krstić et al., 2012; Sant et al., 2016). Interestingly, *Mediocypris* was not found in the Dinarides, but it is widespread in other Middle Miocene regions in Europe and Russia, indicating that the age of the Dinaric Lake System is different from the Serbian one (Krstić, 1987; Krstić et al., 2012; Sant et al., 2016). Among the ostracods of the SLS there is no species that still lives, but some of the fossils have aberrant properties, which indicates

an increased mineralization of water. Taxonomic descriptions of these species from different sites are scarce or often missing (Jovanović, 2012; Krstić et al., 2012).

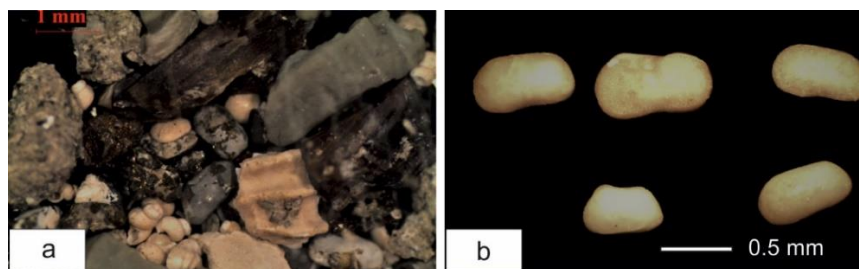


Fig. 6.1.4. (a) The typical fossil association extracted from the silty clay includes ostracods, gastropods, fish bones and teeth, otoliths as well as coal fragments. Besides, a sulphide mineralization present, (b), a characteristic ostracod assemblage with dominant forms of *Ilyocypris* sp., *Candona* sp. and *Ochriedella? sabantae* Krstić, 1974 – below left, with a characteristic "saddle" at the anterodorsal margin.

## STOP 6.2 MATARUŠKA BANJA

Locality: Mataruška banja, 6 km SW of the Kraljevo town

WGS84: 43°41'16"N, 20°37'38"E

Age: Lower Miocene

The Mataruška Banja section is exposed along the Ibar river valley. It is located at the south-eastern margin of the Čačak-Kraljevo basin. The section (Fig. 6.2.1) comprises poorly sorted and immature conglomerates that contain a large compositional diversity of clasts (such as diabase, serpentinite, andesite and their pyroclastites, quartzite, schists, recycled conglomerate and sandstone).



Figure 6.2.1: Alluvial succession near Mataruška banja

The conglomerates are pebble to cobble size, clast- to matrix-supported. They have channel-like geometry (N-S flow direction) and are engulfed in red fine- to medium-grained sandstones and



siltstones. Towards the top, alluvial succession shows coarsening and thickening upward trend. In the upper part of succession alluvial clastics are overlain by grey sandstones and marls deposited in marginal lacustrine environment. The provenance and maturity of clastic material and flow direction suggest that the catchment area of this alluvial system was restricted to the footwall of the basin bounding fault.

## 7. IBAR BASIN

The Lower Miocene freshwater Ibar Basin is located 200 km south of Belgrade, covering an area of approximately 320 km<sup>2</sup>. It is a northwest-southeast elongated tectonic depression with a maximum length of 20 km and width of 12 km. This basin is a member of the Neogene lacustrine systems of the Dinarides (Harzhauser and Mandić, 2008; Krstić et al., 2003) filled by bituminous coal-bearing clastic rocks (Ercegovac et al., 1991; Obradović and Vasić, 2007) deposited over Mesozoic serpentinite and Tertiary volcanic rocks. The basin is situated between two metamorphic domes, Kopaonik and Studenica. Today, it includes several subbasins (Ušće, Tadenje, Jarando, Progorelica, Fig. 7.1).

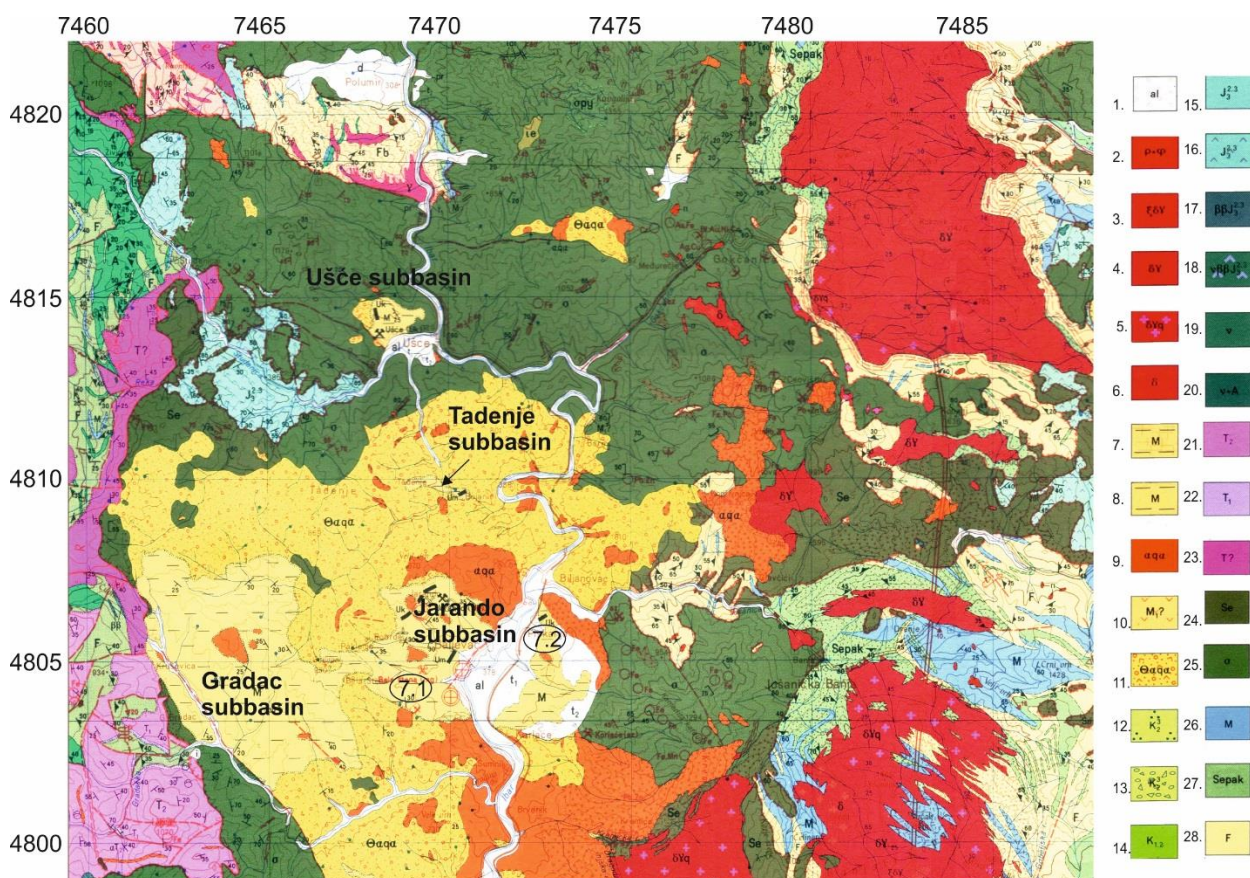


Figure 7.1. Geological map of the Ibar basin area (after Basic geologic map of Serbia, 1:100,000) with field stops 7.1 and 7.2. 1. Alluvium; 2. Pegmatite and aplite; 3. Granite; 4. Granodiorite; 5. Granite and quartzmonzonite; 6. Hydrothermally altered diorite; 7. Massive limestone; 8. Conglomerate, sandstone, claystone and marlstone; 9. Dacite-andesite; 10. Pyroclastic rocks; 11. Flysch; 12. Limestone breccia and conglomerate; 13. Bedded limestone; 14. Ophiolitic melange; 15. Claystone, sandstone, diabas; 16. Diabase, spilite; 17. Gabbro-diabase; 18. Gabbro; 19. Gabbro and amphibolite; 20. Limestone and dolomite; 21. Sandy marlstone and limestone; 22. Limestone, dolomite and marble; 23. Serpentinite; 24. Hartzburgite; 25. Calcschist and marble; 26. Marble; 27. Chlorite-epidot-actinolite schist and metabasite; 28. Sericite-chlorite schist and metasandstone.

Previous studies of the Ibar Basin were related mostly to geology (Đorđević, 1954; Urošević et al., 1973a, b in Obradović and Vasić, 2007) stratigraphy (Čirić, 1962; Gagić, 1995 in Obradović and Vasić, 2007; Pantić, 1961) and sedimentology (Obradović and Vasić, 2007 and references therein), and exploration of coal (Ercegovac et al., 1991 and references therein), boron mineralization (Obradović et al., 1992), and magnesite (Ilić, 1952; Ilić, 1968/1969; Fallick et al., 1991). At present coal is exploited in two underground mines Jarando and Tadenje, and one open pit Progorelica. Borates are currently exploited in the Pobrđe deposit and explored in the Piskanja deposit, and magnesite was exploited in the Bela stena deposit.

The Ibar basin is located in the internal Dinarides. The basement geology emerges as a result of the collision of the Europe and Adria plate creating thrust sheets divided into internal and external Dinarides (Pamić et al., 2002; Schmid et al., 2008). The internal Dinaridic composite units comprise Palaeozoic and Mesozoic rocks of the Adriatic distal passive margin covered by the allochthonous ophiolites and associated accretionary prism (e.g. Đoković, 1985; Sudar and Kovacs, 2006).

During Late Cretaceous to Paleogene shortening these units were together with the syn-contractual trench turbidites involved in out-of-sequence thrusting forming several thrust sheets (i.e. Jadar-Kopaonik and Drina-Ivanjica, Schmid et al., 2008). The latest compressional stage was characterized by production of I-type calc-alkaline granodiorite magmas (Schefer et al., 2011) represented by Kopaonik, Drenje and Željini plutons and associated dacitic/andesitic volcanics and their pyroclastic rocks (e.g. Cvetković, 2002; Mladenović et al., 2015). During Neogene the area was affected by the significant extension which is in general related to the back-arc opening of the Pannonian Basin starting at ~20Ma (Fodor et al., 1999, 2005; Horváth et al., 2006, 2015 and references therein). Aforementioned extension reactivated Late Cretaceous thrusts as a low-angle extensional faults leading to exhumation of greenschist- to amphibolite-grade domes (i.e. Studenica and Kopaonik Metamorphic Series, from 21-17 Ma to 10 Ma,  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dating on micas, zircon and apatite fission track, Schefer 2010) and formation of Ibar basin in the hanging wall (e.g. Andrić et al., 2015).

The decompressional melting due to Studenica dome exhumation gave S-type Polumir granite (18.1-17.4 Ma, U/Pb zircon dating, Schefer et al., 2011). This was followed by the quartz-lattice extrusions and pyroclastic rocks. Coeval, Ibar basin evolution was characterized by heating episode prior to cooling that began at around 10 Ma (Andrić et al., 2015). The heating episode started around 17 Ma and lasted 10–8 Ma reaching the maximum temperatures between 100–130°C. The apatite fission track data also indicate local thermal perturbations, detected in the SE part of the Ibar basin (Piskanja deposit) with the time frame ~7.1 Ma, which probably corresponds to the youngest volcanic phase in the region.

The rejuvenated shortening from late Miocene onwards inverted basin and divided it into four subbasins Ušće, Tadenje (Tadenje and Progorelica coal field), Jarando (Jarando coal field and Piskanja) and Gradac (Fig. 7.1). Post-sedimentary fault tectonics resulted in structural deformations of coal seams and formation of occasionally complex block-structure of coal deposits.

Sedimentation started in the Lower Miocene (Urošević et al., 1973a, b in Obradović and Vasić, 2007) followed by basin subsidence resulting in formation of a 1500 m thick sequence (based on geophysical exploration). The basin is filled with clastic sediments deposited in alluvial and later in lacustrine phase.

The alluvial clastics are represented by breccia, conglomerates, sandstones marlstones and several coal layers. The lacustrine phase is characterized by laminated dolomitic marlstones and claystones, rarely intercalated with sandstones lenses. The deposits of the Ibar basin, as mentioned before, are located within four subbasins (Ušće, Tadenje, Jarando and Gradac).

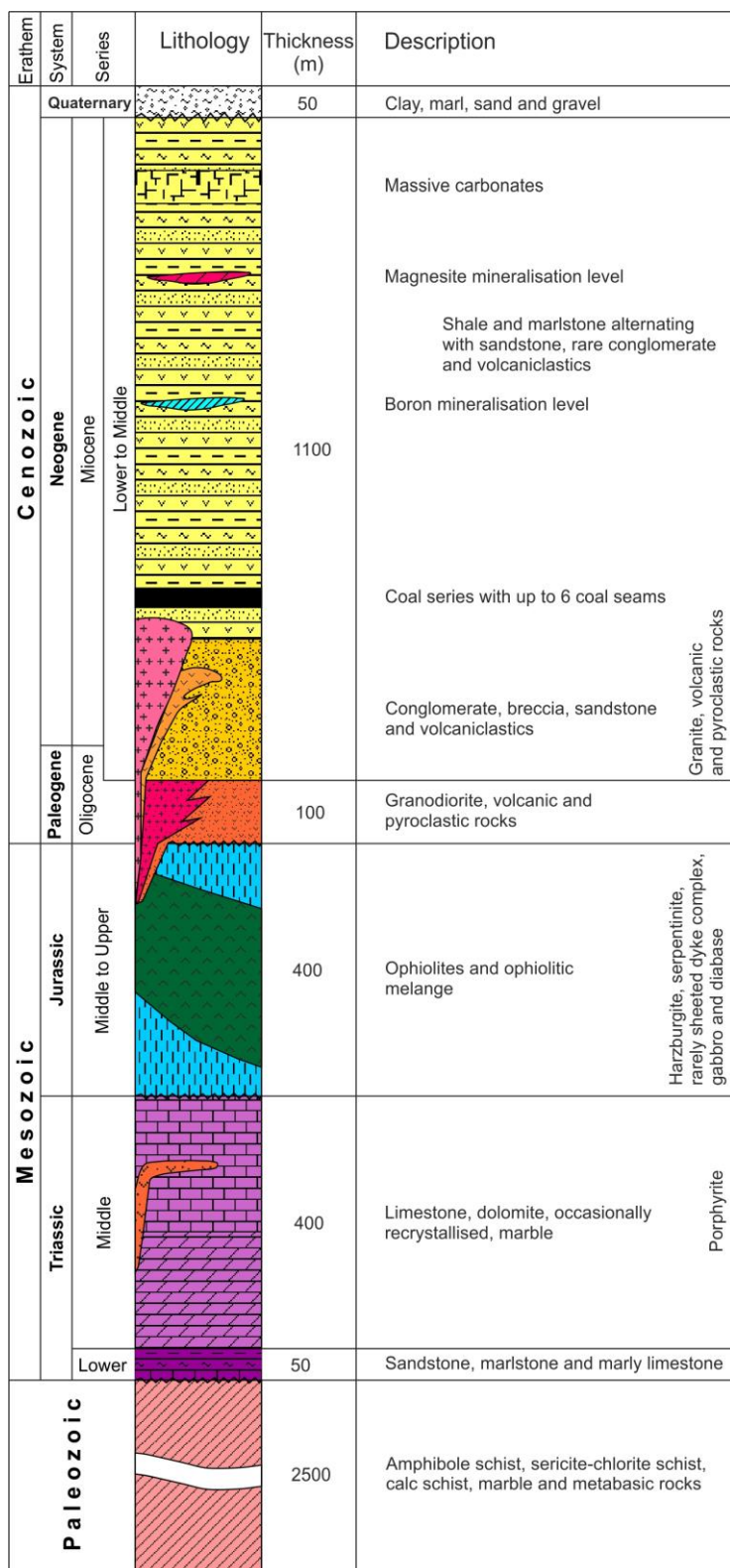


Figure 7.2. Geological column of the Ibar basin

In the Jarando coal deposit sediments are represented by palustrine to shallow-water lacustrine and profundal lacustrine facies. The deposition started with red alluvial clastics (conglomerates and sandstones) which laterally grade into fine-grained grey tuffaceous sediments overlying volcanics and volcanoclastics. The thickness of this unit usually varies between 10 and 30 m (Ercegovac et al., 1991), but occasionally the oldest coal seam lies directly over andesitic paleorelief. Coal series, which comprises up to nine coal seams out of which six have commercial thickness and were named 1 to 6 (top to bottom), is interbedded within marlstones, marly shales, medium- to coarse-grained sandstones and conglomerates. It is situated along the NW margin of the Jarando subbasin. The average thickness of coal seams varies from 1 to 4 m, whereas the cumulative thickness of coal series ranges from 60 to 120 m (Ercegovac et al., 1991).

It is situated along the NW margin of the Jarando subbasin. The average thickness of coal seams varies from 1 to 4 m, whereas the cumulative thickness of coal series ranges from 60 to 120 m (Ercegovac et al., 1991). Previous petrographic and organic geochemical investigations (Ercegovac et al., 1991) were performed on samples from Jarando, Tadenje and Ušće deposits, with mean random vitrinite reflectance of coal 0.83, 0.77, and 0.91, respectively.

Studied samples had a high content of aromatic hydrocarbons (Jarando-50.3%; Tadenje-40.5%; Ušće-52.45%) and lower content of saturated hydrocarbons (Jarando-7.2%; Tadenje-15.3%; Ušće-14.5%), NSO compounds (Jarando-27.9%; Tadenje-23.3%; Ušće-22.65%) and asphaltenes (Jarando-14.6%; Tadenje-20.9%; Ušće-10.5%). In the hanging wall of the coal series shale, marlstone sandstone, and conglomerate were deposited, occasionally with boron layers

(Pobrđe and Piskanja deposits, Obradović et al., 1992, and magnesite (Bela stena, Fallick et al., 1991). The deposition started with alluvial coarse-grained breccia, conglomerate and sandstone, alternating with lenses of marlstone. The transgression continued resulting in widespread laminated dolomitic marlstones, organic rich shales with thin intercalations of fine-grained sandstones and mudstones in the central and eastern part of the basin (i.e. Piskanja deposit). Carbonates are located along the western margin of the central part of the basin. The ostracode remains and tooth of *Mastodon (Bunolophodon) angustiden forma subtapiroidea* suggest freshwater deposition no later than Otnangian to Karpatian (Rögl, 1996; Burdigalian-ISC), even up to Badenian (Langhian-ISC) stage (Čirić, 1962; Gagić, 1995 in Obradović and Vasić, 2007). Pantić (1961) determined approximately the same age based on paleofloral material: *Pinus hepios* (Ung.) Heer, *Alnus kefersteini* (Göpp.) Ung., *Quercus lonchitis* Ung., *Quercus drymeja* Ung., *Quercus neriifolia* A. Br., *Myrica lignitum* (Ung.) Sap., *Carya serraefolia* (Göpp.) Krausel, *Zelkova ungeri* (Ett.) Kov., *Laurus princeps* Heer, *Casia hyperborea* Ung., *Leguminosites* sp., *Acer trilobatum* A. Br., *Crysophyllum atticum* Ung., and *Monocotyledonae* gen. et sp. indet.

The Quaternary sediments include mostly clay, marl, sand and gravel.

## STOP 7.1. BELA STENA MAGNESITE DEPOSIT

Locality: Baljevac, 15 km north of Raška town  
WGS84: 43°23'6.43"N, 20°36'50.70"E  
Age: Miocene

Magnesite deposit of Bela Stena was the first discovered hydrothermal-sedimentary type of cryptocrystalline magnesite in the world (Ilić, 1952). It was explored during 1952, and production started in 1953 and lasted till the end of last century. Today it is possible to see only small remnants of the original ore body (Fig. 7.1.1).



Figure 7.1.1. Overview of the Bela Stena deposit – contact of magnesite with marlstone and shale

The Bela Stena deposit was the largest single magnesite deposit in Serbia and former Yugoslavia, formed as a lens up to 250 m long, up to 190 m wide and up to 120 m thick (Ilić, 1968/1969). It

was mostly massive ore, occasionally brecciated or bedded. It rarely embedded small lenses of marlstone, shale and sandstone.

Magnesite body was underlain by thin-bedded marlstone and shale with intercalations of yellowish and greenish sandstone, and overlain by bedded marlstone, shale and sandstone (Ilić, 1968/1969).

The stable isotope study enabled Fallick et al (1991) to construct the "Yugoslavian magnesite regression line" expressed as  $\delta^{18}\text{O} = 0.508 \delta^{13}\text{C} + 32.3$ , between two end members of  $\text{CO}_2$  reservoirs, the one with low  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in ascending hot groundwater environment with organically derived  $\text{CO}_2$  (vein deposits in ultramafic rocks), and the other with high  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , originating in low-temperature, meteoric water with atmospheric  $\text{CO}_2$  (Bela Stena magnesite type).

More recent researches generally confirmed those results (Zedef et al, 2000; Jurković et al, 2012). Based on stable isotope analysis and trace elements content, particularly REE, Jurković et al (2012) suggested that Bela Stena is of sedimentary origin.

## STOP 7.2. PISKANJA BORATE DEPOSIT

Locality: Baljevac, 15 km north of Raška town

WGS84: 43°23'1.62"N, 20°38'53.75"E

Age: Miocene

Boron mineralisation in the Jarando area was first found in the Pobrđe locality (Stojanović, 1967), and afterwards geologically explored by former GEOZAVOD NEMETALI state-owned institution. It is a small deposit, exploited by Ibar Coal Mines, with total resources of around 170 kt of ore. Main boron minerals are colemanite and howlite (Janković et al, 2003).

Piskanja boron mineralisation was discovered in 1987 by Ibar Coal Mines during realisation of the long-term hard coal exploration programme (Fig. 7.2.1). Today Balkan Gold holds an exclusive exploration license for the Jarando property and the Piskanja boron deposit. Balkan Gold is a Serbian Corporation founded in 2009 and is a wholly owned subsidiary of Erin Ventures Inc. located in Victoria, Canada (Balkan Gold web data, 2017).



Figure 7.2.1. Position of boron deposits in the Jarando subbasin (by courtesy of Balkan Gold)

The Jarando property covers a 35 km<sup>2</sup> directly adjacent to, and between, Balkan's 100% owned Piskanja boron project (covering 3 km<sup>2</sup>) on the eastern edge of the Jarando Basin, and the Pobrđe Boron Mine, some 2.5 km away from Piskanja on the opposite edge of the Jarando Basin. Jarando has the potential to host extensions to the Piskanja deposit and/or the potential to host separate similar boron deposits.

Balkan Golds Piskanja project is a world class, high grade boron deposit with a NI 43-101 compliant mineral resource of 7.8 million indicated tonnes (31.0% B<sub>2</sub>O<sub>3</sub>), in addition to 3.4 million inferred tonnes (28.6% B<sub>2</sub>O<sub>3</sub>). Main boron minerals are colemanite and ulexite (Janković et al, 2003).

Boron mineralisation occurs as several layers within dolomitic marlstone, shale and, subordinately, sandstone, to the depth of cca 350 m (FigS. 7.2.2 and 7.2.3).

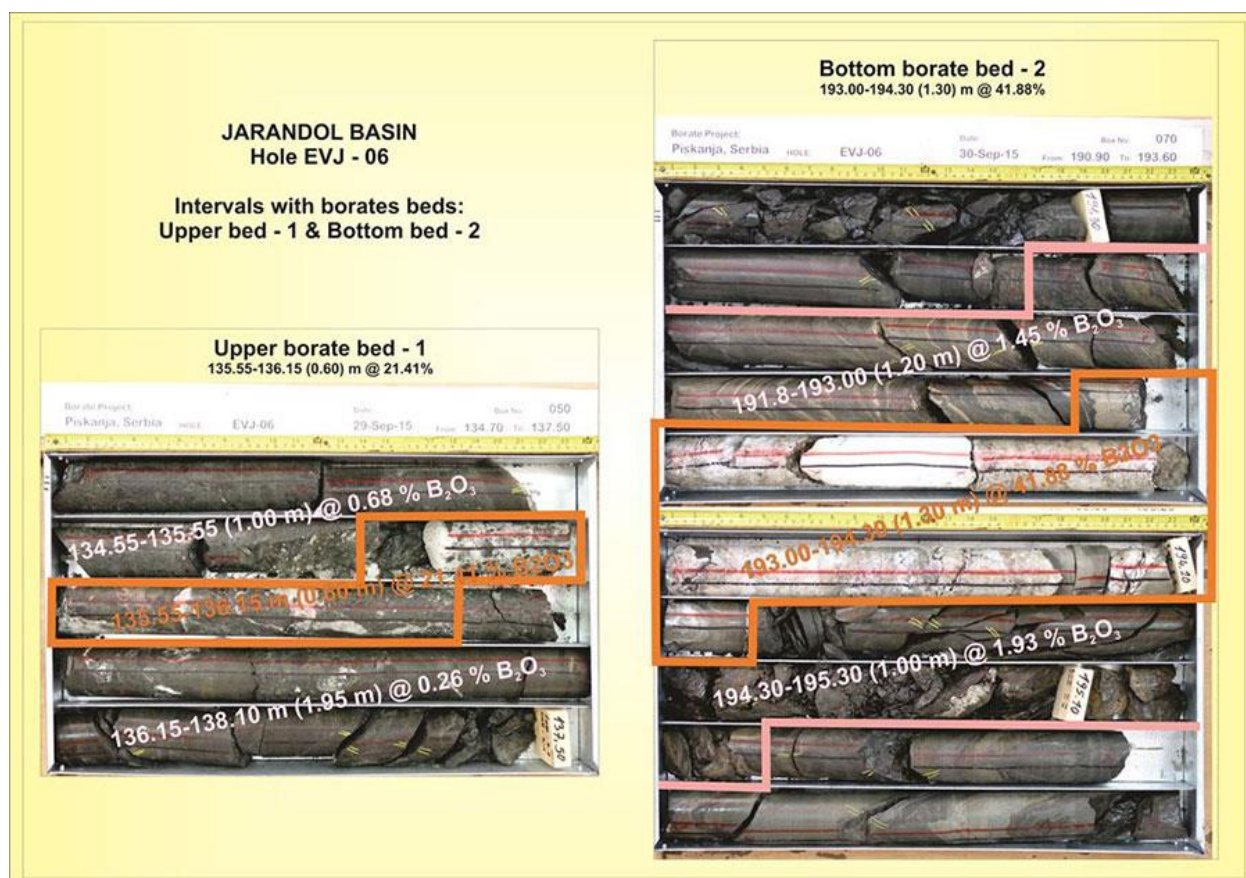


Figure 7.2.2. Example of boron layers in the Piskanja deposit (by courtesy of Balkan Gold)

Recent studies of Piskanja sedimentary sequence included vitrinite reflectance and maceral analysis of dispersed organic matter on eleven shale samples (seven are positioned in lacustrine and four in alluvial facies) from the Piskanja deposit (Andrić et al, 2015). The vitrinite reflectance results vary from 0.63 to 0.90%Rr implying a bituminous stage of organic matter. In the borehole IBM-1 (Piskanja deposit) the vitrinite reflectance values do not show a pronounced depth trend. The data are spread between 0.63% and 0.77%Rr, whereas most values are overlapping within one standard deviation (0.11–0.07%).

Shale samples are characterised by high contents of liptinite (32.5–86.0 vol.%, mmf) and variable amounts of inertinite (1.0–27.3 vol, mmf) and vitrinite (6.1–36.1 vol.%, mmf). Lamalginite (0.3–60.8 vol.%), telalginite (0.4–44.1 vol.%), liptodetrinite (13.1–41.8 vol.%, mmf) and sporinite (6.6–27.4 vol.%) are the most abundant liptinite macerals, whereas cutinite, resinite, suberinite, and

exsudatinite are rare. Fusinite and semifusinite are the most abundant inertinite macerals. Collodetrinite is the most abundant vitrinite maceral, while the content of collotelinite is lower. Contents of pyrite are low in most shale samples.

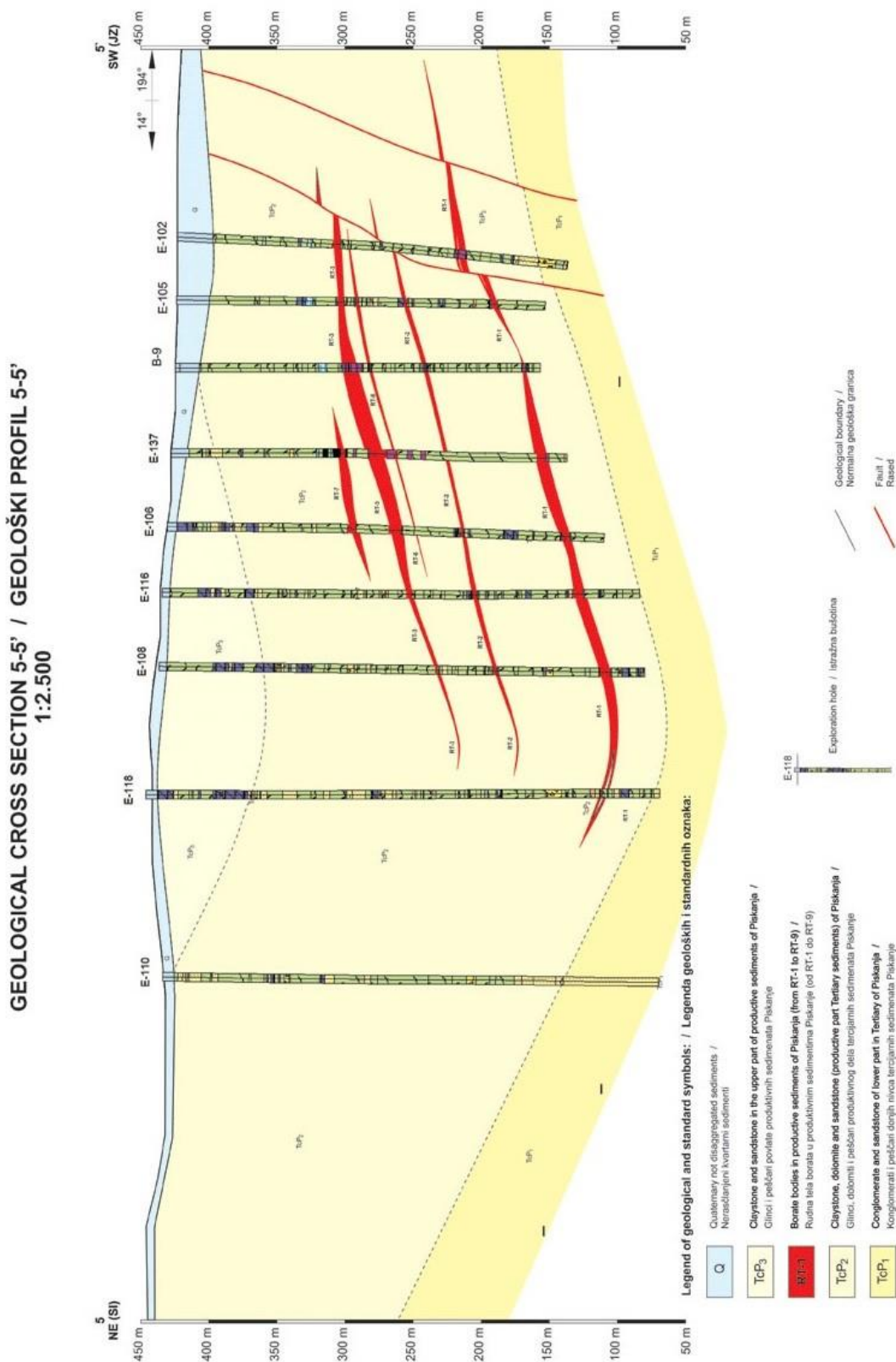


Figure 7.2.3. Position of boron layers in the Piskanja deposit (by courtesy of Balkan Gold)

## 8. THE POTPEĆ CAVE

### STOP 8. THE POTPEĆ CAVE

Locality: The Potpeć village, 14 km from the town of Užice

WGS84: 43°47'44.46"N, 19°55'59.61"E

Age: Quaternary? (Formed in the Middle Triassic limestone)

The Potpeć Cave is protected natural area. It is located in the Potpeć village, 14 km far away from the town of Užice, in the northern area of Drežnicka Gradina (931 m a.s.l.). The Cave is 10 kilometers long, but it is available to visitors on a tour of 555 meters.



Fig. 8.1. Main entrance to the cave (above, left) and an inside out view (above, right) as well as details of the cave ornaments (other photos).



The entrance to the cave is one of the monumental works of nature. It is located on a limestone cliff 72 meters high, waiting for about 200 steps. The vertical entrance in the form of a horseshoe which is about 50 meters height and 12 meters wide (at the bottom part) represents the highest cave entrance in Serbia. Input or downward track has over 700 steps.

The Potpeć Cave is a spring type and it was built by the underground stream of water that sinks in Drežnička valley and after underground stream in distance of 4-5 km (in a straight line), emerges from the caves or springs outside the cave and builds two kilometers long the Petnica-cavernous River.

According to Cvijic (1914), the Potpeć Cave built into middle Triassic limestones that "lying on Werfenian schist". A detailed geological studies and mapping of the area were made by B. Marković (1957, 1968). Triassic limestone has a whitish color, fracture porosity and fine mosaic structure. In the Potpeć Cave there are two main floors of the cave channels: the older - the Upper Cave and younger - Lower Cave. The entrance channel is common to both horizons, since it originated by destruction of the ceiling and their combination. The richness of cave ornaments is one of the very few in the karst caves. In the cave there is an abundance of stalactites and stalagmites, and the forms are reminiscent of dragons, camels, eagles, owls, fish, etc. (Lazarević, 1981).

In morpho-speleological sense, three channels are recognized in the Potpeć cave: fossil (Upper Cave), periodically active (extended portion of the Lower Cave) and constantly active (the latest underground stream).

The mean annual air temperature is 9.5° C. It is assumed that the cave was a human habitat even during the Neolithic period. It was discovered abundant ceramic surfaced antlers and stone weapons. Its residents were in any case able to use its favorable natural characteristics.

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