

# Significance of the Badenian petroleum source rocks from Krndija Mt. (Pannonian Basin, Croatia)



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### ABSTRACT

Discovery of petroleum source rocks at surface exposures of the Badenian deposits on the northern slopes of Krndija Mt. is the first record of petroleum source rocks at outcrop in the Croatian part of the Pannonian basin. Rocks with increased organic matter content have the characteristics of prime source rocks. Positive hydrocarbon potential is the consequence of a favourable type of organic facies. Type II kerogen is of mostly marine algal origin, but with somewhat more pronounced terrigenous lipid content. Source rocks are in the immature, diagenetic period of thermal transformation. Genesis of these rocks is related to the reducing depositional environment in a mostly shallow sea, formed in protected lagoons during the Badenian period, which was reconstructed using palaeogeomorphological, palaeontological, petrographical and organo-geochemical analyses. These new petrological data deserve attention as they highlight the need for additional geological-geophysical-geochemical research of the petroleum potential of the Badenian deposits in the broad area around Našice.

**Keywords:** Petroleum geology, source rocks, Badenian, Krndija Mt., Croatia, Pannonian basin

### 1. INTRODUCTION

According to bioproduction in the sea and on land, the area covered, and the volume of material deposited, the Badenian sediments have a significant petrological potential which has not been sufficiently explored either using boreholes or at outcrops. These outcrops on the edges of mountain massifs, used to form the edges of pools or islands in the Badenian sea. Badenian sediments, which have a thickness of no more than a few dozen metres in the outcrops of the Slavonian Mountains, can attain thicknesses of several hundred metres

in deeper areas of sedimentary basins. Palaeorelief, or more precisely a rugged coastline with numerous lagoons and bays, provided excellent conditions for the accumulation of organic matter in anaerobic conditions necessary to create kerogen. Therefore, the conclusions of HERNITZ et al. (1995) are very indicative, in this respect and contain a detailed analysis of source rocks in the area between Našice and Donji Miholjac. The analyzed rocks are mostly Badenian in age, with a few older sediments, which contain source rocks of 500–600 m thickness.

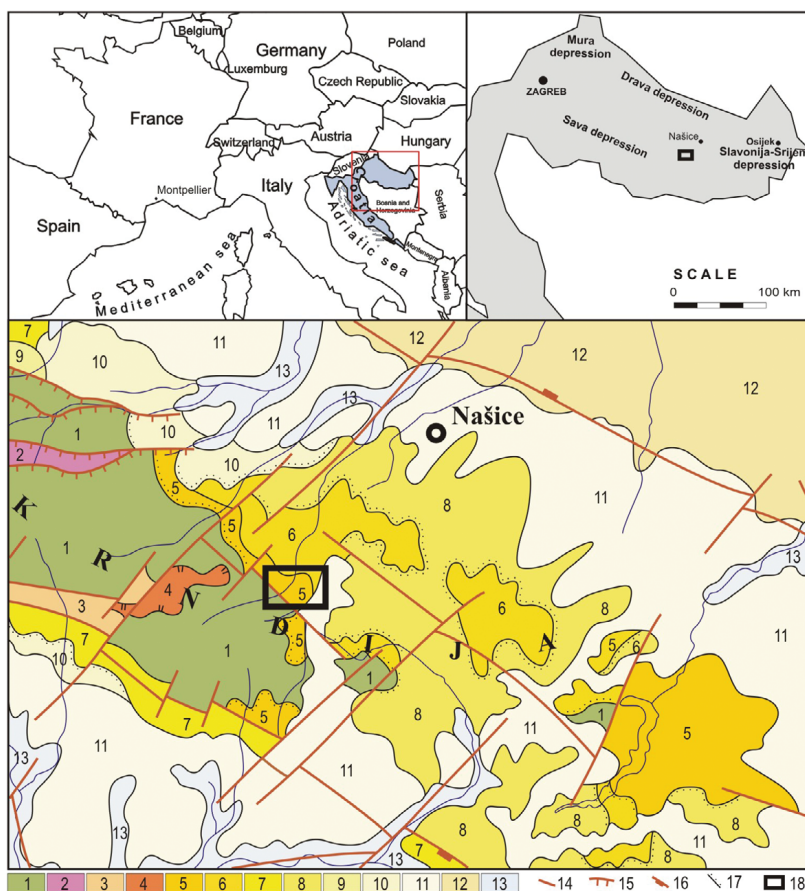
For a complete reconstruction of petrological relationships, research on surface outcrops is necessary, as well as full depth geological research which would encompass not only the Badenian sediments but also the upper parts of the Karpatian and lower parts of the Sarmatian (including the Karpatian/Badenian and Badenian/Sarmatian boundaries). On the trail of such ideas, full research was conducted on the easily accessible Badenian sediments at “Bukova glava” near Našice, on the northern slopes of Mt. Krndija (Fig. 1). A comprehensive analysis and reinterpretation of data provided by the Croatian national petroleum company “INA Oil Industry” from the nearest research boreholes as well as seismic sections of the Drava depression has also been performed.

On the northern slopes of Mt. Krndija, at the site of “Bukova glava” (Fig. 2) stratimetric scans and rock sampling were conducted, in order to ascertain their petrological significance, i.e. determine their caprock properties, reservoir properties and the presence of source rocks. With this goal in mind, samples were collected and used for organo-geochemical research as well as samples for determining permeability and porosity. Palaeontological research served to reconstruct palaeoecological conditions and biostratigraphic subdivision, and data were collected for reconstruction of several geological columns and profiles. Furthermore, samples used to determine the mineral and chemical content were collected from several layers, and on the “Gradac” notch, samples of the “basement rocks”, or rocks from the Preneogene base were also gathered.

The aforementioned data have facilitated creation of a synthetic column, used to correlate the Badenian sediments from “Bukova glava”, with the seismic sections and Badenian sediments defined in certain intervals of the nearest wells in the Drava depression. They were also used for construction of an isopach map (contour map of true thickness) of the Badenian sediments in the broad area around Našice.

Surface and sub-surface regional petrological research into the age and facies of core rocks in the Croatian part of the Pannonian basin, has been undertaken and published by numerous authors including; KRANJEC et al. (1976), HERNITZ (1983), PRELOGOVIĆ et al. (1998), HERNITZ et al. (1993), VELIĆ et al. (2000, 2002.), LUČIĆ et al. (2001), PAVELIĆ (2001) and PAVELIĆ et al. (2003a, 2003b). More recently, there is the work of SAFTIĆ et al. (2003), and VR-SALJKO (2007), while MALVIĆ (2006) published in the field of geostatistics.

Deposits of Neogene age were distinguished in three sedimentary megacycles of the 3rd order, composed of sequences of well defined lithological units in the rank of formations (VELIĆ et al., 2002), (Fig. 3). The first and oldest megacycle, of diverse and varied lithological composition, belongs to the lower and middle Miocene. It contains petroleum source fine-grained clastics and occurs in some of the largest petroleum reservoirs discovered in Croatia such as Beničanci and Molve. The second upper Miocene megacycle is specific by the even alternation of sandstone and marl



**Figure 1:** Geographical location of the Republic of Croatia, showing the broad area with the position of the research area and a geological map of Krndija Mt. (CROATIAN GEOLOGICAL SURVEY, 2009).

**Legend:** Metamorphic rocks, Precambrian; 2. Clastic deposits, Upper Permian; 3. Clastic deposits and carbonates with clastics, Ottangian, Karpatian; 4. Magmatic rocks: andesites and rhyolites, Karpatian and Badenian; 5. Lithothamnion limestone and clastic deposits with volcanic rocks, Badenian; 6. Carbonate-clastic deposits, Sarmatian and Pannonian; 7. Clastic deposits with coal, Pontian; 8. Sands and clays, Miocene and Pliocene; 9. Paludina deposits, Dacian and Romanian; 10. Clastic deposits, Pliocene-Pleistocene; 11. Loess, Pleistocene; 12. Diluvial-proluvial deposits, Holocene; 13. Alluvial deposits, Holocene; 14. Fault; 15. Thrust; 16. Normal fault; 17. Erosional or erosional-tectonic boundary; 18. Location of the studied area.



Figure 2: A photograph of the "Bukova glava" exploitation area.

with all transitional varieties. Many sandstone petroleum reservoirs are located here, of which the ones in the fields of Stružec, Žutica, Ivanić-Grad and Kloštar Ivanić are the largest. The third megacycle is of Pliocene-Quaternary age, and is composed of sand, clay, gravel, and sporadically lignite/tuff. It is currently thought to be of negligible petroleum significance.

Neogene sediments transgressively overlie the Palaeozoic "basement" of Krndija mountain in line with the development of the Croatian part of the Pannonian basin system. These are Miocene breccias, conglomerates, sandstones, limestones, volcanics, tuffs, tuffites, marls and coal, and

Pliocene marls, sandstones, gravels, clays and coal. They are overlain by the so-called "Quaternary cover" composed of gravels, sands, dust, clays and loess.

## 2. MATERIALS, DATA AND METHODS OF RESEARCH

Detailed analysis in the field, and scans of geological columns, has yielded rock samples selected for mineralogical, petrographic, geochemical and organochemical analyses. Three detailed geological columns have been recorded in the quarry near Našice that produces raw material for cement

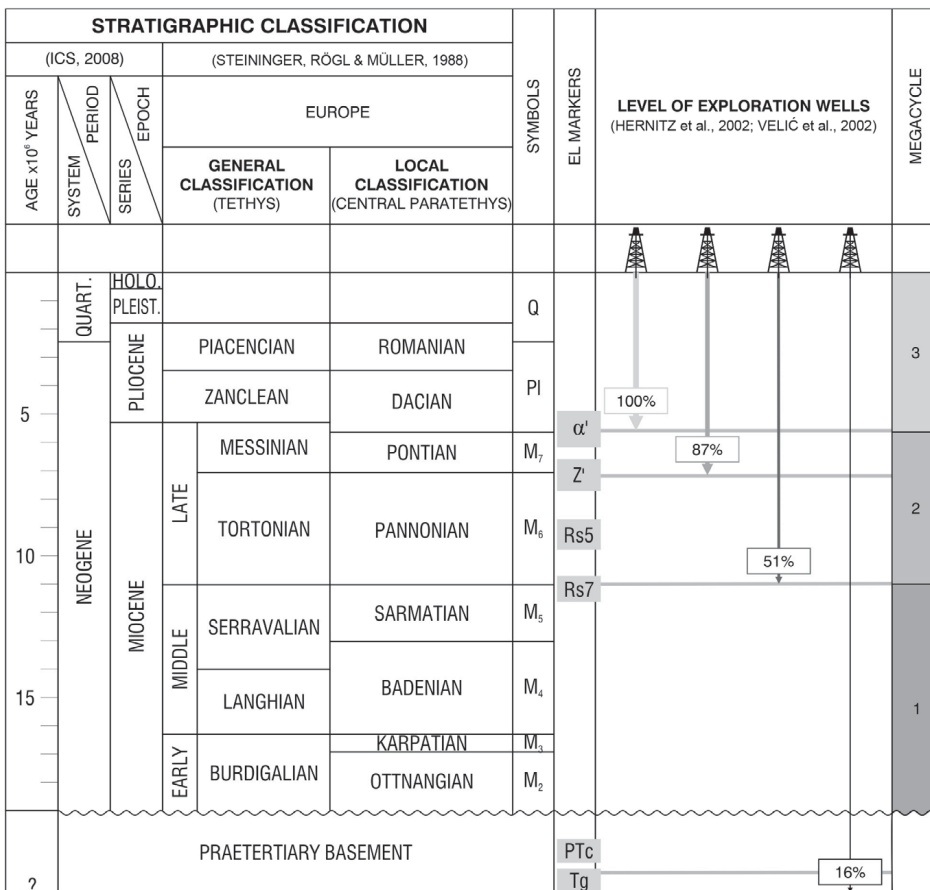


Figure 3: Stratigraphic classification for the range of Tethys and Paratethys with E-log markers and percentages of oil exploratory wells in the Croatian part of the Pannonian basin as well as marked environments of sedimentation and megacycles (updated after STEININGER et al., 1988; VELIĆ et al., 2002; HERNITZ et al., 2002).



production. On the basis of this data and the data collected from shallow boreholes (drilled to estimate reserves of raw cement material), a detailed synthetic geological column has been reconstructed.

### 2.1. Palaeontological methods of determining fossil samples

Samples with macrofossils were isolated in the field, and later refined and prepared for determination. Samples for micropalaeontological analysis were taken from layers with

visible lithological change. In total, 42 samples of approximately 0.5 kg were taken. In the base of the column, where potential petroleum source rocks were perceived in the field, 15 samples were collected at approximately 30 cm intervals. In order to determine the fossil flora and fauna, the following papers were consulted: HÖRNES (1856), GORJANOVIĆ-KRAMBERGER (1891), AGIP s.p.A. (1982), PAPP & SCHMID (1985), CIMERMAN & LANGER (1991), HOTTINGER et al. (1993), RÖGL & BRANDSTÄTTER (1993), HARZHAUSER et al. (2003), MANDIĆ (2004), WESSELIŃGH (2006).

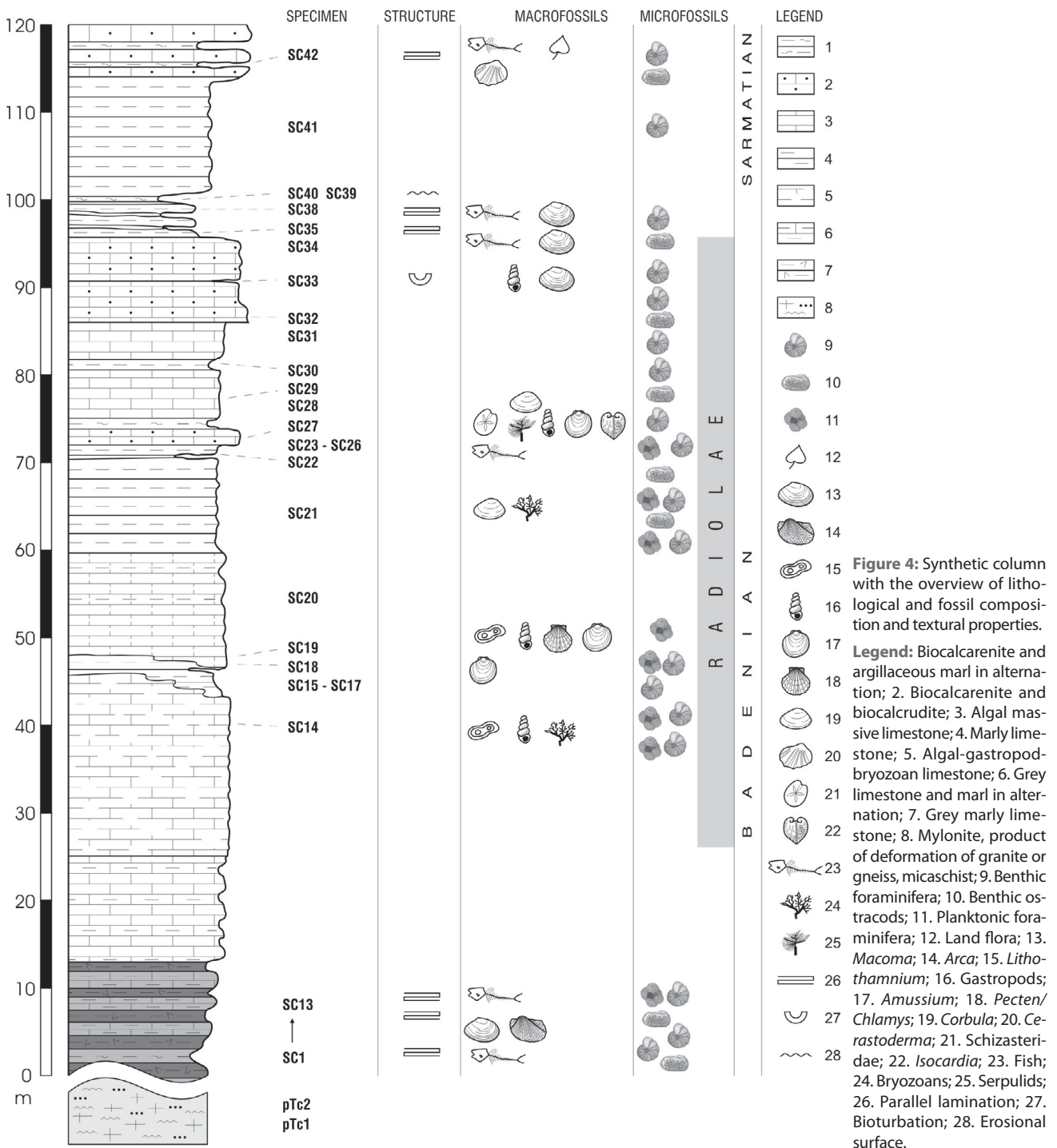


Figure 4: Synthetic column with the overview of lithological and fossil composition and textural properties.

**Legend:** Biocalcarenite and argillaceous marl in alternation; 2. Biocalcarenite and biocalcrudite; 3. Algal massive limestone; 4. Marly limestone; 5. Algal-gastropod-bryozoan limestone; 6. Grey limestone and marl in alternation; 7. Grey marly limestone; 8. Mylonite, product of deformation of granite or gneiss, micaschist; 9. Benthic foraminifera; 10. Benthic ostracods; 11. Planktonic foraminifera; 12. Land flora; 13. *Macoma*; 14. *Arca*; 15. *Lithothamnium*; 16. Gastropods; 17. *Amussium*; 18. *Pecten/Chlamys*; 19. *Corbula*; 20. *Cerastoderma*; 21. Schizasteridae; 22. *Isocardia*; 23. Fish; 24. Bryozoans; 25. Serpulids; 26. Parallel lamination; 27. Bioturbation; 28. Erosional surface.

## 2.2. Petrological analyses

Three samples were prepared for macroscopic and microscopic petrological analyses (pTc1, pTc2 i SC1). Samples pTc1 and pTc2 were collected from the cement quarry “Tajnovac” and the exploitation area “Bukova glava”, on the Požega–Našice road, for the purpose of determining the presence of basement rocks. Sample pTc1 was taken 11 kilometres away from the road, and pTc2 7.5 kilometres from the entrance to the quarry (pTc2 is approximately 4 kilometres in a straight line distance from the top of “Bukova glava”). The locations where both samples were collected are on outcrops by the road below the “Lončarski vis” peak (492 m), in the immediate vicinity of the “Gradac” crossing (355 m). Sample SC1 was taken from the lowest part of the synthetic column, therefore from the oldest available part of the Badenian sediments (Fig. 4).

## 2.3. Methods for determining permeability and porosity

To determine permeability and porosity, six samples were collected from selected locations. Petrophysical testing was performed in the Sector for research and development, Service for evaluation of rocks and reservoir fluids of INA-Oil industry. Two samples had distinct bedding and were sampled both parallel and perpendicular to the bedding plane. From six samples a total of eight cylinders were crafted – five of them 3.84 cm (1½ inch) in diameter and three 2.56 (1 inch) in diameter. Prior to determination of permeability and porosity, the samples were dried at 105°C.

Porosity is determined using a volumetric method in a gas porosity meter crafted by the CoreLab company using nitrogen to fill the empty porous space. This method is based on the expansion of gas from the reference cell to the cell of known volume containing the sample. The pressure drop is equivalent to the volume of solid phases. Measurement is based on Boyle’s law of gas expansion.

Permeability is determined in a gas permeameter by measuring the pressure drop during the flow of nitrogen through the sample. Measurement is based on Darcy’s law of fluid flow through a porous medium in terms of laminar flow. The standard method uses pressure tightening the sam-

ple at 12 bars. The results are then corrected for the Klinkenberg effect. The permeability and porosity results are as shown in Table 1.

## 2.4. Organogeochemical methods

Five chosen samples were analyzed using organogeochemical analysis. Preparation of samples included: washing, drying, grinding in a Fritsch mill and filtering through a screen to a particle size of 315 µm.

The total amount of carbon was determined on a LECO IR 212 carbon determinator. By determining carbon the sample was pre-processed with 18% hot chloride acid in order to remove carbonate material. The ground rock particles were then analyzed on a Rock-Eval 6 pyrolyzer (ESPITALIE et al., 1985). On the basis of the parameters obtained by Rock-Eval pyrolysis (TOC, S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, T<sub>max</sub>, HI, OI, PI) diagrams were produced which offer insight into the richness, generative potential, quality (type of kerogen) and maturity of organic matter.

Isolating organic matter (kerogen) for optical testing, determination of the sulphur content and stable carbon isotopes, was done by standard chemical-physical methods of inorganic component breakdown using HCl and HF acids, and separating heavy metals by a ZnCl<sub>2</sub> solution with a density higher than 1.8 g/cm<sup>3</sup>.

Microscopic testing of organic matter in transitory, reflected and blue fluorescent light was conducted on an Olympus BH-2, Olympus BX-51 microscope and Leitz MPV-3 microscope photometer. The arithmetic mean of vitrinite reflection was measured. In a maceral system, amorphous organic matter was discerned (fluorescent-nonfluorescent), and also liptinite macerals (alginite, dinoflagellates, sporinite, liptodetrinite), vitrinites and inertinites.

The sulphur content in the kerogen was determined on a sulphur analyzer Leco SC-144 DR using the accredited method ASTM 4239-05. Soluble organic matter (bitumen) was procured by extracting ground samples of rock in a Soxhlet apparatus by chloroform reflux over 36 hours. Excess solvent was removed using rotational evaporation at 50°C, and the quantity of bitumen was determined after drying in a vacuum desiccator.

The extractable organic matter (EOM) content of the ground samples was determined using a 36-hour long Soxhlet extraction by chloroform. Chromatographic-gas analysis of the alkali fraction of bitumen was done on a gas chromatograph Varian 3900 equipped with a capillary column (50 m x 0.25 mm).

## 2.5. Interpretation of seismic sections and documentation regarding deep borehole cores – petroleum geological research

Seismic sections and documentation regarding cores from exploration boreholes were analyzed and interpreted with the goal of correlating Karpatian, Badenian and Sarmatian sediments at depth in the Drava depression with the Badenian and Sarmatian sediments discovered at “Bukova glava”.

**Table 1:** Results of basic petrophysical analyses

Sample	Porosity* %	Permeability* horizontal	
		vertical	vertical
SC42	15.5	0	0.04
	16.1	2.2	0
SC38	53.6	0	0
SC34	35.8	5,714.00	0
SC27	24.9	0.22	0
SC 21	12.4	0	<0.01
	11.4	<0.01	0
SC14	21.2	0	0

\*-mD = 1 x 10<sup>-3</sup> µm<sup>2</sup>

On the seismic sections, the basement mountains were denoted, that is to say the E-log datum Tg and the boundary between the first and second Neogene megacycle (VELIĆ et al., 2002), or more precisely E-log marker Rs7. With the data obtained from seismic sections as well as from documentation regarding core analyses from deep boreholes, a clearer picture on the distribution and thickness of Badenian and Sarmatian sediments was gained. Data from the boreholes Bankovci-1, Bankovci-2, Koška-2, Đurđenovac-1 and Našice-1, as well as seismic sections BK-5V-84, CR-2V-84, BV-25-94, KLOK-16-81, NA-1-94 and IS-2-84 were analyzed. Locations and the spatial distribution of deep boreholes and seismic sections in regards to the site of "Bukova glava" are shown on Fig. 13.

## 2.6. Analysis of documentation of shallow boreholes

Lithological and chemical data were interpreted from cores of the 18 shallow boreholes drilled for calculation of material reserves and also to enable correlation of sediments and compile the data into a single unit, i.e. a synthetic column. Data regarding the content of SiO<sub>2</sub> and CaCO<sub>3</sub> were particularly useful and interesting as they facilitated reliable correlation both laterally and vertically in terms of geological age.

## 3. RESEARCH RESULTS

### 3.1. Results of palaeontological research

At "Bukova glava" numerous macrofossils and microfossils were recovered. Among the macrofossils molluscs including *Amussium*, *Macoma*, *Corbula*, and *Cerastoderma* are particularly numerous, together with snails, polychaetes (*Serpula*), bryozoans, urchins (*Schizaster*) and fish. Various fragments of fossil macroflora are also commonly present.

Among the microfossils collected, foraminifera are the most numerous with a total of 29 species, of which 28 are of benthic and one of planktonic origin (Table 2). In the basal 12m of the column, in which petroleum source rocks were defined, dark green and light gray laminae of marl alternate, and samples (SC1-SC13) were collected at 30 centimetre intervals. Foraminifera are rare in these sediments, and mostly concentrated in lighter laminae, and the eurivalent taxa *Elphidium* and *Cibicides* are dominant. Samples taken in the middle part of the column (SC15 do SC26) contain small benthic taxa (*Bolivina*, *Bulimina*, *Uvigerina*) typical for the *Bulimina-Bolivina* zone of the Upper Badenian. The planktonic foraminifera *Globigerina bulloides* appears for the first time in a layer from which sample SC13 was taken, and is more frequent in samples SC15-SC18, which indicates a deepening and/or a strong connection with open seas.

The genus *Globigerina* appears for the last time in sample SC26, and is completely absent in subsequent samples, which suggests a shallowing upward trend and a change of the regime of sedimentation in the pool. In the upper third

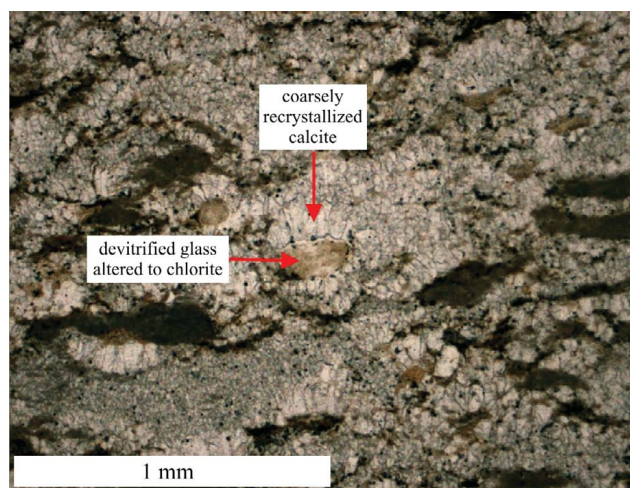


Figure 5: Fragments of volcanic glass in the devitrification process altered to chlorite. They are surrounded by coarsely recrystallized calcite.

of the column, biodiversity decreases, and foraminifera are slowly replaced by ostracods. Among the foraminifera, the tolerant taxa *Elphidium* and *Cibicides* are prevalent.

### 3.2. Results of petrological analyses

Two samples, pTc1 and pTc2 were analyzed, to correlate the data from rock outcrops on the northern slopes of Mt. Krndija with the data obtained from bore holes located in the deeper parts of Drava depression in order to determine the composition of basement highs.

On the basis of microscopic investigation, sample pTc1 was classified as mylonite, which originated by intensive deformation of granite or gneiss. Sample pTc2 is also metamorphic rock, having been deformed under the influence of relative high pressure and temperature and is determined as a tourmaline garnet micaschist. Both samples belong to the "basement highs", namely to rocks underlying the Neogene sequences.

Microscopic investigation of sample SC1 revealed that it is tuffaceous carbonate sandstone. Fragments of volcanic glass being completely devitrificated by chlorite formation are present in the sample (Fig. 5). Usually, coarsely recrystallized calcite is visible around such devitrificated fragments. It is possible, that this calcite recrystallization was not only the consequence of diagenesis, but also of elevated temperature. Numerous rock fragments having lenticular form and parallel orientation with respect to each other occur in this sample (Fig. 6), and are most likely marls in composition. Sometimes, rims of thinly and unequally distributed brown altered biotite and black kerogen (Fig. 6) are developed around these rock fragments. Also, rare muscovite and grains of quartz and zircon occur in the sample. The cement is calcitic, but calcite grains have an uneven grain size.

### 3.3. Permeability and porosity results

Basic petrophysical analysis of six samples (SC42, SC38, SC34, SC27, SC21 and SC14), as shown in Table 1 was per-



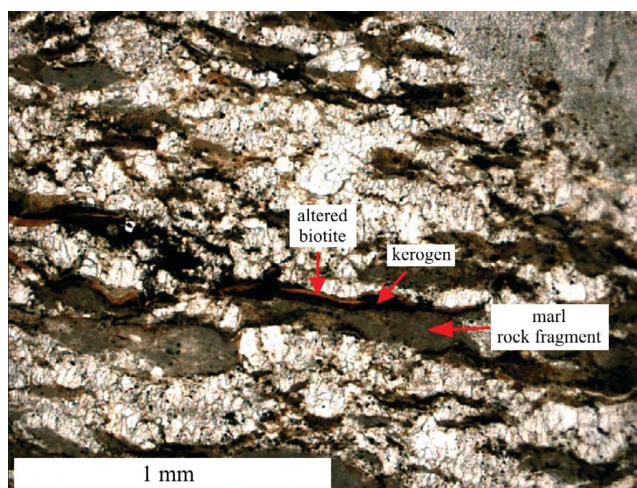
Table 2: Determined Miocene foraminifera at the "Bukova glava" locality

DETERMINED FORAMINIFERAL TAXA	ABUNDANCE/SAMPLE																																						
	SC6	SC7	SC7a	SC8	SC9	SC9a	SC10	SC11	SC12	SC13	SC14	SC14	SC15	SC16	SC17	SC18	SC19	SC21	SC22	SC23	SC24	SC25	SC26	SC27	SC28	SC29	SC30	SC31	SC32	SC34	SC35	SC36	SC37	SC38	SC39	SC40	SC41	SC42	
PHYLUM : PROTOZOA																																							
CLASSIS : RHIZOPODA																																							
SUBCLASSIS : FORAMINIFERIDA																																							
ORDO : FORAMINIFERIDA EICHWALD, 1830																																							
<b>SPECIES</b>																																							
<i>Globigerina bulloides</i> D'ORBIGNY																																							
<i>Uvigerina peregrina</i> CUSHMAN																																							
<i>Uvigerina</i> sp.																																							
<i>Bolivina dilatata</i> REUSS																																							
<i>Bolivina</i> cf. <i>compressa</i> D'ORBIGNY																																							
<i>Bolivina</i> sp.																																							
<i>Bulimina elongata</i> D'ORBIGNY																																							
<i>Bulimina marginata</i> D'ORBIGNY																																							
<i>Bulimina</i> cf. <i>elegans</i> D'ORBIGNY																																							
<i>Glandulina ovata</i> D'ORBIGNY																																							
<i>Globulina gibba</i> D'ORBIGNY																																							
<i>Lenticulina</i> sp.																																							
<i>Nodosaria</i> cf. <i>urnula</i> D'ORBIGNY																																							
<i>Pyramidulina</i> sp. (D'ORBIGNY)																																							
<i>Cibicides lobatulus</i> (WALKER & JACOB)																																							
<i>Nonion commune</i> (D'ORBIGNY)																																							
<i>Elphidium crispum</i> (LINNE)																																							
<i>Elphidium aculeatum</i> (D'ORBIGNY)																																							
<i>Elphidium macellum</i> (FINCHTEL & MOLL)																																							
<i>Elphidium</i> cf. <i>regnum</i> (D'ORBIGNY)																																							
<i>Ammonia inflata</i> (SEGUEENZA)																																							
<i>Amphistegina hauerina</i> D'ORBIGNY																																							
<i>Heterolepa dutemplei</i> (D'ORBIGNY)																																							
<i>Hoeglundina elegans</i> (D'ORBIGNY)																																							
<i>Melonis</i> cf. <i>pomplioioides</i> (FICHTEL & MOLL)																																							
<i>Spirolina</i> cf. <i>austriaca</i> (D'ORBIGNY)																																							
<i>Pygo chryseata</i> (D'ORBIGNY)																																							
<i>Tritoculina gibba</i> (D'ORBIGNY)																																							

ABUNDANCE/SAMPLE

○ - low   ● - medium   ● - high

Middle (?Early) Badenian  
 Upper Badenian (Bulimina-Bolivina zone)  
 Badenian-Sarmatian transition  
 Sarmatian



**Figure 6:** Rock fragments (probably marls in composition) are characterized by rims of thinly and unequally distributed brown altered biotite and black kerogen.

formed in order to determine their petrological characteristics i.e. analysis on the basis of permeability and porosity, and characterization as collector or cap rocks. Four samples (SC38, SC34, SC27 and SC14) are defined by a porosity greater than 20%, while the remaining two (SC42 i SC21) have a porosity below 20%.

Indirect comparison of the synthetic column with the displayed fossil and lithological content (Fig. 4) and the table of results of the basic petrophysical analyses (Tab. 1) illustrates the petrophysical and lithological characteristics of rocks which contain individual fossil communities.

### 3.4. Results of organic geochemical analyses

Five rock samples were chosen from the lowest part of the synthetic column and subjected to organic geochemical analysis (Fig. 7).

The organic matter content in collected samples varies from 0.48 to 13.5 % TOC. Samples SC16 (a, b) contain 0.48 and 0,52% organic carbon respectively, are of low generative potential, ( $S_2$ , Tab. 3), and their organic matter was partially changed by oxidation (OI, Tab. 3). As per pyrolytic and optical parameters, the organic matter is immature, and kerogen is of type III (Fig. 8). There are no characteristics of source rocks.



**Figure 7:** Display of part of the outcrop at Bukova Glava on which the lower part of the synthetic column was recorded with the location of sample SC13 indicated.

In contrast, samples of silty marls SC13, SC3 and SC1 (Table 3) show high levels of organic matter content which resulted in increased residual potential values ( $S_2$ , Tab. 3). Analytical results highlight the similarity between the samples. Values of genetic potential are in line with the organic matter contents. The sample containing the highest organic matter content also has the highest value of residual potential, as confirmed using Rock Eval pyrolysis ( $S_2=74.52$  mg HC/g rock).

A fair generative capability was also confirmed using pyrolysis on the extracted samples. It can be concluded that the rocks from all three layers of the lowest part of the column have very good to excellent characteristics of source rocks (HUNT, 1995; WAPLES, 1985). Increased hydrocarbon potential is the effect of a favourable type of organic facies, e.i. type II kerogen (Fig. 8).

Microscopic evaluation of the isolated organic matter determined that the rocks contain mostly (75–80%) amorphous organic matter of an uneven, but intense colour of fluorescence ranging from ochre yellow over yellow orange to brown orange. In its maceral structure, there is an extremely high content of hydrogen rich liptinite macerals of sporinites and liptodetrinites (15–20%), while vitrinite macerals only form up to 5% with a trace of inertinite macerals of fusinites and semifusinites (TYSON, 1995; TAYLOR et al, 1998).

Liptite macerals have marked yellow fluorescence. The Vitrinite maceral group is represented by two different macerals: a low-reflecting desmocolinite and telocolinite. The low reflection of desmocolinites is connected with submi-

**Table 3:** Results of determining organic carbon content, Rock Eval pyrolysis and extraction for samples SC1, SC3, SC13, SC16a and SC16b.

Sample *—extracted sample	TOC <sub>Leco</sub> %	TOC <sub>RE</sub> %	$S_1$	$S_2$	$S_3$	$T_{max}$ °C	$P_1$	$S_2$ $S_3$	HI	OI	MIN C %	Extract ppm
			mg HC g rock	mg HC g rock	mg CO <sub>2</sub> g rock				mg HC g TOC	mg CO <sub>2</sub> g TOC		
SC16b	0.48	0.55	0.08	1.26	1.05	407	0.06	1.2	229	191	3.14	400
SC16a	0.52	0.61	0.08	1.47	1.09	404	0.05	1.35	241	179	2.83	994
SC13	8.9	7.62	2	48.82	4.61	409	0.04	10.59	641	60	3.29	2844
SC3	7	6.47	1.29	35.93	3.32	417	0.03	10.82	555	51	2.28	3172
SC3*	0	5.9	1.23	34.62	3.47	416	0.03	9.98	587	59	2.25	0
SC1	13.5	12.28	3.65	74.52	4.69	416	0.05	15.89	607	38	1.65	4598
SC1*	0	12.35	3.34	73.41	5.11	414	0.04	14.37	594	41	1.35	0



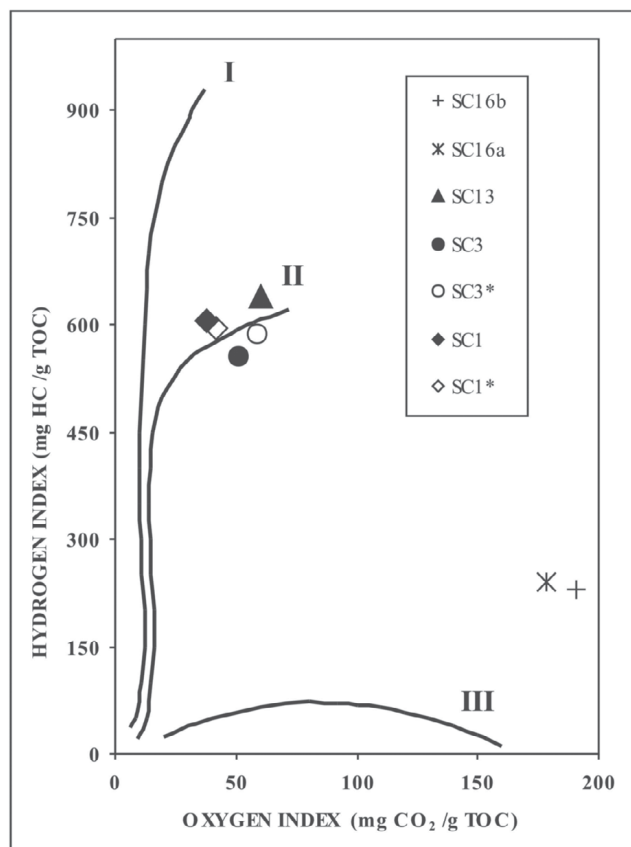
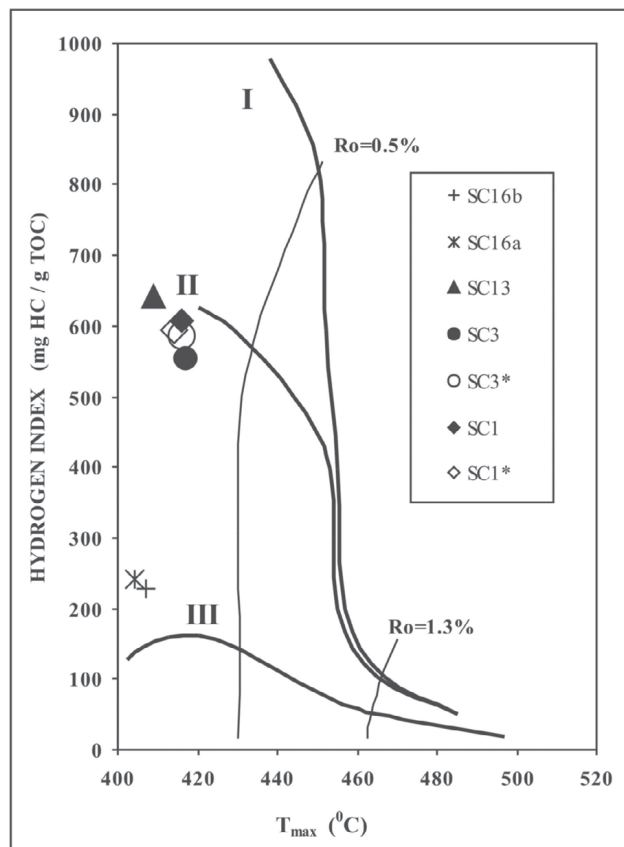


Figure 8: Modified VAN KREVELEN diagram.

Figure 9: Modified HI-T<sub>max</sub> diagram.

croscopic lipid intercalations which derive from the anaerobic (bacterial) breakdown of cellulose (TAYLOR et al., 1998).

Microscopically a rare occurrence of sulphur in the form of pyrite (framboidal pyrite) was also determined, and the remaining sulphur is chemically bound within a macromolecule of kerogen. The concentration of total sulphur in the kerogen is 8.77–13.02 %, which supports the theory of sedimentation in a marine environment.

Optical maturation parameters TAI ( $1^{+}-2^{-}$ , conversion  $<0.35\%Ro$ ), the yellow-orange hue of fluorescence as well as of measured vitrinite reflection (0.25 and 0.26 % Ro) indicate an immature, diagenetic phase of thermal transformation of organic matter. The value of maximum temperature of pyrolysis ( $T_{max}$  409–417°C; Tab 3, Fig. 9), further supports this. Therefore, the samples have the characteristics of an immature core rock.

In the analysed samples, a heightened quantity of less soluble bitumen was also determined 2844 to 4598 ppm. High n-alkane content and a hydrocarbon chain spanning  $C_{11}-C_{35}$  characterize a gas chromatograph profile of the bitumen. However, these results show signs of a bimodal distribution, but loss of hydrocarbons of the lower molecular domain is probable.

The bimodality of the distribution determines a mixed origin and suggests a heightened content of terrestrial lipids in an originally algal organic matter. The prevalence of HCs in a higher molecular domain ( $C_{27}$ ,  $C_{29}$ ,  $C_{31}$ ) as well as the domination of uneven HCs over the even ones ( $CPI >> 1$ )

confirm the results of the microscopic analysis, i.e. the heightened content of hydrogen rich lipids of the higher plants and the immaturity of bitumen (TISSOT & WELTE, 1984).

The Pr/Ph relations speak in favour of an anoxic to sub-oxic environment of organic matter sedimentation. As a result of the absence of lighter hydrocarbons (the sample in question is a surface sample) determining the maturity of bitumen is dubious.

With certain reservations regarding the bitumen maturity, it can still be safely concluded that the aforementioned parameters of bitumen are in accordance with the defined organic facies and the generative potential of the core rock.

### 3.5. Results of petroleum-geological research

Stratigraphic, micropalaeontological, geochemical, bitumenological-luminiscent, and similar data was used in order to reconstruct the geological and petrological conditions of Neogene sediments within the deeper parts of the Drava depression, as mentioned previously by KRANJEC et al. (1976).

It should be noted that chronostratigraphic analysis of the Neogene during the drilling of the aforementioned boreholes was somewhat different, layers had different names and ranges. A similar situation is applicable to the Badenian period (previously known as the Tortonian) which is today subdivided into Lower, Middle, and Upper, (while the Tortonian was subdivided into the Lower and Upper divisions). Ban-1 and Ban-2 (Bankovci-1, -2) boreholes can be subdivided into Lower Middle and Upper on the basis of bore-

hole documentation, because the lithology (and to a lesser extent the relatively comprehensive palaeontological content) of the Badenian and the Sarmatian sediments in these two wells was also identified in the “Bukova glava” synthetic column. An attempt at such analysis was made (but with limitations) for the Đurđenovac–1 and Koška–2 boreholes. Comparison with the “Bukova glava” column is not easy to achieve because of different lithological characteristics and poor palaeontological data.

It must also be mentioned that there is a 500m interval (from 1350–1850m depth) that contains no samples and is therefore chronostratigraphically undetermined in the Đurđenovac–1 well. Within this interval, there is a boundary between the basement rocks and the first Neogene megacycle which can be confirmed and located on the basis of seismic data, and as such is integrated in the table display of the Đurđenovac–1 borehole within the stratigraphic range of deep boreholes.

Data for the Na–1 (Našice–1) borehole are the poorest and exist only in the form of a short text description of the borehole. It was drilled 50 years ago and has no graphic or stratigraphic description, and the palaeontological data are generalized and for the Badenian base restricted to a few lines of text. Despite these problems, thicknesses of the 1<sup>st</sup> Neogene megacycle (Fig. 2) can be displayed with a high percentage of accuracy for all five analyzed boreholes. The “Bukova glava” column is best correlated with the stratigraphic display in the research borehole Bankovci–2 (Ban–2) shown in Fig. 12.

Hydrocarbons were not detected in the boreholes, nor were petroleum source rocks, which does not definitely exclude the possibility of their past or present occurrence. For example, in the Đu–1 (Đurđenovac–1) borehole samples from 1207–1210 m (top part of the 1st megacycle bordering the 2nd megacycle), contain elevated total organic matter (>0.5 %), above the contiguous in estimation of source rocks, in relation to deeper intervals. However the results of pyrolysis indicate a very small quantity of residual organic matter; in other words they don't suggest the possibility of gas and oil generation. Organic matter is on the border of maturity ( $T_{max}=434^{\circ}C$ ).

On this basis it can only be partially deduced that the drilled Badenian sediments have no petroleum source intervals, nor an interval with adequate sedimentary properties.

As the Badenian sediments on the northern slopes of Mt. Krndija on the “Bukova glava” are good petroleum source rocks, the question arises as to whether source rocks lie more to the edge of the depression where organic matter was deposited in isolated lagoons and coves. These are areas where alongside the original organic matter of aquatic, i.e. algal origin, a significant amount of lipid components of prevalently terrigenous origin is also represented (for example in the Badenian sediments of the lower synthetic column, SC1–SC13, dinocysts of bisaccates occur – *Pinus*, *Picea* and *Abies*).

Thicknesses of Badenian sediments increase from the edges towards the deeper parts of the depression, but the pe-

troleum source potential of the sediments decreases, which can be connected to the distance from the coastline to which depositional, i.e. palaeoecological conditions favourable for the accumulation and preservation of organic matter are tied.

### 3.6. Results of the analysis of shallow borehole documentation

Lithological and chemical data from the cores of 18 shallow exploratory boreholes drilled by the “Nexe grupa” company in the “Tajnovac” quarry, were analysed in order to correlate the deposits and determine the relationships between SiO<sub>2</sub> and CaCO<sub>3</sub> in space and time. A relative increase of the SiO<sub>2</sub> component with regards to CaCO<sub>3</sub> was noted in the sequence of sediments ranging from the youngest to the oldest, and a relative increase of the proportion of the SiO<sub>2</sub> component in relation to CaCO<sub>3</sub> ranging from north to south.

## 4. DISCUSSION

### 4.1. Biostratigraphic discussion

The fossils recovered at “Bukova glava” belong to the first Neogene megacycle (lower-to-middle Miocene) according to VELIĆ et al. (2002). The diverse microfossil assemblage in the middle part of the column is of particular interest.

The oldest sediments outcropping at the surface are laminated marls. Lighter laminae are interbedded with darker laminae of tuffitic marls and sandstones. In the darker laminae there is virtually no trace of life, while in lighter laminae *Macoma* and *Arca* bivalves were discovered, as well as carbonized fish and rare members of tolerant taxa of foraminifera (of which the genera *Elphidium* and *Cibicides* are the most common). Palynological analysis has shown that a large percentage of pollen grains of conifers, transported from land, occur alongside marine dinocysts *Lingulodinium machaerophorum*, *Systematophora placacantha* and *Spiniferites ramosus*, (K. BAKRAČ, pers. comm.).

Due to the stressful environment, there are no index taxa in these sediments. Their age is older than the Upper Badenian, because the *Bulimina–Bolivina* zone was proven in the overlying deposits. ĆORIĆ et al. (2009) link the tuffitic volcanism in this region to the Lower Badenian, so we can assume the age of these sediments, or at least a part of them, to be Lower Badenian.

Fossiliferous marls and marly limestones in the middle part of the column (samples SC15–SC26) contain flora and fauna characteristic of the lower part of the Upper Badenian, the *Bulimina–Bolivina* zone (Đ. PEZELJ, pers. comm.). *Bolivina*, *Bulimina* and *Uvigerina* genera dominate, as they are represented by a larger number of species (Tab. 1), and there is a high percentage of the planktonic species *Globigerina bulloides*. The accompanying flora and fauna is also typical of the upper Badenian in Paratethys, as coralline algae, bivalves (*Chlamys*, *Amussium*, *Corbula*) snails, bryozoa, polychaeta (*Serpula*) and urchins (*Schizaster*, numerous radiolae) frequently occur.

In the layer from which sample SC27 was taken there is an abrupt decrease of fossils, and subsequently only *Cibicides* and *Elphidium* can be found in marls, up to the level of sample SC38. The foraminiferal assemblage of Sarmatian age appears from the horizon with sample SC27 onwards (Đ. PEZELJ, pers. comm.). In the same samples, ostracods and snails appear, together with the bivalve *Macoma*, as well as carbonized fish. Bioturbation and parallel lamination, low biodiversity, and the prevalence of opportunistic euryhaline species, suggest a shallowing upward trend and increased input of fresh water into the pool.

Echinoid radiolae can still be discovered in the sediments, which were probably redeposited from older horizons. Sediments between horizons SC28–SC38 are marked as transitional, because they contain only opportunistic microfossil species of low stratigraphic value, typical for stressful environment. The upper boundary of this sediment package is marked by an erosional surface. In sample SC38 Prasinophyceae appear for the first time, such as *Mecsekia* sp, *Cymatiosphaera miocenica* and *Cymatiosphaera* sp., together with terrigenous palynomorphs. In samples S39 and SC40 there are neither macrofossils, nor foraminifera, and in sample SC42 the bivalves *Cerastoderma latisulcum* and *C. vindobonense vindobonense* occur. Therefore the sediments in the upper part of the column (above horizon SC38) were designated to be of Sarmatian age.

#### 4.2. Petroleum – geology discussion

Deposition of petroleum source rocks in the lower part of the synthetic column (ranging from SC1 to SC13) (Fig. 4) occurred in lagoon conditions in rugged environments of low water energy (Fig. 11), where sedimentation of calcitic clay, silt, and sand (grey-white layers) took place. Periodic volcanic activity in the form of an eruption and release of volcanic ash in the region of the Slavonian mountains (and possibly more remote regions as well) led to a cyclic pattern of sediments – tuffaceous calcitic marly sandstones ranging from dark green to black in colour with a grey-white calcitic clays, marls and marly sandstones. Tuffaceous marly sands were deposited in reducing conditions as indicated by the presence of framboidal pyrite. Reduced pH conditions with a lack of  $\text{CaCO}_3$  component are related to more pronounced sedimentation of  $\text{SiO}_2$  detritus.

A few small individuals of the genus *Elphidium* occur, in the grayish-white sediments represented by *Elphidium crispum*, *E. aculeatum* and *E. macellum*, while in the dark green tuffaceous layers there are virtually no foraminifera. During deposition of these sediments open marine influences are lacking, and the planktonic foraminifera *Globigerina bulloides* only appears in layer SC13.

The proximity and impact of land is indicated by a considerable amount of liptinites of terrigenous origin (sporinite), as are traces of a maceral of the huminite-vitrinite variety in the content of organic matter, and the increased percentage of hydrogen rich lipids of higher plants in the molecular distributions from segregated extracts (molecular area  $C_{27}$ ,  $C_{29}$ ,  $C_{31}$ ). Microscopically, rare chemical compounds of sulphur



Figure 10: System of normal microfaults of the domino-type in the lower part of the synthetic column.

in the form of pyrite (framboidal pyrite) were also determined, while the remaining sulphur was chemically bound within a macromolecule of kerogen. These parameters determine an anoxic marine environment of deposition.

Fine lamination and lack of sedimentary textures, including bioturbations, are typical for this formation. The sedimentary area expanded during the deposition of the Badenian rocks, which indicates a system of syndimentary normal microfaults of the domino-type in the lower part of the synthetic column, ranging from layers SC1 up to SC13 (Fig. 10).

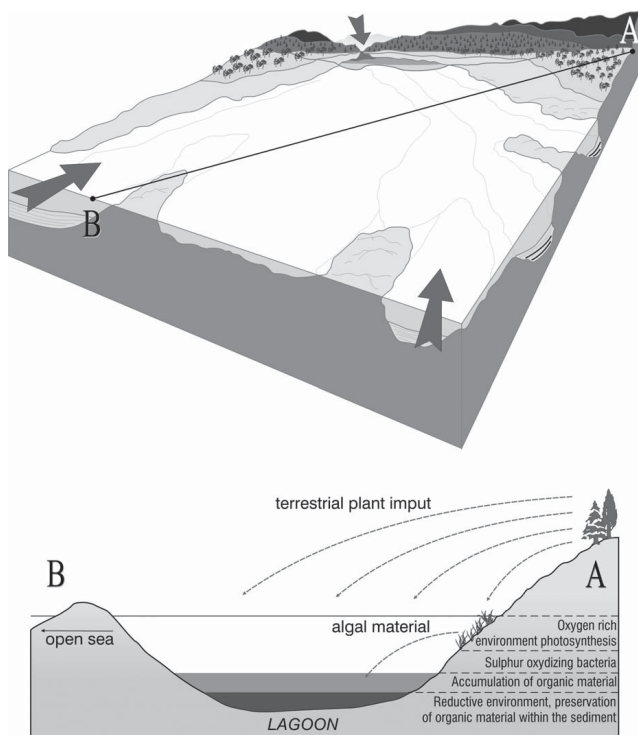
On the basis of lithological and textural attributes and the fossil content, it can be concluded that the sediments in question belong to a protected lagoon (Fig. 11) or a partly closed bay, in which rivers and precipitation carried clastic material from the slopes of Mt. Krndija.

Figure 11 shows the process of organic matter accumulation, which took place in the lower Badenian during formation of layers SC1–SC13. Because the Lower Badenian sediments reach a pronounced palaeorelief with a crystalline base, they fill the area with large sideways shifts in thicknesses in the coastal regions. In the background lie the Krndija massif and a stream/river flow. On the same picture the position of section A–B is shown, together with the model of organic matter accumulation in a partially protected lagoon. The occasional and limited influence of the open marine environment on the lagoon and large stream or river flow, which transported detritus from the slopes of Krndija into the lagoon is depicted using arrows.

Accumulation and transformation of organic matter took place in the deeper parts of the protected lagoon, together with sedimentation of tuffaceous calciferous marly sandstones, and salty marls ranging from dark green to black in colour, i.e. accumulation and sedimentation of volcanic ash, or grey white calciferous clays, marls, and marly sandstones in between volcanic eruptions (Figs. 11a, 11b).

The petrophysical attributes of certain rocks which chronologically, superpositionally overlie the basal deposits of the column (SC1–SC13) have the characteristics of prime





**Figure 11:** An idealized display-reconstruction of the environment in which the processes of production, accumulation and transformation of organic matter in an aquatic surrounding (lagoon) took place.

reservoir rocks. These are especially pronounced in samples SC14, where porosity reaches 21.2%, SC34 with a porosity of 35.8% (permeability  $5.714,00 \times 10^{-3} \mu\text{m}^2$ ) and SC38 with a porosity of up to 53.6%, (a very high value which should be analysed by further research).

The stratigraphic display (Fig. 12) of the research borehole Bankovci–2 (Ban–2) situated approximately 13 km north of the “Tajnovac” cement plant, is similar to the lithology of the open profile on the “Bukova glava” section. The mountains granite core is overlain by pyroclastics, then by marly sandstones, and finally by very fossiliferous marls, as in the synthetic column.

Three locations in the analyzed interval from the stratigraphic display of the research borehole Bankovci–2 have source rock attributes. The “Tortonian” (Badenian) basement, in the stratigraphic display is 247 metres thick and is classified as the “Lower Tortonian”. The interval within the research borehole Bankovci–2 (1436–985 m) which contains Pre-Tertiary basement (granites), pyroclastics, marly sandstones and sandy fossiliferous marls, can be correlated with the synthetic column on the “Bukova glava”.

On the basis of foraminifera, the interval could be determined as Upper Badenian in age, because it contains a microfossil community of the *Bulimina*–*Bolivina* zone. The genera *Bolivina* and *Elphidium* are absent from the community, which leads to the conclusion that the borehole Bankovci–2 reached sediments deposited away from the Badenian coastline.

It is interesting to note that in the stratigraphic display of the research borehole Bankovci–2, the pyroclastics which lie on the basement rocks are placed slightly below the “Tortonian” (Badenian). However, we consider that the pyroclastics in the borehole Bankovci–2 can be determined as Badenian (in the synthetic column they are marked as the Lower Badenian). In addition to the superpositional location within the synthetic column and the fossil composition which indicates a Badenian age, there are a number of papers which place the pyroclastics of Mt. Krndija and the surrounding

ŠIMON, 1974			ZEČEVIĆ, 2008			LITHOLOGY
AGE	interval [m]	thickness [m]	AGE	interval [m]	thickness [m]	
Upper Badenian (previously U. Tortonian)	985-1030	45	Upper Badenian	985-1160	175	
Middle Badenian (previously M. Tortonian)						
Lower Badenian (previously L. Tortonian)	1030-1232	202				
?	1232-1341	109	Middle Badenian	1160-1200	40	
			Lower Badenian	1200-1341	141	
Pretertiary basement	1341-1436	95	Pretertiary basement	1341-1436	95	
						GRANITE

**Figure 12:** A comparison of the stratigraphic subdivision of part of the deep borehole Bankovci–2 by the original analyst (ŠIMON, 1974) and the stratigraphic subdivision of the cores from the borehole in light of the new data.

mountains mostly into the Lower, or Lower and Middle Badenian (KRKALO & MUTIĆ, 1978; PAMIĆ & PECSKAY, 1996; KRKALO, 1998).

Also, it is significant to note that on the stratigraphic display of the research borehole Bankovci-1 which is situated only a few kilometres away from borehole Bankovci-2, the pyroclastics which lie on the basement rocks (micaschist) were indicated as being of “Lower Tortonian” age. On the profile through the boreholes Bankovci-1 – Bankovci-2 – Koška-2 – Đurđenovac-1 – Našice-1, the pyroclastics in the research boreholes Bankovci-1 and Bankovci-2 are correlated, i.e. were deposited at the same time and over the same area. It can be assumed that they belong to the lower part of the Lower Badenian as well as the pyroclastics in the synthetic column on the site of “Bukova glava”.

The stratigraphic display in the deep research borehole Bankovci-2 therefore differs significantly from the interpretation and provisions of ŠIMON (1974) who had placed the “Tortonian” (Badenian) sediments mostly in the “Lower Tortonian” (with the exception of the borehole Bankovci-2 where alongside “Lower Tortonian” “Upper Tortonian” was also displayed) or just defined as “Tortonian” without subdividing the aforementioned geological epoch.

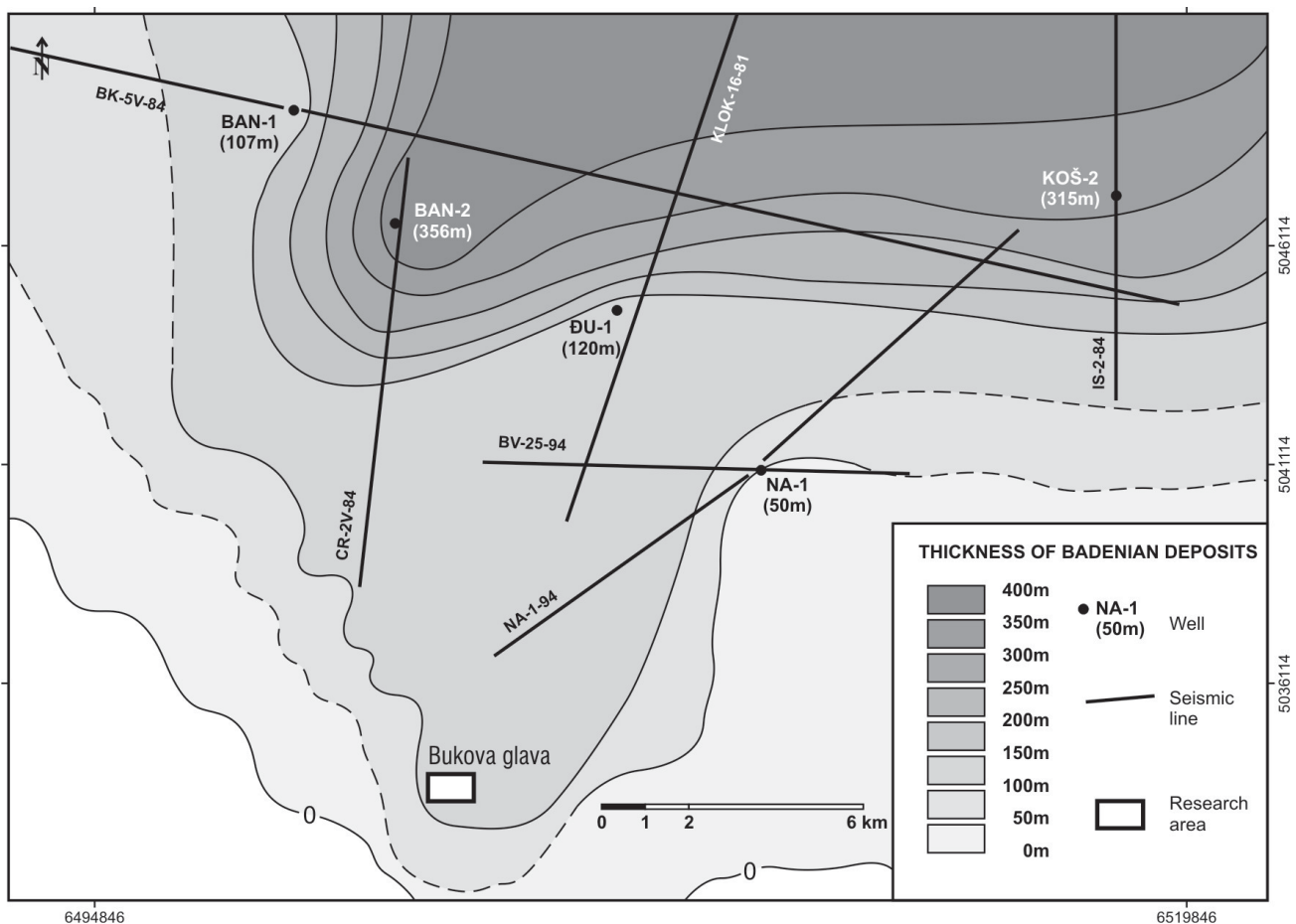
According to the graphically displayed conclusions of PERKOVIĆ (1975, 1978); ŠIMON, (1974) and BRODARIĆ,

(1985), the “Upper Tortonian” (Upper Badenian) and Sarmatian are completely absent from the deeper part of the Drava depression around Našice. This does not agree with the all-encompassing research carried out by KRANJEC et al. (1976), nor with the geophysical and hydrogeological research on the slopes and boreholes carried out by ŠUMANOVAC et al. (2003) at “Seona” on the northern slopes of the Mt. Krndija.

Differing standards of subdivision and definition of the “Tortonian” (as well as the Neogene), at the time when the boreholes were drilled, and lack of comparison with surface outcrops, are the most likely explanations for the discrepancy in thickness.

The isopach map (Fig. 13) of the Badenian sediments was created in accordance with the data which were collected in the field and laboratory research on the “Bukova glava”. During the creation of this map, the data from the “Seona” (ŠUMANOVAC et al., 2003) were taken into account, as was the data from the regional research published by KRANJEC et al. (1976), as well as the seismic sections as spatially distributed as shown in Fig. 13.

On the isopach map, an expected thickening of the Badenian sediments towards the centre of the Drava depression is visible. Badenian sediment thickness north of Našice increases rapidly from 150 to 350 metres.



**Figure 13:** Isopach map of the Badenian sediments of the northern slopes of Mt. Krndija and the southern boundary area of the Drava depression in the vicinity of Našice with the marked locations of exploration wells, seismic sections and the site of “Bukova glava”.

## 5. CONCLUSION

The development of the Badenian sediments on the northern slopes of Mt. Krndija was characterized by very diverse environments on a slightly sloped basement on which synsedimentary tectonics had a significant influence.

The well-developed palaeorelief of Mt. Krndija played a crucial role in the creation and modification of the depositional environment, as reflected in the flanking and vertical changes of facies. Furthermore, synsedimentary tectonics and the dynamics of the depositional area, particularly elevation of Mt. Krndija and the spread and subsidence of the depositional basin during the Badenian, together with regression in the uppermost part of the Badenian caused by synergistic activities of land rise and sea level fall were also important.

As a consequence of tectonics and eustatic changes in Paratethys, a shallowing upward trend occurred in the study area on numerous occasions. It is also likely that there was an emersion phase as well (visible at the boundary between layers SC38 and SC41).

Badenian sediments are characterized by the greatest variations in thickness of all the geological stages of the Miocene. The Badenian sediments which overlap periclinally on the Papuk–Krndija massif mostly match the former sea belts or environments of sedimentation such as bays and lagoons, where the changing sea levels are strongly reflected, together with spatial extension and the rise of massifs and subsidence of the depositional basin.

Since the sedimentary area during the Badenian steadily subsided and was broadened, the shifting of the coast line and the space of clastic deposition was caused by an uneven transport of material due to the seasonal influence of rains, as well as the varying intensity of erosion of parts of the rising terrain/land.

Contours of sedimentary elements visible on the seismic profiles mark periclinal overlaps on the northern slopes of Mt. Krndija as a consequence of the aforementioned palaeogeographical circumstances.

The diversity of environments, i.e. the environment of the protected lagoon/bay and a high rate of bioproduction, created ideal conditions for the accumulation of organic matter which was displayed in the petroleum geological model (Figs. 11a,b). An increased organic carbon content and the favourable hydrocarbon potential of these rocks are the consequence of a particular type of organic facies, type II kerogen, mostly of marine algal origin, but with an increased content of terrigenous lipids.

The presence of tuffites in the rocks with a considerable concentration of carbon suggests that volcanic activity influenced anoxic conditions (a decrease in pH) and significant changes of palaeoecological conditions, which occurred cyclically.

Additional evidence of a marine environment and anoxic conditions of sedimentation are the increased quantity of framboidal pyrite, and the increased content of organically bonded sulphur and the domination of phytane over pristane in the gas chromatographic distributions of bitumen extracted from the source rocks.

The genesis of this part of the analyzed sediments is tied to very reducing conditions of sedimentation which govern in protected lagoons/bays of relatively shallow seas.

The lithological composition of rocks on the edges of the Slavonian mountains can serve as input data for the creation of a 3d computer model which could by analyzing palaeostructural and palaeotectonic relationships simulate the time and possible routes of hydrocarbon migration. This provides the possibility for collecting new information for petroleum exploration. Furthermore, the data on rock permeability and porosity can be used in various geostatistical analyses of the Badenian sediments, to correlate the data from the boreholes in the Drava depression with those obtained on the edge of Mt. Krndija.

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