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MINERALOGICAL-GEOCHEMICAL CHARACTERISTICS OF THE NEOGENE SEDIMENTS AT THE COAL MINE OF ŽIVOJNO IN THE PELAGONIA DEPRESSION

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A b s t r a c t: This study gives a first-time detailed analysis of the mineralogical and geochemical characteristics of the Neogene sediments found at the coal mine of Živojno in the Pelagonija depression based on tested samples of cores recovered in the investigation of the coal series from this region. For the determination of the mineralogical composition we used the x-ray diffraction method while for the determination of the detailed geochemical characteristics we tested the presence of trace elements with the ICP-MS method. The presence of the following main mineral stages was recorded: muscovite/illite, chlorite, quartz, albite, orthoclase and epidote. The presence of these rare elements ranges from (in ppm): Mn (1684); Sr (250); Ba (598); Zn (121); Pb (36); Cr (34); Co (22); Ni (39); Cd (0.65); Cu (55); As (9.7); Li (32); V (121); Mo (2.1); Sb (1.2); Be (3); Bi (1); Ge (0.38); Sn (2.97); Ag (3.3); Ti (1.41); Rb (157); Cs (8.5); Th (15.9); U (3.93).

Key words: sediments; Neogen; Pelagonia; mineralogy; x-ray diffraction

INTRODUCTION

The tested samples have been taken in the course of the investigation of the coal mine of Živojno, which is located in the south-western part of the Republic of Macedonia and is a part of the Pelagonia coal basin (Fig. 1). The coal mine is at around 30 km in the south-eastern direction of the city of Bitola, around 10 km from the already open surface pit of Brod–Gneotino and 20 km from the thermal power plant of Suvodol. The investigated region falls under the territory of the villages of Živojno. Bach and Germijan in the immediate vicinity of the Macedonian-Greek border.

The borders of the coal mine are not clearly defined. In the south and south-west the coal mine continues towards Greece, in the east and north-east it wedges out whereas in the north-west it continues towards the coal mine of Brod–Gneotino. From the western side, the coal mine hasn't been contoured and as the result of the preliminary investigations it has started to sink considerably. The coal mine itself takes up an area of more than 20 km^2 and is located in the uppermost south-eastern part of the Pelagonia coal basin.

GEOLOGIC CHARACTERISTICS OF THE WIDER REGION

From a geologic point of view, the peripheral portion of the Pelagon and the paleorelief of the coal mine are built out of Precambrian gneiss and micaschists, Paleozoic quartz-graphite schists, phyllites and argilloschists whereas the basin is composed of Neogene and Quaternary sediments that lie transgressively and discordantly on top of the paleorelief.

Lithologically, the gneiss-micaschistic series is the most present in the wider region. It's quite heterogeneous and composed of several lithological media, the most common of which are the gneiss and micaschists along with their varieties.

Graphite micasists (Sgr) are most present in the wider region of the coal mine (Fig. 2). These highly metamorphous rocks have been found at the location between the Macedonian–Greek border and the village of Živojno, north-east of the village of Bach, i.e. they make up the north-eastern border of this Neogene coal basin. In the field, they're quite brittle, degraded in places and dark gray to black schistic rocks, composed of quartz, muscovite and graphite and more rarely from albite and garnet. There are also transitions towards garnet micaschists. These metamorphous varieties contain the presence of white quartz veins of various thickness and orientation direction most commonly along the foliation planes (N-NW–S-SE).

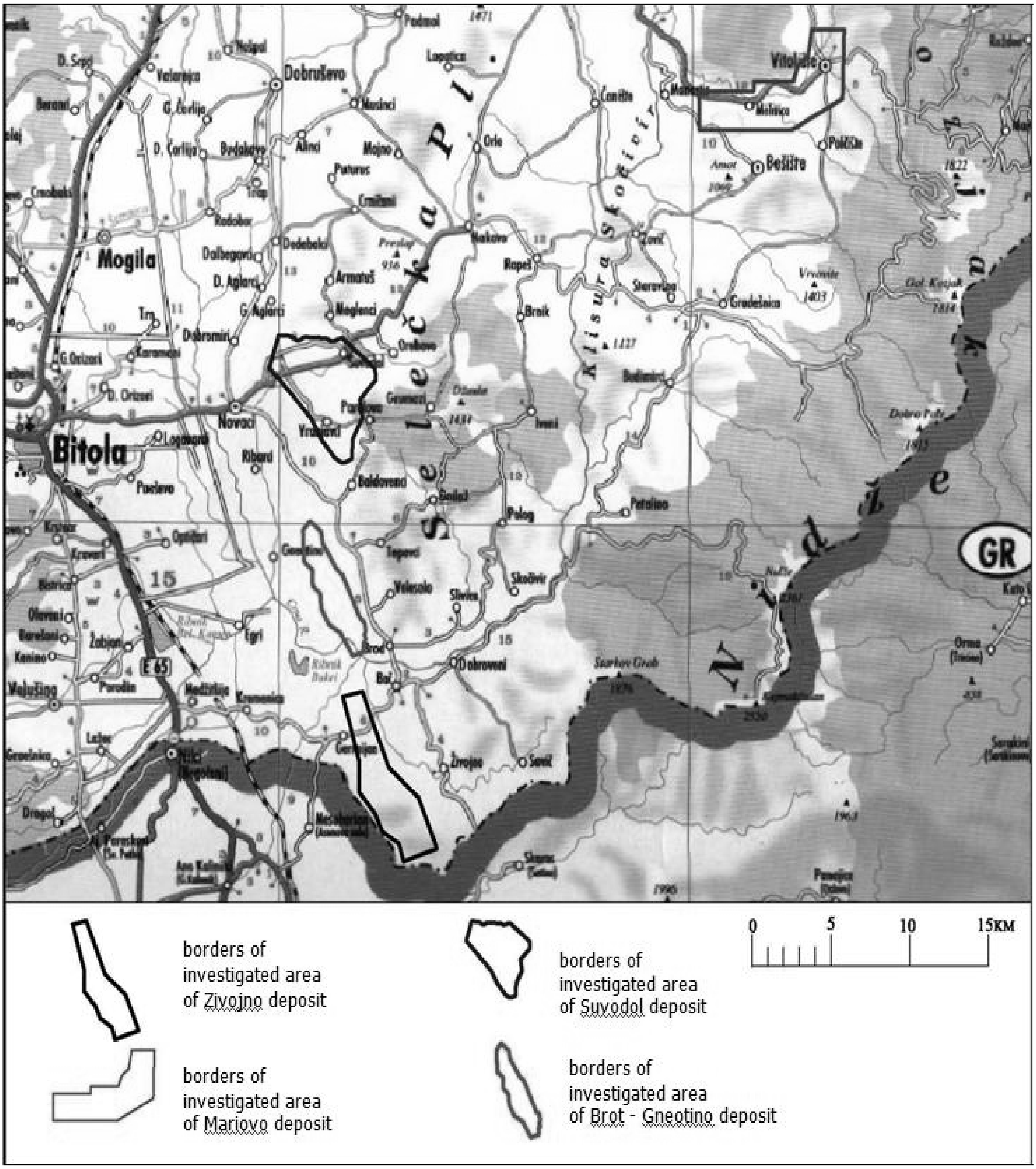
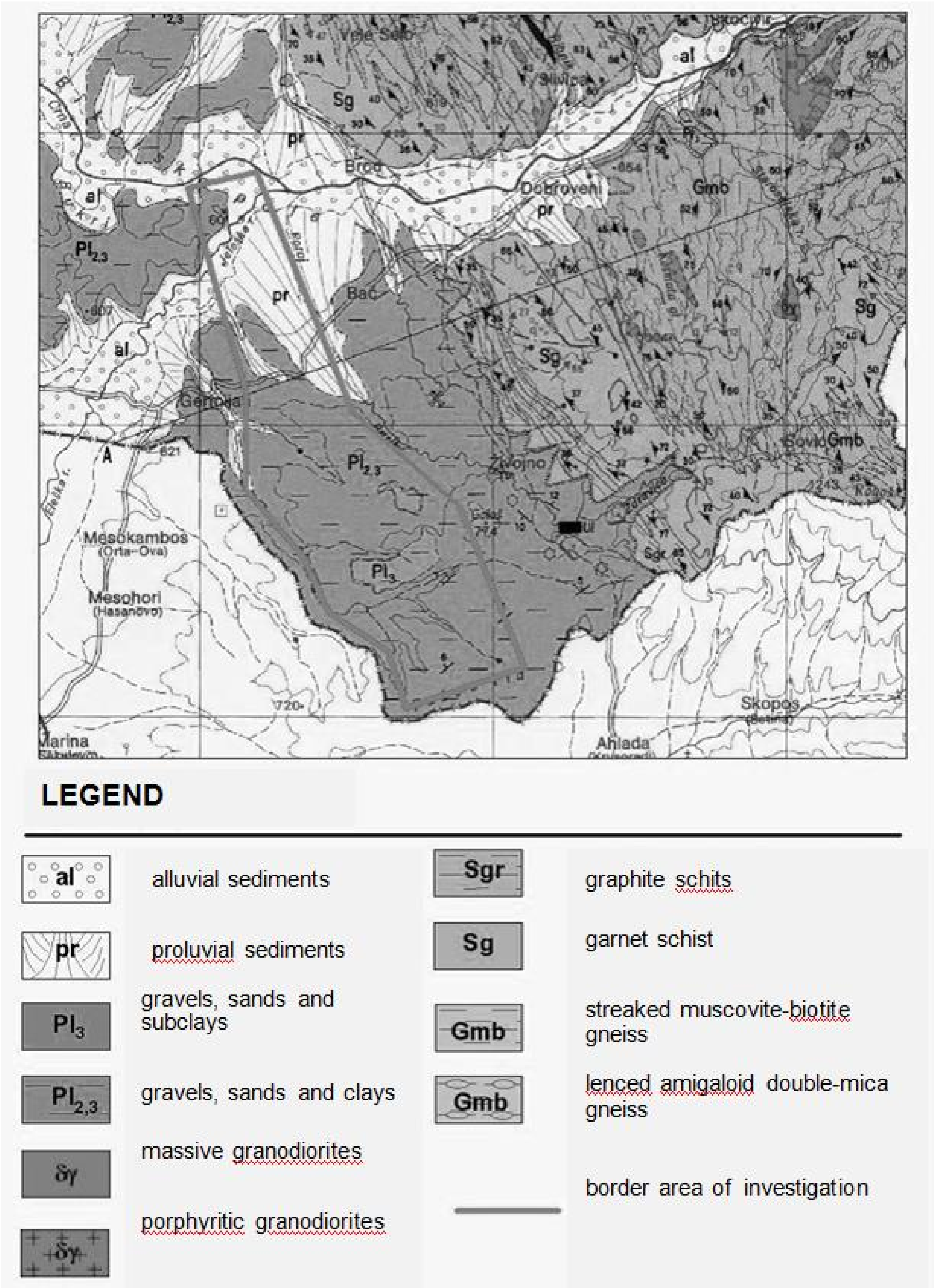


Fig. 1. Overview map of coal deposits in Pelagonia



Fig, 2. Geological map of the wider region of the Živojno coal mine

On top of the highly-crystalline metamorphous rocks lie transgressively and discordantly thick Neogene (Miocene-Pliocene) lake sediments. The thickness of these sediment deposits in the deeper (more central) parts of the Pelagon is over 700 m. These sediments mostly consist of two facies:

– lower facies (gray series) composed of gray well-stratified gravels, sands, sandy clays, clays and aleurolites with layers of coal (Upper Miocene sediments) and

– upper facies (yellow series) composed of yellowish poorly-sorted and poorly stratified gravels, sands (Pliocene sediments).

The lower facies (M_3) is the basic part of the Pelagonia depression, which starts with transgressive materials consisting of gravel and gravel sands. On top of this layer, which is around 10 m thick, are gray to gray-greenish well stratified layers and interbeds of sands, sand clays, aleurolites and clays which are interchangeable and gradually wedge out both in the vertical and horizontal direction.

The age of these sediment formations has been identified as upper Miocene based on the leafy flora and fossil remains consisting of diatom algae (Dumurdzanov, 1997), (Dumurdzanov and others, 2003, 2004 and 2008).

In the aleurolite layers, which overlie the coal layers, we've identified leafy fossil flora of Upper Miocene origin, such as: *Taxodium distikhum*, Juglan sacuminata, *Castanea atavia*, *Quercus pseudocastanea*, *Q. cerisaecarpa*, *Q. sosnowski*, *Q. mediteranea*, *Q. species* 2, *Pinus hepios*, *Gliptostrobus europius*, *Ulmus cf. ruskovensis*, *Ulmus species*, *Dictylofillum* sp. (Mihajlovic & Lazarevic, 2004) (Fig. 3).

In the section overlying the coal we also identified the presence of the diatom algae *Ciclotella iris* and *Ciclotella* sp. 1 – a massive type in the Upper-Miocene sediments of the Pelagonia basin (Ognjanova-Rumenova & Dumurdzanov, 2008). *Actinocylus gorbunovii* (Sheshuk) and its accompanying types *Malosir aundulata*, *M. undulata* var. *normannii* Ariott, and *Fragilaria leptostauron* (Ehr.) Hust, *F. leptostauron* var. *fossilis* (Pant.) Rehak *F. leptostauron* var. *rhomboids* (Grun.) Hust., *Diploneis carpathorum* are also found, but much more rarely.

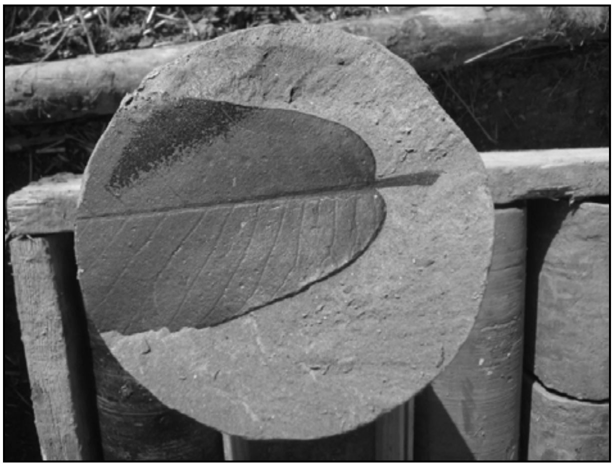


Fig. 3. Leafy fossil flora

The upper facies (PI) lies directly on top of the Upper Miocene sediments and is composed of light-gray and yellowish poorly-sorted and poorly stratified gravels, silts and sands. In the lower sections there are well stratified and well-sorted sediments, light gray in color (white aleurolites – "trepel" and well-stratified fine-grained and in places clayey aleurolites). In the higher sections there are mostly yellowish gravels, gravel sands, aleurolites and sands. The upper facies is a continuation of the sedimentation of the lower facies. Its thickness depends a great deal on the morphology of the terrain, the structural-tectonic characteristics as well as the degree of erosion. In some sections of the investigated region this facies is almost completely eroded making the lower facies exposed at the very surface of the terrain. The origin of this series has been identified as Pliocene based on the flora found – *Tapirus priskus* var. *macedonica* (Laskarev 1950).

The lake sediments in some sections of the terrain are covered with **Quaternary deposits (Q)**. These deposits are of small thickness, up to several meters and are mostly represented by diluvial, proluvial and alluvial deposits. They're composed of clay sandy slope and river material mixed with unrounded or poorly rounded pieces and blocks of various rocks that make up the surrounding terrain.

APPLIED METHODOLOGY

There were 37 core samples recovered from the boreholes, each weighing around 2 kg. All samples were prepared in accordance with standard ISO-14869/1. The concentration of rare elements has been determined with the use of the ICP-MS method under the following conditions.

Conditions for ISP-MS, 7500, Agilent

Sample introduction	
Sprayer	PEEK, Babington-type
Spraying chamber	Glass, double pass, spraying chamber temperature 2^0C
Injector of ISP torch	Quartz, 2.5 mm
Programme conditions	
Plasma power	1500 W
Pump velocity	0,1 rps
Aux flow of Ar for plasma	1,0 L/min
Carrier gas flow Ar	0,9 L/min
Sampler cone	Nickel
Skimmer cone	Nickel
Sample depth	7.4
Points/mass	3
Integration time	0,3 s
Total acquisition time /replicates	8 s
Replicates	3
Total acquisition time/sample	24 s

Element/mass

Element	m/z	Element	m/z
Li	7	As	75
Be	9	Sr	88
Al	27	Mo	95
Ti	48	Pd	106
V	51	Cd	111
Cr	53	Cs	133
Mn	55	Ba	137
Co	59	Tl	205
Ni	60	Pb	208
Cu	63	Bi	209
Zn	66	Th	232
Ga	69	U	238
Ge	72	Sn	120
Sb	121		

The mineralogical composition has been determined based on the x-ray diffraction method of three samples marked BOEY-1, BOEY-2 and BOEY-3 under the following conditions:

Portion of each pulverized sample was packed into a standard holder. The quantities of the crystalline mineral phases were determined using the Rietveld method. The Rietveld method is based on the calculation of the full diffraction pattern from crystal structure information. The X-ray diffraction analysis was performed on a PanalyticalX'Pert Pro diffractometer equipped with Cu x-ray source and an X'Celerator detector and operating at the following conditions: 40 kV and 40 mA; range 4 – 80 deg 2 θ; step size 0.017 deg 2 θ; time per step 50.165 sec; fixed divergence slit, angle 0.5^0; sample rotation 1 rev/sec.

RESULTS

Mineralogy

Sample BOEY-1/(126-126.6 м) is dominantly composed of muscovite/illite and contains minor amounts of chlorite, quartz and albite. SEM observations combined with EDS analysis showed that illite mostly occurs as fine grained particles (<20 µm). Some of the illite and/or muscovite as well as chlorite are in the form of platy particles.

Samples BOEY-2/(73.0-73.6 м) and BOEY-3/(37-22) are dominantly composed of feldspar and quartz, while muscovite/illite and chlorite are minor components. The samples also contain minor amounts of epidote and traces of amphibole. Traces of mixed-layer illite-smectate were indentified based on peak at 12.1 Å. Quartz, feldspar and epidote occur as angular particles and most of the muscovite and chlorite as platy particles larger than 20 µm in size. The morphological observations suggest detrital origin of the minerals. The mixed-layered illite-smectite may also be of detrital origin being formed from weathering of muscovite. The absence of diagenetic mineral formation is supported by the shallow depths and unconsolidated nature of the sediments.

The minerals identified in the samples and their semi-quantitative amounts are in Table 1.

Table 1

Minerals identified in the samples and their semi-quantitative amounts (wt %)

No/probe	Muscov/ Illite	Chlorite	Quartz	Albite	Orthoclase	Epidote
BOEY-1/ 126-126.6, A11-12190-1	49	18	14	18	trace	n.d.
BOEY-2/ 73.0-73.6, A11-12190-2	14	12	18	37	8	11
BOEY-3/ 37-22, A11-12190-3	11	11	20	36	6	15

Note: n.d. = not detected

Whole rock geochemistry

Table 2 shows the results of the macro- and microelement content in the Neogene sediments from Živojno, the composition of the neighboring gneiss-granite from the Pelagonia metamorphous complex (PMC) (lit), the average composition of the upper crust (UC) (Taylor and McLennan, 1985) as well as the composition of the North-American clayey sediments (NASC) (Gromet et al., 1984).

The results clearly show that the composition of the main elements of the Neogene sediments in the area of Živojno is very close to the composition of the gneiss-granite of the PMC and at the same time very close to the composition of the upper crust (UC). The same conclusions which refer to the origin of the material of the Neogene sediments at Živojno, can be drawn with the use of the diagrams (A-CN-K; A-CNK-FM) (Nesbit et al, 1996). These diagrams (Fig. 4) clearly show the trend of the weathering processes of the gneiss-granite and the formation of the Neogene sediments as well as the difference in the presence of the Al_2O_3, CaO, Na_2O and K_2O in these sediments compared to the gneiss-granite. These differences are a result of the weathering processes of the metamorphous rocks and the fast mobility of the Ca, Na, Sr.

Trace elements geochemistry

The concentration processes of the rare elements in the course of sedimentation are quite complex and generally depend on several factors of the weathering process of rocks, such as: material classification, adsorption, diagenesis and transport of the material (Garrels and Mackenzie, 1971; Taylor and McLennan, 1985). The concentration of the rare elements (see Table 2) shows a wide range of variations in relation to the UC and many similarities with the NASC. The thorium and uranium have a different mobility in the weathering processes, which is why the Th/U ratio is within the 3.5 – 5.0 range (McLennan et al., 1993). Some of the presence of V, Zn, Ni, Cr is a lot similar to the presence found in the NASC. Also the presence of Co, Cu, Rb, Sr, Cs, Ba is a lot similar to the presence found in NASC with the exception of the relatively increased presence of Sr, which is a result of the fast weathering of the plagioclase. The small presence of clay minerals in the Neogene sediments basically predetermines the distribution and concentration of the rare elements.

Table 2

Major elements as wt % and trace elements in ppm (by ICP-MS)

Sample	Živ-1	Živ-2	Živ-3	Živ-4	Živ-5	Živ-6	UC	NASC	PMC
SiO_2	64.21	68.13	64.18	64.58	65.41	65.74	66.00	64.80	66.22
Al_2O_3	16.8	13.6	15.7	15.9	13.6	14.7	15.20	16.90	19.80
CaO	1.23	1.23	1.40	3.08	1.68	1.37	4.20	3.63	1.60
MgO	1.66	1.42	1.60	0.96	1.29	1.21	2.20	2.86	2.26
Na_2O	1.49	1.16	1.49	2.84	1.28	1.13	3.90	1.14	2.30
K_2O	1.69	1.21	1.52	1.21	1.21	1.21	3.40	3.97	6.00
TiO_2	0.78	0.58	0.81	0.93	0.60	0.56	0.50	0.70	0.12
FeO	6.6	7.6	5.7	6.6	5.3	5.5	5.0	5.65	1.18
MnO	0.23	0.34	0.11	0.46	0.21	0.11	0.08	0.06	0.11
P_2O_5	0.04	0.02	0.03	0.04	0.05	0.03		0.13	0.07
H_2O	5.50	5.11	7.56	3.91	9.37	8.44			0.58
Total	**100.23**	**100.40**	**100.10**	**100.51**	**100.00**	**100.00**	**100.48**	**99.84**	**100.24**
Sr	155	174	231	176	108	164	350	142	
Ba	586	624	678	609	457	606	550	636	
Zn	109	112	108	118	93	120	71	115	
Pb	23	26	24	23	14	23	25	25	
Cr	116	114	110	113	60	116	35	125	
Co	27	31	27	29	17	27	10	25	
Ni	30	37	34	38	33	33	20	58	
Cd	0.54	0.57	0.88	0.58	0.53	0.49	25		
Cu	52	51	53	58	43	45	1.5	50	
As	5.3	9.8	5.7	8.6	6.3	9.4		7.6	
Li	37	39	44	35	33	38	60		
V	116	140	175	159	103	161		130	
Mo	1.2	1.2	1.5	2.5	0.82	0.87	0.2		
Sb	0.58	0.68	0.71	0.76	0.81	0.47		2.09	
Be	2.6	3.2	3.2	3.8	2.7	3.1			
Bi	1.6	0.78	0.79	1.9	0.65	0.54			
Ge	0.35	0.24	0.29	0.19	0.21	0.34			
Sn	3.2	2.8	3.5	5.4	3.9	2.1			
Ag	1.3	1.5	1.2	1.3	1.4	1.2			
Rb	163	219	211	258	140	166	112	125	
Cs	5,8	7.1	6.9	12	3.7	3.8	3.7	5.6	
Th	17.7	17.4	19	30	16	20	10.7	12.3	
U	3.5	5	4.5	6	4.9	7.5	2.8	2.66	
Cr/Th	6.55	6.55	5.7	3.7	3.75	5.8	3.27	10.16	
Th/U	5.0	3.48	4.22	5.0	3.26	2.66	3.80	4.62	

UC – Upper Crust (Taylor and McLennan, 1985)
NASC – Average Nort American Shale (Gromet et al, 1984)
PMC – Pelagonian Metamorphic Complex (lit)

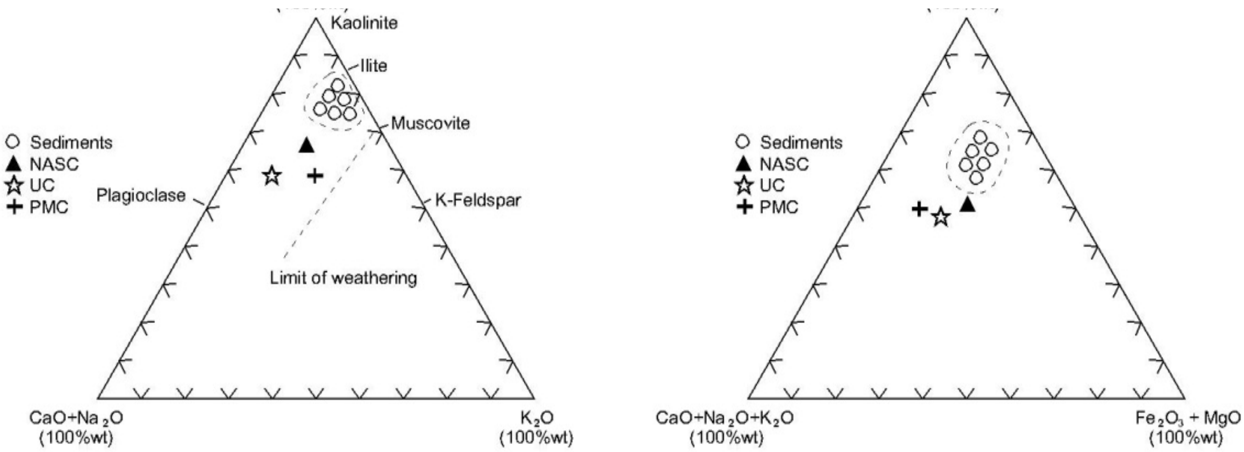


Fig. 4 Al_2O_3-($CaO+Na_2O$)-K_2O and Al_2O_3-($CaO+Na_2O+K_2O$)-Fe_2O_3+MgO plot of sediments samples (after Nesbitt and Young, 1996), compared with upper crust (UC) given by Taylor and McLennan (1985); and North American Shale Composite (NASC) given by Gromet et al. (1984).

CONCLUSION

The mineralogical and geochemical investigations which were conducted on a certain number of samples from the Neogene sediments found in the vicinity of the Živojno coal mine point to the following: the main minerals identified in the Neogene sediments are K-feldspar, quartz, muscovite/illite, chlorite and small quantities of epidote and amphibole. The morphological forms of the minerals points to the fact that these are detritic forms. The minerals of the mixed layers illite/smectite are also of detritic origin and were formed with the decomposition of muscovite. Therefore, the specified mineralogical composition of the Neogene sediments is very close to the composition of the neighboring gneiss-granite of the Pelagonia metamorphous complex.

The content of the macro- and micro-elements clearly indicates the relation between the Neogene sediments and the neighboring metamorphous rocks and the weathering processes and mobility of these elements in the same processes.

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Р е з и м е

МИНЕРАЛОШКО-ГЕОХЕМИСКИ КАРАКТЕРИСТИКИ НА НЕОГЕНИТЕ СЕДИМЕНТИ ВО НАОЃАЛИШТЕТГО ЗА ЈАГЛЕН ЖИВОЈНО ВО ПЕЛАГОНИСКАТА КОТЛИНА

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Клучни зборови: седименти; неоген; Пелагонија; минералогија; рендгенска дифракција

Во трудот за прв пат се објавени детални минералошки и геохемиски анализи на неогените седименти од околината на наоѓалиштето за јаглен Живојно во Пелагониската Котлина. Минералошката детерминација е направена со примена на методот на рендгенска дифракција и притоа е одредено присуството на следните минерални фази: мусковит/илит, хлорит, кварц, албит, ортоклас и епидот. Одредбата на елементите во траги е направена со методот ICP-MS и на база на добиените резултати може да се констатира дека неогените седименти во овој дел од Пелагониската Котлина водат потекло од околните метаморфни карпи.