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СОДРЖИНА

Geologica Macedonica	Год.	25	Број	1	стр.	1–84	Штип	2011
Geologica Macedonica	Vol.		No		pp.		Štip	

TABLE OF CONTENTS

GEOME 2
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Original scientific paper

TOTAL DEPOSITED DUST AS A REFLECTION OF HEAVY METALS DISTRIBUTION IN AREA WITH INTENSIVELY EXPLOITED COPPER MINERALS

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A b s t r a c t: The "Bučim" copper mine environ was monitored for assessing the heavy metals distribution. For that issue characterization of 17 elements content in total deposited dust was performed. The element contents were determinate using atomic emission spectrometry with inductively coupled plasma (ICP-AES). Bučim and Topolnica Villages and the town of Radoviš were chosen as sampling spots. It was determinate that in some period's trough the year large amounts of dust deposits in mine environ. The annual average values of dust deposition in the villages of Bučim and Topolnica are 489 mg m^{-2} d^{-1} and 309 mg m^{-2} d^{-1}, respectively. Maximum value for the total deposited dust (815 mg m^{-2} d^{-1}) was obtained at the sampling site in the Bučim village. The close vicinity of the Radoviš town was not exposed on dust deposition (97 mg m^{-2} d^{-1}). Characterization of elements contents showed higher contents of some heavy metals (with emphasis on Cu and Pb) in deposited dust. Maximum value for the content of Cu was obtained in dust from Topolnica village (1183 mg kg^{-1}) and maximum value for Pb content was obtained in deposited dust from Radoviš.

Key words: air pollution; monitoring; heavy metals; total deposited dust; copper mine; Republic of Macedonia

INTRODUCTION

Emissions of heavy metals into the environment happen through several processes. The emission of heavy metals into the atmosphere is one of the greatest threats to human health. Large amounts of dust are generated during blasts and excavations of mining minerals, whereas they are distributed in the air by the winds. People are directly exposed to the effects of heavy metals through inhalation of airborne micro-particles from atmospheric dust (Jarup, 2003; Godish, 2004). Atmospheric particles affect the human health when they enter into the respiratory system. The polluted air slows down the development of pulmonary functions in children (Gauderman et al., 2000; Gauderman et al., 2004). Senior citizens, especially those with a weakened cardiovascular and respiratory system are a high risk group too. Another risk group is patients with chronic pulmonary emphysema, asthma or cardiovascular diseases (Vallero, 2008).

Heavy metals in the atmosphere originated mainly from dust dispersion from metal refining, fossil fuel combustion, vehicle exhausts, and other human activities and stay in the atmosphere until they are removed by a variety of cleansing processes (Agarval, 2009). Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust. Copper mine with open ore pit type present a potentially emission source of heavy metals in the air. Main processes that allow it are: minerals blasting, drilling and crushing, their loading and transportation to processing and flotation plants. From other hand, large amounts of ore waste and flotation tailings are deposited at open, continuously exposited to air flow and winds caring-out. Heavy metals emitted in the atmosphere by combustion processes usually have relatively high solubility's and reactivity's; especially under low-pH condition (Athar and Vohora, 1995; Hršak et al., 2003; Hou et al., 2005). They can be carried to places far away from the sources by wind, depending upon whether they are in gaseous form or as particulates. Metallic pollutants are ultimately washed out of the air by rain and deposited on the land.

Total deposited dust is commonly used as monitor for this purpose. These kind of monitoring have been performed as part of a large number of analytical studies for a long time, but their application in recent decades has taken a swing. This is due to the fact that monitoring does not require the use of expensive technical equipment. Analytical results reflect the real situation of heavy metal distribution in the investigated area.

Deposited dust refers to any dust that falls out of suspension in the atmosphere. Solid and liquid particles or dust that falls out of suspension in the atmosphere can get into the environment and lead to its contamination. Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic elements introduced into the atmosphere (Čačković et al., 2009). Fine powder with a high content of heavy metals is generated as a result of emissions from the ore processing and metallurgical process and is distributed as a result of wearing the wind. Many investigations have focused on the chemical composition and the content of toxic substances in deposited dust (Morselli et al., 2003; Avila and Rodrigo, 2004; Polkowska et al., 2005; Vike, 2005, Stafilov et al., 2010).

In order to determine the amount of fine dust contained in the air, samples of total deposited matter (deposited dust) were collected at three locations in the area of Bučim copper mine, Republic of Macedonia.

INVESTIGATED AREA

Investigations were conducted in the eastern part of the Republic of Macedonia (Fig. 1), where the appearance of some metals (Au, Mg, Al, Sc, Ti, V, Cu) in the air is related to the presence of a copper mine and flotation plant, “Bučim”, near the town of Radoviš (Barandovski, et al., 2008; Balabanova et al., 2009, 2010, 2011; Stafilov et al., 2010). In this area an influence from the former iron mine, Damjan, has also been determined (Serafimovski et al., 2005). As a result of these anthropogenic activities, distribution of certain heavy metals in air and their deposition in the environs were expected. Moderate continental climate characterized the region of the study area. The altitude varies between 350 and 1000 m. The average annual temperature is around 10°C. The average annual rainfall amounts to 563 mm with large variations from year to year. The most frequent winds in the region are those from the west with a frequency of 199 ‰ and speed of 2.7 m s^{-1}, and winds from the east with a frequency of 124 ‰ and speed of 2.0 m s^{-1} (Lazarevski, 1993).

The "Bučim" mine and the ore processing plant have been functioning since 1979 and it is assumed that the mine has about 40 million tons of ore reserves. Ore tailings are dropped out by the dampers from the open ore pit at open site near the mine. The ore tailings deposit occupies a surface of 0.80 km^2, located southwest of the open ore pit, near the regional road Štip–Strumica. The ore tailings deposit has about 130 million tons of ore tailings. Exposure of this great mass of ore tailings to constant air flow and wind, leads to the distribution of large amounts of dust in the air. The flotation plant produces 4,000,000 tons of copper ore annually. In the process of flotation of copper minerals, the average annual amount of flotation tailings created is approximately 3.95 million tons. These tailings are drained and disposed of on a dump near the mine (2.2 km).

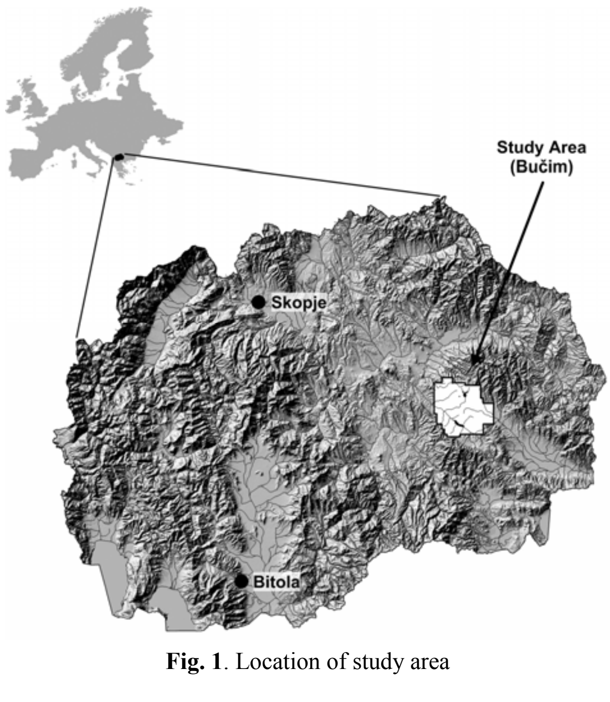

Fig. 1. Location of study area

Geological description

At the study area the following main geotectonic structural units have been identified: (1) the Kriva Lakavica basin, the Smrdeš–Gabreš syncline, the Radoviš basin, the Radoviš anticline divided to the Štip Block and the Bučim Block (Hristov et al., 1965; Stefanova et al., 2004; Stafilov et al., 2010). The Radoviš anticline represents the eastern boundary of the Vardar zone towards the Serbian–Macedonian mass. These two large structural units are separated by a deep NW-SE fault (Hristov et al., 1965). The Bučim–Damjan–Borov Dol area is divided into two tectonic blocks. The Bučim tectonic block and the southern tectonic block Damjan are a part of the Vardar zone. The blocks are divided by a fault of first order in the SE direction. Despite the disposition in two different tectonic blocks, the metallogenic area is unified based on the similarities of Tertiary magmatism and the analogous ore mineralizations. The Bučim copper-porphyry deposit with additional gold mineralization is found in the northern block (Stefanova et al., 2004).

EXPERIMENTAL

Sampling and sampling preparation

In order to determine daily amount of deposited dust, samples of total deposited matter (deposited dust) were collected. The town of Radoviš and the Bučim and Topolnica villages (Fig. 2) were the three monitoring spots around Bučim copper mine. The total quantity of the deposited dust was monitored monthly in 2009. Samples of total deposited matter (wet and dry deposition) were collected using the dust deposition gauges. This method measures dust deposition rate and involves the passive deposition and capture of dust within a funnel and plastic container. Data is usually collected over monthly periods and results are expressed mg m^{-2} d^{-1} (i.e. the mass of dust deposited per m^2 per day). This method enables determination of the relative 'dustiness' of sampling locations.

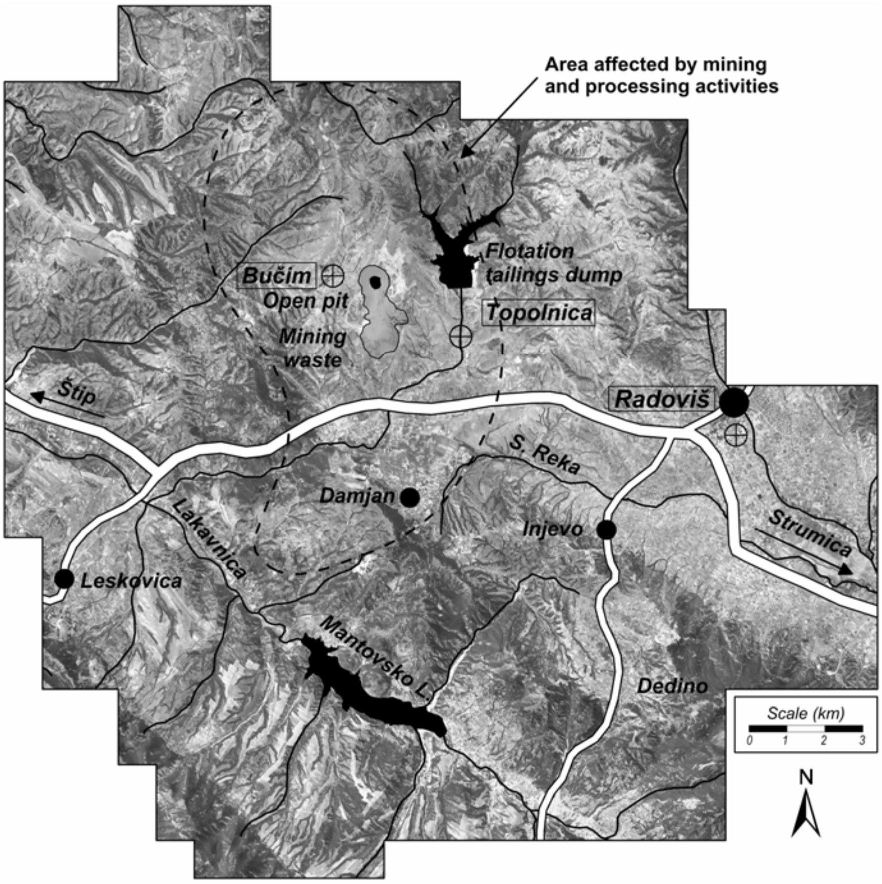

Fig. 2. Location of the sampling points for deposited dust

A deposit gauge, which comprises a 28±1 cm diameter funnel inserted into a plastic container (at least 5–10 liters in size) through a rubber stopper. Stand approximately 2 m tall and a canister which holds the plastic container to protect it from sunlight. The plastic container may also collect rainwater and other material such as bugs and leaf litter, etc. This does not contaminate the sample and should not be removed in the field. After 30±2 days, any deposited matter in the funnel was washed into the plastic container using distilled water. The aliquot of each sample was evaporated near dryness and then 3–5 ml of nitric acid, *p.a.* (MERCK, Germany) was added and collected into the 25 ml volumetric flasks.

Chemical analysis

Seventeen elements (Al, B, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V and Zn) were determined by using atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian 715-ES). The optimal instrumental parameters for this technique were previously given (Stafilov et al., 2010). For ICP-AES instrument calibration and quantitative determination of each element in deposited dust, a commercial standard mix solution (11355-ICP Multi Element Standard IV, Merck) was used. The correlation coefficient of calibration curve for each element was 0.999. In order to check for possible background contamination, blank samples were used and processed simultaneously with field samples. The method detection limit was calculated based on average measuring of the blank sample. For all laboratory samples and standard solutions, treated ultra pure water was used. The QC of the applied technique was performed by standard addition method, and it was found that the recovery for the investigated elements ranges between 98.5–101.2 %.

Data processing

For the statistical analysis of data parametric and nonparametric statistical methods were used (Hollander and Wolfe, 1999). The obtained values for the contents of the investigated elements were statistically processed using basic descriptive statistics. Data distribution was examined with the application of normality tests. Line and bar/colon plots were used for better visibility of elements content and trends of dust deposition through the year.

RESULTS AND DISCUSSION

The amount of total deposited dust that is spread in the air is presented in Fig. 3. It is evident that a large amount of deposited dust were recorded in the close vicinity of the mine (Bučim and Topolnica villages) in some periods in the year where the values are above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}). Maximum value for the total deposited dust (815 mg m^{-2} d^{-1}) was obtained in August in the Bučim village. This is the highest value for the amount of total deposited dust compared to the other two places. The annual average for the total deposited dust in the vicinity of the Bučim village is 489 mg m^{-2} d^{-1}, for Topolnica is 309 mg m^{-2} d^{-1} and accounted for Radoviš is 97 mg $m^{-2}d^{-1}$. A lower value was obtained for the amount of the total deposited dust in Topolnica village environ, while for Radoviš was obtained a much lower value (Fig. 3).

The obtained values for 17 elements content were proceed using descriptive statistics (Table 1). As it can be seen, median values for the copper in deposited dust samples taken from the studied area is 158 mg kg^{-1} and the min/max range of values shows much higher content of this element in the samples from the mining area (ranges from 52 to 1182 mg kg^{-1}). Similar results were obtained for the distribution of Fe, Pb and Zn thereby the median value and the min/max range for these elements indicate their increased content.

Because of high ore content of Cu (0.3 %) and large amount of copper in flotation tailing (Serafimovski et al., 2005) it was expected this element to have significantly higher content in samples of deposited dust compared to the other elements. As it can be seen from the data presented in Table 2, the median values for Cu in samples of deposited dust taken from the Radoviš area is 396 mg kg^{-1} and the ranges (from 94.8 to 1171 mg kg^{-1}) for the Topolnica village the median values in samples of deposited dust is 150 mg kg^{-1} with ranges (from 52.5 to 1183 mg kg^{-1}) and for the Bučim village the median values in deposited dust samples is 145 mg kg^{-1} and the ranges from 85.3 to 317 mg kg^{-1}. The maximum value for the content of Cu was obtained from Topolnica village (settlement near by the flotation tailings landfill) (Fig. 4). Even the amounts of deposited dust was not above the maximum permitted level in the town of Radoviš higher contents of Cu were found at the beginning of the year (max. value was obtained in May), with descending trend to the end of the year. These high contents of Cu are not only due to mining works, but also the town works, the traffic and industry. The developed technological processes allow emission of higher contents of Cu in the air and it deposition in Radoviš environs. In general, villages are less affected with these potentially emission sources of copper.

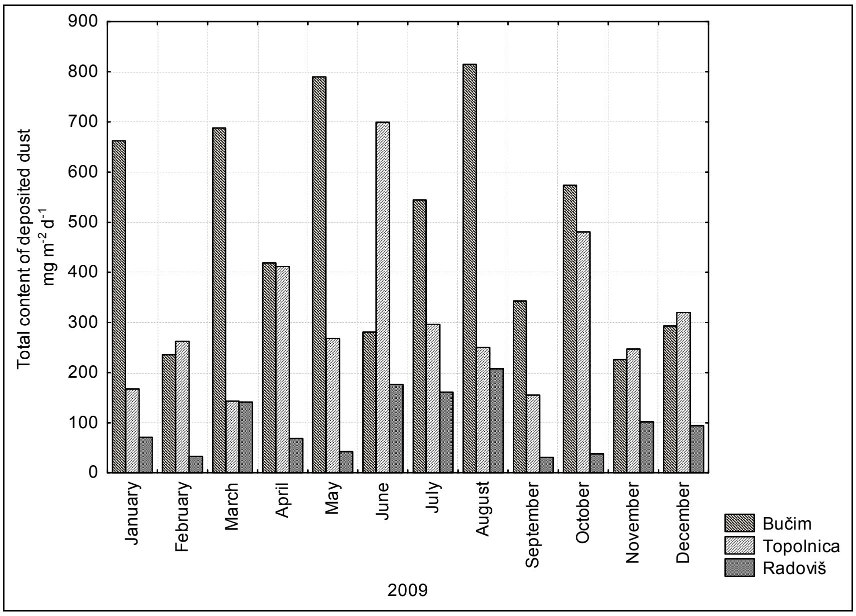

Fig. 3. The total content of deposited dust

Table 1

*Descriptive statistics of measurements (**N** = 36, 17 elements)*
Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg^{-1}

Element	*N*	*X*	*Xg*	*Md*	Min	Max	P_{10}	P_{90}	*s*	*A*	*E*
Al	36	0.2	0.16	0,17	0.02	0.57	0.07	0.3	0.13	1.51	2.16
Ca	36	6.20	4.01	4.17	0.52	21.9	1.01	14.6	5.65	1.30	1.19
Fe	36	0.32	0.26	0.27	0.05	1.00	0.14	0.66	0.20	1.59	2.77
K	36	1.21	0.84	0.77	0.12	6.21	0.28	2.20	1.23	2.62	7.14
Mg	36	0.48	0.44	0.44	0.15	1.36	0.24	0.81	0.24	1.56	3.71
Na	36	0.51	0.35	0.35	0.06	2.42	0.08	1.06	0.48	2.06	5.71
B	36	443	195	188	8.91	3085	38.3	1427	654	2.52	7.02
Cr	36	8.61	6.60	6.69	0.96	41.2	3.17	17.8	7.36	2.75	10.4
Cu	36	310	210	158	52.5	1182	84.1	861	313	1.70	1.95
Li	36	3.70	1.99	2.06	0.27	60.3	0.95	3.83	9.77	5.89	35.1
Mn	36	183	162	151	50.8	459	95.7	362	98.9	1.37	1.53
Mo	36	4.25	2.73	3.59	0.50	15.7	0.50	9.57	3.70	1.37	1.91
Ni	36	21.7	13.5	12.9	1.78	148	5.39	35.3	28.8	3.24	11.5
Pb	36	49.3	35.1	28.6	7.19	189	14.6	122	47.3	1.83	2.61
Sr	36	212	128	132	16.9	887	34.0	572	223	1.59	1.79
V	36	9.35	8.01	7.24	2.31	27.1	4.34	16.8	5.47	1.27	1.76
Zn	36	259	176	149	38.9	1045	72.7	665	275	2.04	3.29

N – number of samples, *X* – arithmetical mean, *Xg* – geometrical mean, *Md* – median, Min – minimum, Max – maximum, P_{10} – 10 percentile, P_{90} – 90 percentile, *s* – standard deviation, *A* – skewness, *E* – kurtosis

Table 2

Statistical parameters for annual average of the content of chemical elements in samples of deposited dust (Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg^{-1})

Element	*N**	Sampling site					
		Bučim village.		Topolnica village		Radoviš	
		Median	Range	Median	Range	Median	Range
Al	12	0.13	0.02–0.19	0.15	0.07–0.58	0.25	0.16–0.56
Ca	12	9.12	1.74–2.19	1.32	0.53–4.74	7.25	1.56–20.9
Fe	12	0.23	0.05–0.34	0.27	0.10–1.02	0.36	0.14–0.77
K	12	0.76	0.12–4.71	0.86	0.28–6.21	0.69	0.23–2.12
Mg	12	0.43	0.15–0.84	0.34	0.21–0.84	0.48	0.19–1.36
Na	12	0.16	0.06–0.92	0.31	0.08–0.87	0.77	0.24–2.41
B	12	203	8.91–1427	93.4	34.7–305	454	101–3085
Cr	12	4.22	0.96–7.78	6.32	1.74–20.1	12.6	6.42–41.2
Cu	**12**	**145**	**85.3–317**	**150**	**52.5–1183**	**396**	**94.8–1171**
Li	12	1.17	0.27–2.11	2.13	1.20–5.16	2.79	0.95–60.3
Mn	12	128	50.8–459	148	69.8–411	197	98.4–419
Mo	12	3.53	0.50–6.91	2.51	0.50–12.3	4.18	0.50–15.7
Ni	12	6.94	2.81–14.1	13.5	6.49–27.8	26.9	1.79–148
Pb	**12**	**25.7**	**12.1–56.6**	**26.8**	**7.20–184**	**69.5**	**20.1–189**
Sr	12	303	70.7–888	46.4	16.9–269	170	34.1–572
V	12	5.49	2.31–8.23	8.63	4.34–27.1	13.1	5.23–18.5
Zn	12	217	92.5–1045	89.0	38.9–240	176	86.6–665

*N – number of samples

Similar results were obtained for the content of Pb. With previously investigations in the same study area, Cu and Pb were separated as anthropogenic introduced elements in the Bučim mine environ (Balabanova et al., 2009, 2010, 2011; Stafilov et al, 2010). Maximum value was obtained from the town of Radoviš (189 mg kg^{-1} in February) and varies during the whole year (Fig. 5). This discontinuity of the monthly values for lead contents in deposited dust, indicates that to Pb emissions contribute town characteristic factors (special emphasis is given on traffic and industry). Despite the large amounts of total deposited dust from Bučim village, lead contents were insignificant. Maximum value (184 mg kg^{-1}) for the lead content in deposited dust from the Topolnica village was obtained in March, when starts' decreasing of lead content and the trend is retained until the end of the year (Fig. 5).

The ultimate effect is that despite large amounts of deposited dust, population in Bučim and Topolnica villages is not affected with high content of anthropogenic introduced metals (Cu and Pb) due to copper mining works. Deposited dust collected in the town of Radoviš, despite small amounts of deposited dust, has higher content of Cu and Pb.

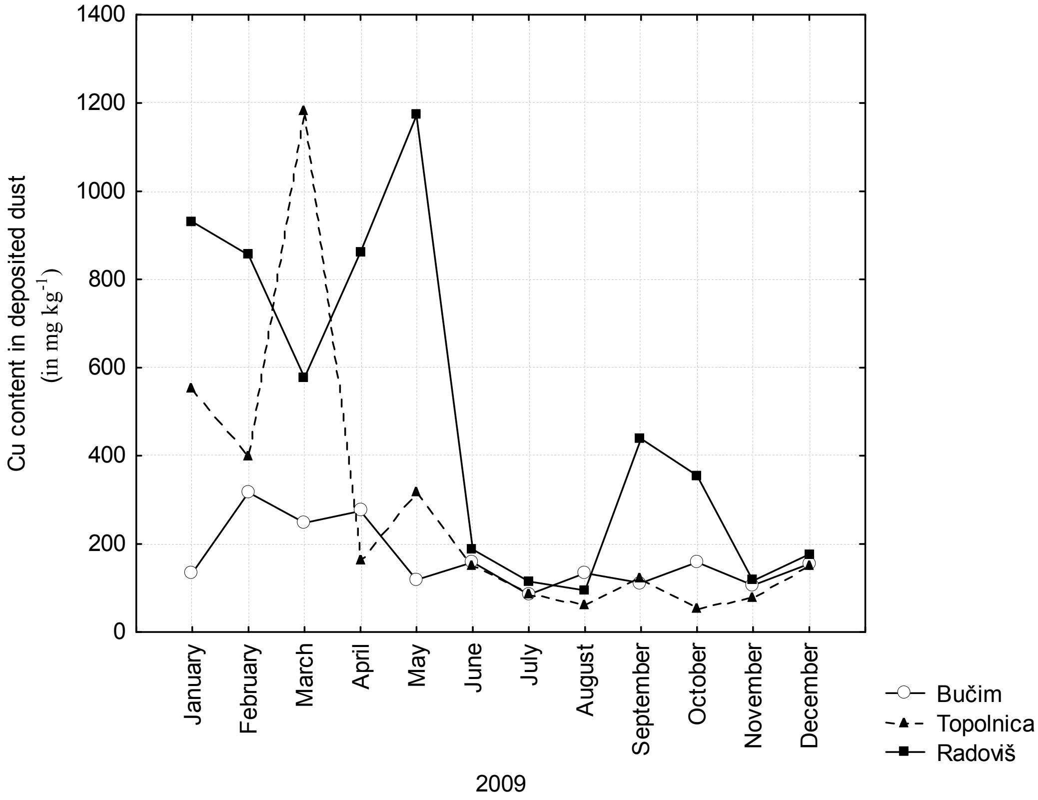

Fig. 4. Trends of copper content in deposited dust through the whole year

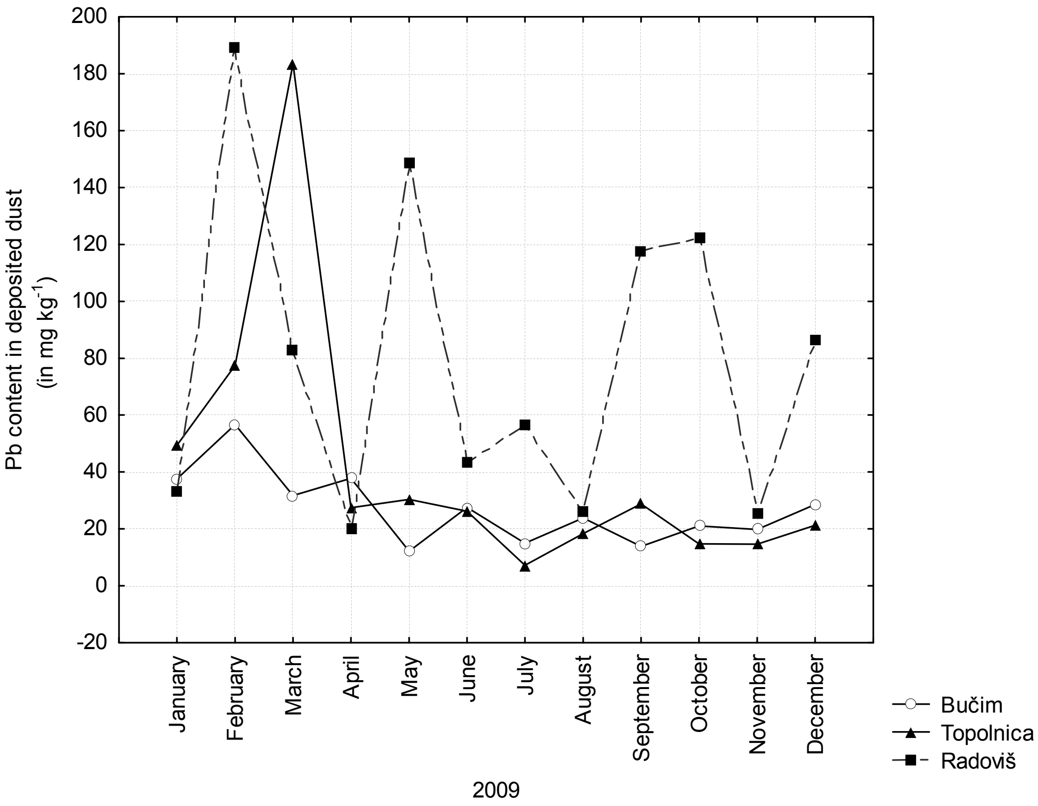

Fig. 5. Trends of lead content in deposited dust through the whole year

CONCLUSION

Total deposited dust has proved to be very effective environmental media sample for monitoring present distribution of heavy metals in area with intensively exploited of copper minerals. In this investigation, obtained data about element contents showed that copper mine contribute to dust distribution in it's environ. Conducted monitoring with deposited dust samples showed that anthropogenic introduced elements (with emphasis on Cu and Pb) deposit in higher content in close vicinity of their hot spots (open ore pit, ore waste and flotation tailings landfill). In the copper mine environ, there were some values above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}). Annual average for the total deposited dust in the vicinity of the Bučim village was 489 mg m^{-2} d^{-1}, for Topolnica 309 mg m^{-2} d^{-1} and for Radoviš 97 mg m^{-2} d^{-1}. Maximum value for the Cu content was obtained from Topolnica village (settlement near by the flotation tailings landfill). In the town of Radoviš deposited dust was not above the maximum permitted amount for dust powder, but higher content of Cu and Pb contents were found (max. values 1171 mg kg^{-1} and 189 mg kg^{-1}, respectively). The higher contents of Cu and Pb are not only due to mining works, but also the town works, the traffic, industry and developed technological processes alow emission of higher amounts of these heavy metals in air.

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Р е з и м е

СЕДИМЕНТЕН ПРАВ КАКО РЕФЛЕКСИЈА НА ДИСТРИБУЦИЈАТА НА ТЕШКИ МЕТАЛИ ВО ОБЛАСТ СО ИНТЕНЗИВНО ИСКОРИСТУВАЊЕ НА БАКАРНИ МИНЕРАЛИ

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Клучни зборови: загадување на воздухот; тешки метали; седиментна прашина; рудник за бакар; Република Македонија

Во околината на рудникот за бакар „Бучим“ беше спроведен мониторинг за да се утврди дистрибуцијата на тешки метали. Во примероците на седиментен прав беше утврдена содржина на 17 елементи. Анализата на содржината на елементите беше направена со примена на атомска емисиона спектрометрија со индуктивно спрегната плазма (ИСП-АЕС). Како мерни места беа избрани селата Бучим и Тополница и градот Радовиш. Беше утврдено дека во одредени периоди од годината во околината на рудникот „Бучим” доаѓа до депозиција на релативно големи количества прав. Просечните вредности на седиментниот прав во селата Бучим и Тополница изнесуваат 489 mg m^{-2} d^{-1} и 309 mg m^{-2} d^{-1}, соодветно. Максимална вредност за вкупен седиментен прав е добиена од мерното место с. Бучим. Блиската околина на градот Радовиш не е изложена на дистрибуцијата на прав од рудникот (средна вредност од 97 mg m^{-2} d^{-1}). Карактеризацијата на содржината на елементите покажа повисока содржина на бакар и олово во седиментниот прав. Максималната вредност за содржината на Cu е добиена од примероците на седиментен прав од селото Тополница (1183 mg kg^{-1}), а максималната вредност за содржината на олово е добиена во седиментен прав од градот Радовиш.

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Original scientific paper

ROCKFALL HAZARD ASSESSMENT FOR ACCESS ROAD TO DAM "SVETA PETKA" USING ROCKFALL HAZARD RATING SYSTEM (RHRS)

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A b s t r a c t: Large number of roads in our country are constructed in mountainous and hilly terrains. Execution of cuts in the hard rock masses is inevitable. In light of the geological nature of the rocks, processes like rockfalls and landslides in different forms and magnitude are very usual. They occur during construction activities and afterwards in exploitation of the roads. Correct protective measures must be undertaken in order to secure the safety of traffic and people using this roads. One such case is the access road to Dam "Sv.Petka", where constant rockfalls, result of great rupture tectonics and steep cut angles built in marbly limestones, endanger the safety of traffic and construction workers using this road. In order to stress out the hazard invoked by rockfalls and the need of protective measures, we used the well established Rockfall Hazard Rating System (RHRS). Posted speed limit has great influence. Along other possibilities that this method offers is the planning of annual programs for protection measures, with separation of most dangerous zones according the classification, before any undertaking of geotechnical analyses of slope stability. Further software modeling is needed in order to get a better understanding of the nature of rockfalls.

Key words: rockfall; safety; hazard; RHRS classification

INTRODUCTION

As one of the most frequent geological hazards with real risks to the environment and the goods, in recent years, numerous classifications treat rockfall hazard among wich Brawner and Wyllie (1975) and Wyllie (1987), Pierson *et al*. (1990), Scesi et al., (2001), P. Budetta (2004), Jovanovski, Gapkovski (2006).

Hydro Power Plant "Sveta Petka" began construction in 2005. The first phase of construction included completion of the sites access road in 2007.

The nature of the method of creating cuts for the access road has resulted in the marbly limestone rockmass being at a steep sloping angle to the road, this together with intense tectonics and vibrations from through traffic and construction work at the dam which all together cause rock movement on the cliff face and therefore constant rockfalls to the roadway surface.

Investigation into the most hazardous areas and the extent of rockfall in these areas is necessary to decide on remedial action with the aim of diminishing the danger completely. This is vital to ensure the safety of vehicles and passengers travelling this road. We used the Rockfall Hazard Rating System (RHRS) which will provide a method for the road agency to react to hazards rather than accidents. The RHRS will also provide economical planning of remedial works in the future. In order to be most efficient and effective the Hazard Rating System should be an ongoing constant process where conditions or notoriously hazardous areas are monitored in the way of keeping accurate records and photographs of current conditions and any change of conditions occurring.

ASSESSMENT AREAS

In general, the roadway under investigation is deemed very hazardous in terms of rockfalls. Therefore in order to minimize the extent of investigation the areas deemed most hazardous were singled out and investigated individually. It was decided the most hazardous areas were those on sharp bends in the road or areas where it would seem drivers would have difficulty because of a lack of sight distance. Sections where screed deposits are present were also of great focus because of the unpredictable and unreliable nature of this material. Table 1 shows the selected hazard zones for analysis. Each hazard zone varies in length, from 30 m to 224 m.

Initial exploration into data collection for the site and particular situation lead us to discover that the majority of rockfalls occur during the morning and early evening, leading to the belief that the displacement of these rocks is caused by temperature changes throughout the day – from low temperatures in the early morning to high temperatures in mid afternoon, returning to lower temperatures again in the early evening and night.

Table 1

Analyzed hazard zones

Zone	Cross section	Height, m	Average height, m
1	17	10,3	10,7
	22	9,9	
	23	10,3	
	24	12,2	
2	39	20,3	15,5
	40	20,6	
	42	17,5	
	54	9,7	
	57	9,6	
	61	15,2	
3	103	4,5	4,9
	105	5,2	
4	143	10,5	12,9
	145	15,2	
5	156	14,2	15,7
	157	17,2	
6	166	19,1	18,8
	167	21,75	
	170	22,2	
	174	12,2	
7	195	16,8	11,4
	196	7,1	
	197	12,4	
	201	12,6	
	203	8,2	
8	214	16,7	14,7
	215	12,7	
9	226	16,2	16,2
10	242	11,2	11,7
	243	10,25	
	245	13,7	
11	251	14,5	15,4
	253	11,25	
	256	14,25	
	257	13	
	258	13,6	
	260	14,1	
	261	18	
	262	16	
	264	14	
	265	25,6	
12	270	24,4	25,7
	272	25	
	273	27,6	
13	280A	17,25	17,5
	281	12,8	
	282	16,9	
	283	19,8	
	284	20,7	
14	295	10,1	12,7
	296	15,5	
	297	13,3	
	300	16,2	
	301	14,3	
	302	11,2	
	303	11,4	
	304	9,8	
15	308	6,7	9,6
	308A	7,75	
	309	7	
	309A	6,85	
	310	7,8	
	311	11,15	
	312	13,25	
	313	16,15	
16	320	12,5	13,9
	321	12,75	
	321A	12,5	
	322	13,5	
	325	13,5	
	326	18,5	
17	333	19,1	20,0
	334	21,1	
	335	19,7	
18	340	17,8	25,3
	340A	22,2	
	341	25,1	
	343	25,2	
	344	26,9	
	349	22,2	
	350	37,75	
19	355	30,5	28,6
	356	38,2	
	357	32,75	
	358	13,1	

Seventy vehicles, on average, use the road per day, the majority of which are construction vehicles utilizing the road in the morning which coincides with the natural daily temperature increase. Vibrations created by passing construction vehicles together with the temperature increase enhance the possibility of rockfalls occurring during this particular time of the day.

Many traffic accidents, particularly on sharp corners where the driver's decision sight distance is greatly impaired, have been recorded along the access road as well as one fatality during the first phase of construction of the dam in 2006. Subsequently, this is a very serious problem that will continue to deteriorate unless addressed in an effective and efficient way. For the rockfall hazard assesment Rockfall Hazard Rating System (RHRS) according Pierson *et al*. (1990) was modified in a suitable manner for the particular investigation.

ASSESSMENT METHOD

The Oregon Department of Transportation developed the Rockfall Hazard Rating System in 1984. This is a standardized methodology to provide a rational way for agencies to make informed decisions on where and how to most beneficially spend construction funds along areas of roadway which pass through man made steep terrain very susceptible to dangerous rockfall. As well as highlighting the most hazardous regions, the program also lends opportunity for road agencies to put in place systems to monitor, manage and maintain the road in question as well as help to predict which areas should be of particular concern in the future. This will obviously economically benefit agencies in the future in terms of saving cost on roadway repair and the labor required for this.

As a first step in the evaluation we made an inventory of the slopes on the base of formerly executed geological field works and obtained geological maps as well as field observation on the site itself.

Then according RHRS the preliminary rating system was decided in order to define most interesting areas of the access road. In this stage we made a modification of the system where among other criteria listed in Table 2, we decided on the priority for investigation based also on the extent and sharpness of bends in the road as well as the presence of screed deposits on the slopes adjacent to the road. Typical Engineering geological map is presented on Figure 1.

Table 2

Preliminary rating system

Criteria \ Class	A	B	C
Estimated potential for rockfall on roadway	High	Moderate	Low
Historical rockfall activity	High	Moderate	Low
Bends on the road	Sharp	Straight	No bends
Scree deposit adjacent to the road	Large	Small	Absent

Then based on this inventory we grouped rockfall sites into three broad categories A, B and C.

It was determined that there were nineteen zones sown on Table 1 witch are presenting a danger to drivers and vehicles altogether.

The rating system involves ten categories that allow a number of rock slopes to be evaluated and scored in order, from the least hazardous to the most hazardous. Slopes with a higher score present a greater risk.

The point system has been divided into four columns wich correspond to logical breaks in the increasing hazard associated with each category. The scores increase exponentially from 3 to 81 points and are representative scores of a continuum of points from 1 to 100. Using this exponential system, distinguishing the difference between the most hazardous and least hazardous zones becomes more apparent.

The ten categories are as follows:

1. Slope height
2. Ditch effectiveness
3. Average vehicle risk (AVR)
4. Percent of decision sight distance (DSD)
5. Roadway width

6./7. Geological character

8. Block size or Quantity of rockfall per event
9. Climate and presence of water on slope
10. Rockfall history.

Some of the categories can be measured directly on the field while for others corresponding formulae exist wich can be found in Pierson *et al.* (1990), Scesi et al. (2001), P. Budetta (2004).

The various heights of the cross sections within each hazard zone were similar and therefore taking their average deemed an adequate representation of the overall hazard zone height.

Photo 1. Typical screed deposit

The specific length of each hazard zone was found and calculations were performed to find the average vehicle risk (AVR) using the value known for the average traffic per day and the posted speed limit, 30 km/h and 10 km/h.

The percent of decision sight distance (DSD) was found for each of the nineteen hazard zones using the actual sight distances for each cross section (judged and measured from the road plan) and taking the decision sight distance as 90 m for a posted speed limit of 30 km/h and 26 m for a posted speed limit of 10 km/h. The percent of decision sight distance was calculated for each cross section within the specific hazard zone being investigated. As these values were similar, they could be evaluated within the same scoring points bracket. The remaining categories were also scored accordingly.

Table 3 presents the total scoring for hazard zone 4. In same manner calculations for all other 18 analyzed hazard zones were conducted for speed limits 30 km/h and 10 km/h respectively.

T a b l e 3

RHRS for hazard zone 4 on the access road to dam "Sveta Petka"

CATEGORY		RATING CRITERIA AND SCORE 3 POINTS	9 POINTS	27 POINTS	81 POINTS	Total	
SLOPE HEIGHT		7.5 Metres	15 Metres ✓	22.5 Metres	30 Metres	**9**	
DITCH EFFECTIVENESS		Good catchment	Moderate catchment	Limited catchment ✓	No catchment	**27**	
AVERAGE VEHICLE RISK		25% of the time	50% of the time ✓	75% of the time	100% of the time ✓	**9** **81**	30 kmh 10 kmh
PERCENT OF DECISION SIGHT DISTANCE		Adequate sight distance, 100% of low design value	Moderate sight distance, 80% of low design value	Limited sight distance, 60% of low design value	Very limited sight distance, 40% of low design value ✓	**81**	
ROADWAY WIDTH INCLUDING PAVED SHOULDERS		13.5 Metres	11 Metres	8.5 Metres	6 Metres ✓	**81**	
GEOLOGIC CHARACTER – CASE 1	STRUCTURAL CONDITION	Discontinuous joints, favorable orientation	Discontinuous joints, random orientation ✓	Discontinuous joints, adverse orientation	Continuous joints, adverse orientation	**9**	
GEOLOGIC CHARACTER – CASE 1	ROCK FRICTION	Rough, irregular	Undulating ✓	Planar	Clay infilling, or slickensided	**9**	
GEOLOGIC CHARACTER – CASE 2	STUCTURAL CONDITION	Few differential erosion features	Occasional erosion features	Many erosion features	Major erosion features		
GEOLOGIC CHARACTER – CASE 2	DIFFERENCE IN EROSION RATES	Small difference	Moderate difference	Large difference	Extreme difference		
BLOCK SIZE VOLUME OF ROCKFALL/EVENT		0.3 Metres 2.3 cubic metres	0.6 Metres 4.6 cubic metres	0.9 Metres 6.9 cubic metres	1.2 Metres 9.2 cubic metres ✓	**81**	
CLIMATE AND PRESENCE OF WATER ON SLOPE		Low to moderate precipitation; no freezing periods; no water on slope	Moderate precipitation or short freezing periods or intermittent water on slope ✓	High precipitation or long freezing periods or continual water on slope	High precipitation and long freezing periods or continual water on slope and long freezing periods	**9**	
ROCKFALL HISTORY		Few falls	Occasional falls	Many falls	Constant falls ✓	**81**	
				TOTAL SCORE (30 kmh)		**396**	
				TOTAL SCORE (10 kmh)		**468**	

The posted speed in the time of design of the road was 30 km/h, but from security reasons because of the many bends on the road, it was decided in the zone which is closer to the construction site of the dam this speed to be reduced to 10 km/h. So in order to compare the influence of the reduced speed limit we did the scoring for both speeds. Another modification to the RHRS was done by reducing the points for urgent remedial action required from 500 to 400 having in mind the still active construction site on the dam under the road.

T a b l e 4

Priority for remedial action required

<300	Keep areas under observation
300 – 400	Remedial action priority in these areas
>400	Urgent remedial action required

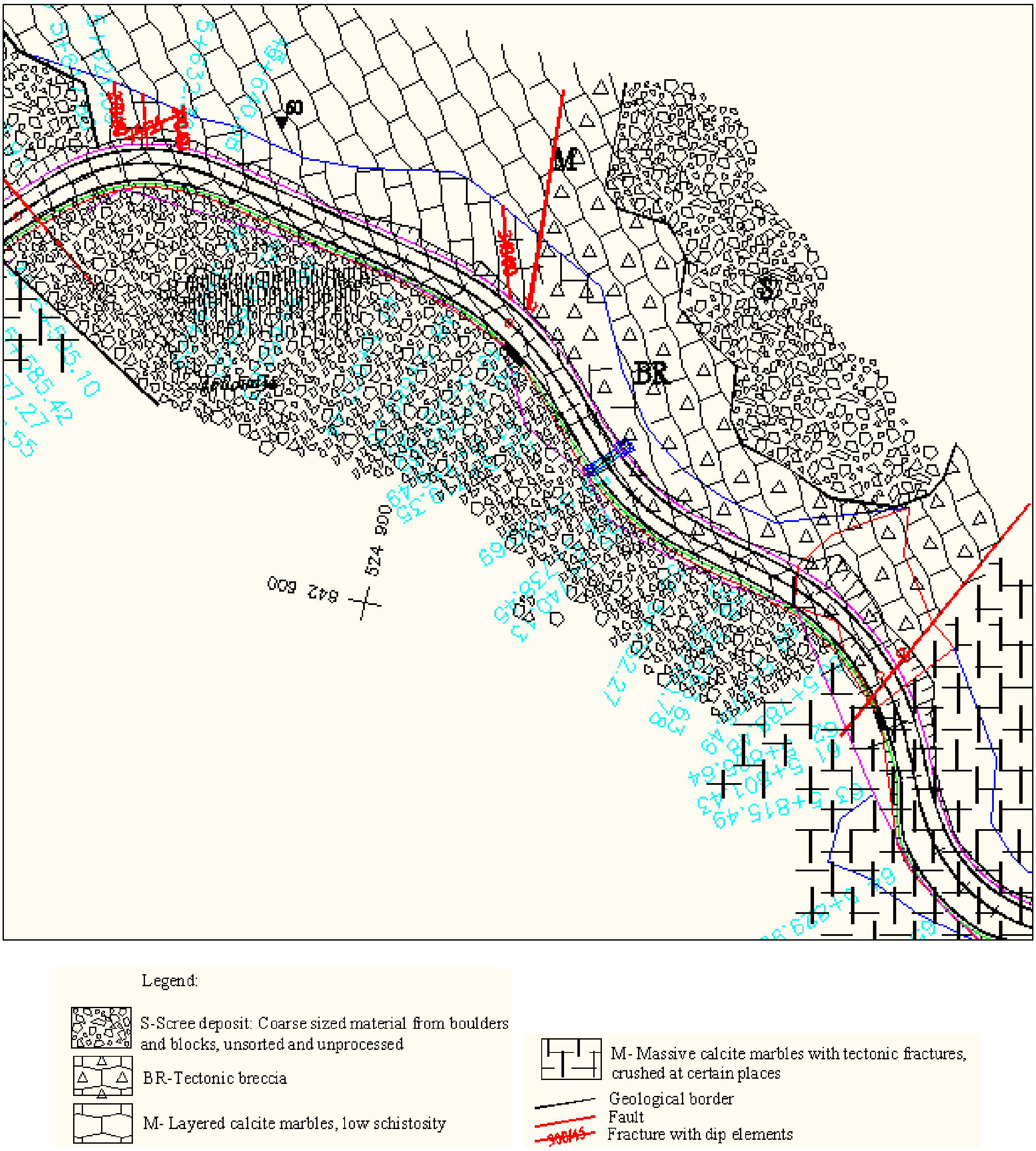


Fig. 1. Engineering geological map for access road to dam Sv. Petka (Chainage km.5+595 – km.6+854)

RESULTS

The obtained scores for each hazard zone are presented in tables 5, 6 and graph 1. Most of the zones should be taken as priority when considered for remedial action. However it's very noticeable how the posted speed limit has a great influence on the results. As expected, more zones become more dangerous as the vehicle travels through at a slower pace.

The number of zones for urgent treatment increases from two to nine with the decrese of speed. Thus spending more time in a hazard zone heightens the likelihood of being struck by one or more falling rocks. However, as the lower speed would cause less vibrations into the ground these results would suggest that vibrations caused by traffic travelling through the hazard zone does not pose as much of a threat as was expected. The time spent in the hazard zone is more of a risk

Table 5

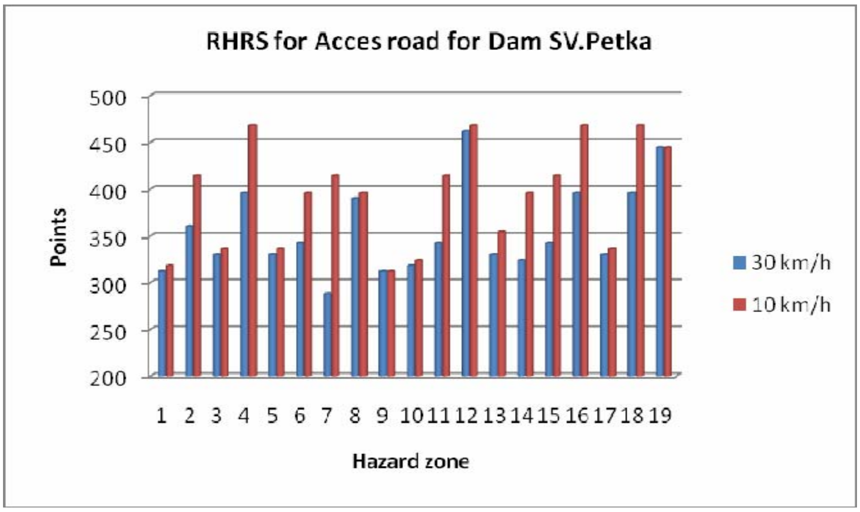
Results for posted speed of 30 km/h

Score	Hazard zone	Inspection rating
288	7	Observe
312	1, 9	Priority
318	10	
324	14	
330	3, 5, 13, 17	
342	6, 11, 15	
360	2	
390	8	
396	4, 16, 18	
444	19	Urgent (2)
462	12	

Table 6

Results of analysis with posted speed of 10 km/h.

Score	Hazard zone	Inspection rating
312	9	Priority
318	1	
324	10	
336	3, 5, 17	
354	13	
396	6, 8, 14	
414	2, 7, 11, 15	Urgent (9)
444	19	
468	4, 12, 16, 18	



Graph 1. Total scores for RHRS rating for 30 and 10 km/h

REMEDIAL ACTION

According all analysis, the possible remedial action that can be performed on a problematic slope are various. The choice of action should be case specific and of course should depend of the extent of hazard presented by the slope. A few of these engineering solutions include:

– ripping of instable blocks, attachment of double road net, along with nonsystematic anchoring,

– anchoring in potentially unstable zones in combination with shotcrete and steel net,

– cleaning of scree deposits and possible cementing with shotcrete,

– construction of reinforced concrete type of gallery protection,

– support with reinforced concrete columns, wich are reinforced with anchors in the cuts,

– concrete supports,

– blasting should be excluded from any action because it further develops conditions for disturbance of the rock masses, i.e. the possibility of additional rockfall manifestations.

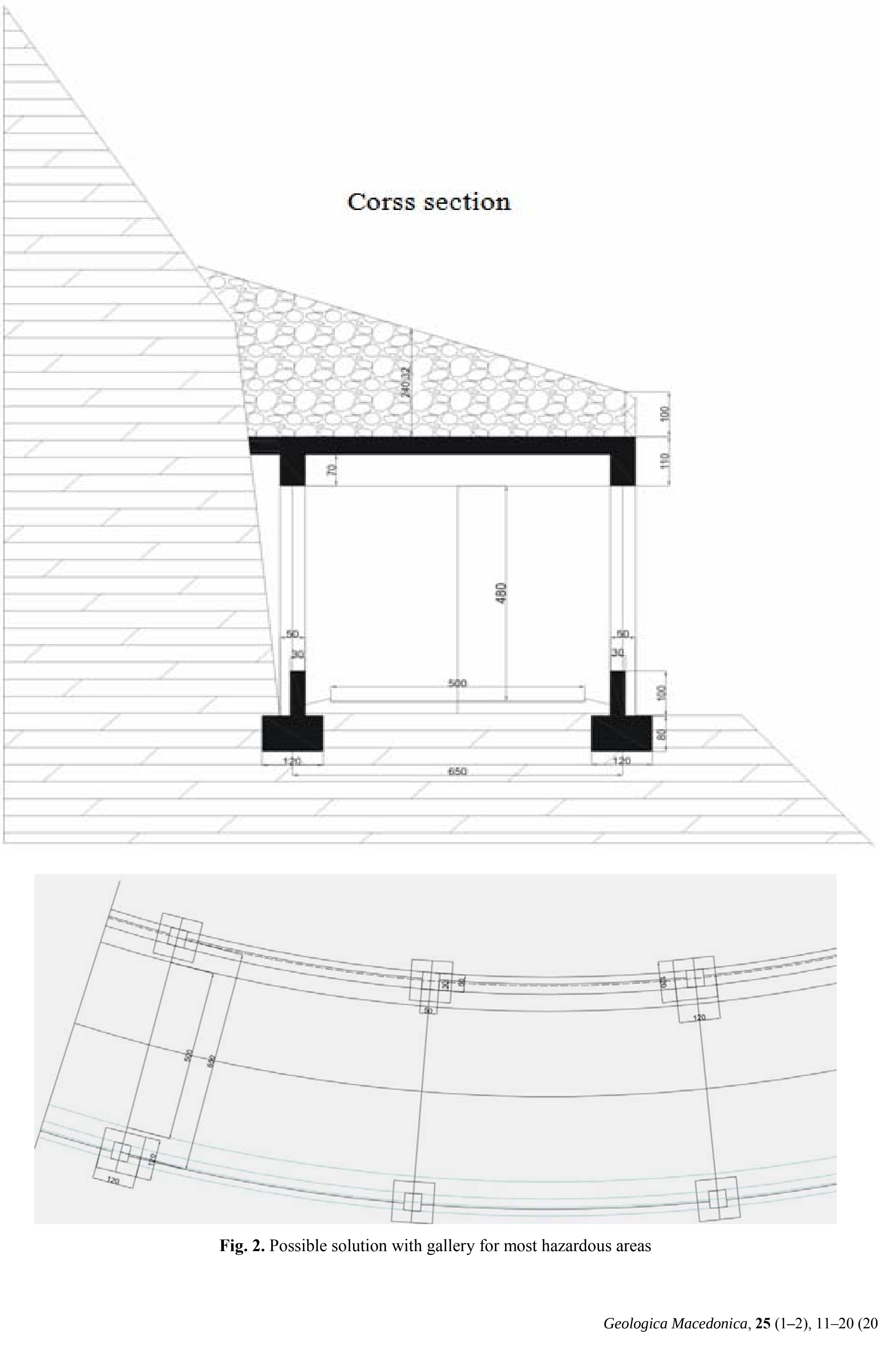


Fig. 2. Possible solution with gallery for most hazardous areas

It is important to determine the most appropriate stabilization methods with not only the aim to repair the problem in the present but to continue to remedy the problem into the foreseeable future, of course in economically feasible manner. This should involve the setting up of an Annual Stabilization Program to ensure continual monitoring of the condition of all problematic areas and consistent action throughout the year. It should also involve the monitoring of areas which have the potential to become dangerous so as action can be applied before the problem becomes more difficult and costly to remedy.

FUTURE WORK

The goal in every project is to be as cost effective as possible. In order to select the appropriate remedial measures from this perspective we propose further analysis by taking the next steps:

1. Use of the evaluation software like Rockscience RocFall to simulate the most hazardous cross sections in order to provide a more informed future prediction of the behavior of hazardous areas.

2. A more in depth investigation into a more specific and accurate size and volume of rocks falling in each hazard zone.

3. Annual Stabilization Program is to be initiated for the entire access road.

5. Research into the possible use of electronic slope monitoring systems and using these to keep maintenance labor and costs to a minimum.

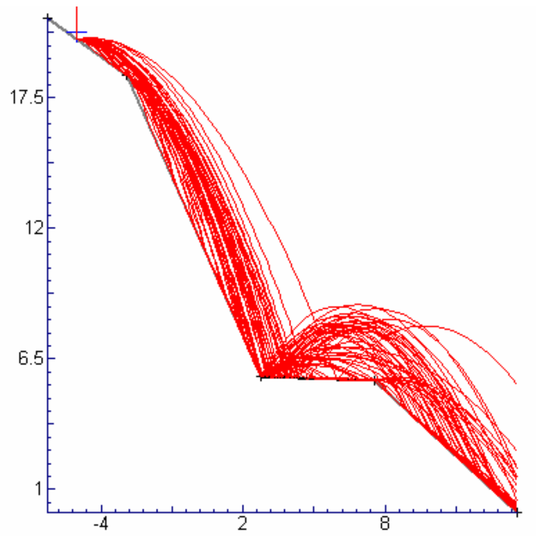


Fig. 3. Output of Rocscience program RocFall from detailed analysis

CONCLUSIONS

Hydro Power Plant "Sveta Petka" began construction in 2005. The sites access road was finished in 2007. The roadway is deemed very hazardous in terms of rockfalls.

Rockfall Hazard Rating System (RHRS) according Pierson *et al*. (1990) was modified in a suitable manner for the particular investigation.

Classification was made for 19 analyzed hazard zones with posted speed limits of 30 km/h and 10 km/h respectively in order to see the effect of reduction of speed.

The number of zones for urgent treatment increases from two to nine with the decrease of speed.

Engineering solutions for remedial works are presented.

Setting up of an Annual Stabilization Program is essential in order to ensure continual monitoring of the condition of all problematic areas throughout the year.

Additional work should be done in order to get a more detailed insight of the rockfall's nature, and usage of software is recommended to model the behavior of falling rocks on the roadway. The posted speed limit sign on one section from the access road of 10 km/h should be replaced with 30 km/h.

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Р е з и м е

ПРОЦЕНА НА ОПАСНОСТА ОД ОДРОНИ НА ПРИСТАПНИОТ ПАТ ДО БРАНАТА „СВЕТА ПЕТКА“ КОРИСТЕЈЌИ ГО СИСТЕМОТ ЗА ПРОЦЕНУВАЊЕ НА ОПАСНОСТА ОД ОДРОНИ (RHRS)

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Клучни зборови: одрон; безбедност; опасност, класификација РХРС

Голем број на патишта во нашата земја се изградени во планиско-ридски подрачја. Ископот на засеци во цврстите карпести маси е неизбежен. Геолошката природа на карпите, а секако и инженерската, активност се причина појавата на геолошки процеси како што се одрони и свлечишта со различна форма и големина да е многу честа. Тие се појавуваат за време на самата изградба на патиштата и за време на нивната експлоатација. За да се обезбеди сигурноста на сообраќајот и луѓето кои ги користат овие патишта треба да бидат преземени соодветни заштитни мерки. Еден таков случај претставува пристапниот пат до браната „Света Петка“, каде постојаните одрони, резултат на голема руптурна тектоника и стрмните засеци изведени во мермеризираните варовници, ја загрозуваат безбедноста на сообраќајот и на градежните работници кои во време на изведба на браната го користат овој пат. Со цел да се нагласи ризикот кој го предизвикуваат одроните, како и потребата од заштитни мерки, искористен е добро познатиот систем РХРС. Заклучено е дека поставеното ограничување на брзината има големо влијание врз опасноста. Помеѓу другите можности кои ги нуди овој метод се и годишни програми за преземање заштитни мерки со издвојување на најопасните зони според класификацијата, а пред преземање на какви било геотехнички анализи за стабилноста на косините. Потребни се понатамошни софтверски моделирања за подетално утврдување на природата на одроните.

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GEOCHEMICAL STUDY OF THE MINERALIZED SYSTEM BUKOVIK–KADIICA, EASTERN MACEDONIA

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A b s t r a c t: In accordance with the performed regional and detailed geochemical studies of the stream sediments, soils and rock chips, at the wider area of the Bukovik–Kadiica locality near Pehčevo town, Eastern Macedonia, regional and local polymetallic geochemical anomalies of elements such are Cu, Fe, S, Mo, Au, Pb, Zn, Sn, As, Sb, Ti, V, Co etc were detected. However, copper, molybdenum, silver, lead and zinc, appeared to have most standard values which coincides with the former geochemical studies. This data directly point to an existence of the copper mineralization in a wider area that coincides with the structural-metallogenic features of the Bukovik–Kadiica area, also. Detailed studies allowed calculation of the correlation factors of the most frequent elements in the area of interest. Especially significant correlation factors were detected for the elemental pairs such as Cu-Ag, Fe-Cu, Zn-Au, Pb-Ag and Pb-As.

Key words: primary halos; stream sediments; metalometry; polymetallic mineralizations; Bukovik–Kadiica locality

INTRODUCTION

The mineralized area Delčevo–Pehčevo–Berovo has been subject of numerous geochemical explorations and studies during the past 4 decades. The first studies of this kind were performed in 1974–1975 when the Geological Survey–Skopje performed preliminary explorations, on the net-like scheme, it was sampled with one sample per a square kilometer. Some of the later geochemical studies concerning this area of interest can be found in the works of Hadži-Petrušev (1985), Stojanov et al. (1995) etc.

Synthesized up to date numerous and complex studies in which geochemical studies took special place, have shown all the complexity of the area, in question as well as findings concerning perspective areas from the mineralization(s) point of view.

Geochemical studies have confirmed the existence of large dislocations, where along them were intruded magmatites and volcanites, as well as post-magmatic hydrothermal processes deposited mineralization and sometimes remobilized them (Hadži-Petrušev, 2008). Geochemical explorations and studies of this region could be divided to:

– systematic regional (and half-regional) explorations and studies of the whole region, and

– separate detailed explorations of particular localities.

Geochemical explorations outlined in this manner enabled regionalization of the terrain in regard of metallic mineral resources, lithological, structural and temperature factors. The existence of the mega-structure of northwest-southeast direction was defined in that manner while at the same time the activities of northeast-southwest and east-west direction were highlighted. Also, the problems of erosion processes were opened where it the presence of copper mineralization was sensed. As very characteristic areas appeared Bukovik–Kadiica, Dvorište and a wider area around the town of Berovo (Vladimirovo, Rusinovo). In that direction was the existence of the aforementioned mega-structure.

REGIONAL GEOCHEMICAL RESEARCH

Geochemical half-regional studies were performed for the necessities of the OGK-2 (Basic Geological Map-2) of the ore region Delčevo–Pehčevo–Berovo (Hadži-Petrušev et al., 2008). Geochemical studies were performed on heavy fractions panning material and soil material (secondary halos of dispersion) along the stream network. Separate geochemical studies from the half-regional and detailed point of view were performed several times at different terrains and localities. Most important of them appeared to be the studies of lead-zinc occurrences in the northern parts of the area, then primary and secondary studies of copper and other mineral resources near Dvorište, Pančarevo, Bukovik–Kadiica, presence of Fluor in Berovo (Maleševo area) and Delčevo (Stamer–Dzvegor–Grat) region. Special attention during the half-regional studies was given to the rare elements (tungsten, tin, molybdenum) near Delčevo (Kulata) and Berovo (Maleševo Mountains). Also, the studies of gold along the Pekljanska river, Bukovik, Dvorište, Laki and other streams were of great importance.

Information obtained from the statistical analysis of the studied elements enabled preparation of graphical interpretation of each element, getting an idea about their lithogeochemical features in comparison to the adjacent areas, as well as about their spatial distribution and concentration within particular localities (Figure 1).

In regards to their spatial distribution and paragenetic grouping of elements and mineral association, the studied region could be divided into four segments: Vetren–Dzvegor–Bukovik–Kadiica –Dvorište; Plačkovica-Maleševo Mountain, southeastern part of the Sasa zone (Kostin Dol), Mitrašinci–Virče. In this preview we are going to pay special attention to the most important geochemical features of the first zone mentioned above, where the copper anomalies around the Bukovik–Kadiica mineralized system stand out. The Vetren–Dzvegor–Bukovik–Dvorište anomalous zone has been characterized by volcanic emanations of dacite to andesite composition, intensive alterations and hydrothermal changes within the volcanic aparatuses and adjacent lithological settings where they have been intruded. Geochemical association has been represented by wide range of elements such as Cu, Pb, Zn, Mo, Ag, Ba, Au and Fe. Mineral associations are represented by chalcopyrite, chalcocite, bornite, covellite, tetrahedrite, lead and zinc sulfides, molybdenite, malachite, azurite, pyrite, native gold and some other minerals. The mineralogical diversity allowed distinction of three geochemical sub-groups:

Dvorište metallogenic field with Cu, Pb, Zn, Mo, Ba ± native Au.

Vetren–Dzvegor–Istevnik metallogenic field with Cu, Pb, Zn, Mo, Ag, Ba.

Bukovik metallogenic field with Cu, Pb, Zn, Mo, Ba, Ag ± native gold and W.

At Maleševo Mountains, around 2.5 km SE from the Dvorište village the so called Dvorište formation composed of dacite, tuff, breccia and aglomerates has been developed. Within this formation and its close vicinity polymetallic Cu, Pb, Zn, Mo, Fe, Au mineralization determined. The polymetallic mineralizations were deposited along the faulting structures located in two-mica and muscovite gneiss. The most important occurrences are: Zabelski Potok, Vrli Čukar, Džuarec, Slivata, Srbnica and Bela Voda. Within all the aforementioned occurrences identical hydrothermal alterations and ore veins filled with pyrite appear, chalcopyrite, chalcocite, bornite, Pb-Zn sulfides, Mo, Ag etc. All of them should be studied in more detail. The volcanic activity around the Vlaina area has been determined as the bearer of polymetallic mineralizations grouped around the volcanic masses at Gabrovo–Dzvegor, enclosed in rocks of the Riphean-Cambrian complex and Triassic limestones and within the volcanic products itself. Near the Gabrovo and Dzvegor villages intensive hydrothermal alterations such are kaolinitization, silicification, and limonitization of the localities occur: Lazovi Kući, Belite Kamenja, Popov Čukar, Karakol, Turćinska Maala, Čukata–Ostrec, Grčina, Okno etc. The mineral paragenesis has been represented by pyrite, chalcopyrite, chalcocite, covellite, sphalerite, galena, magnetite, hematite, titanite, ilmenite, secondary malachite, azurite etc. Minerals at particular localities appear in form of veins while at some other appear they as impregnations.

The volcanic activity at the Bukovik–Orlovec –Kadiica–Kadan Bunar is the bearer of the primary mineralization. At the source area of the Pehčevska River at the contact between volcanics with green schists of the Rusinovo formation hydrothermal alterations with polymetallic mineralizations of pyrite, chalcopyrite, tetrahedrite, galena, sphalerite, molybdenite, malachite, limonite, magnetite and gold occur.

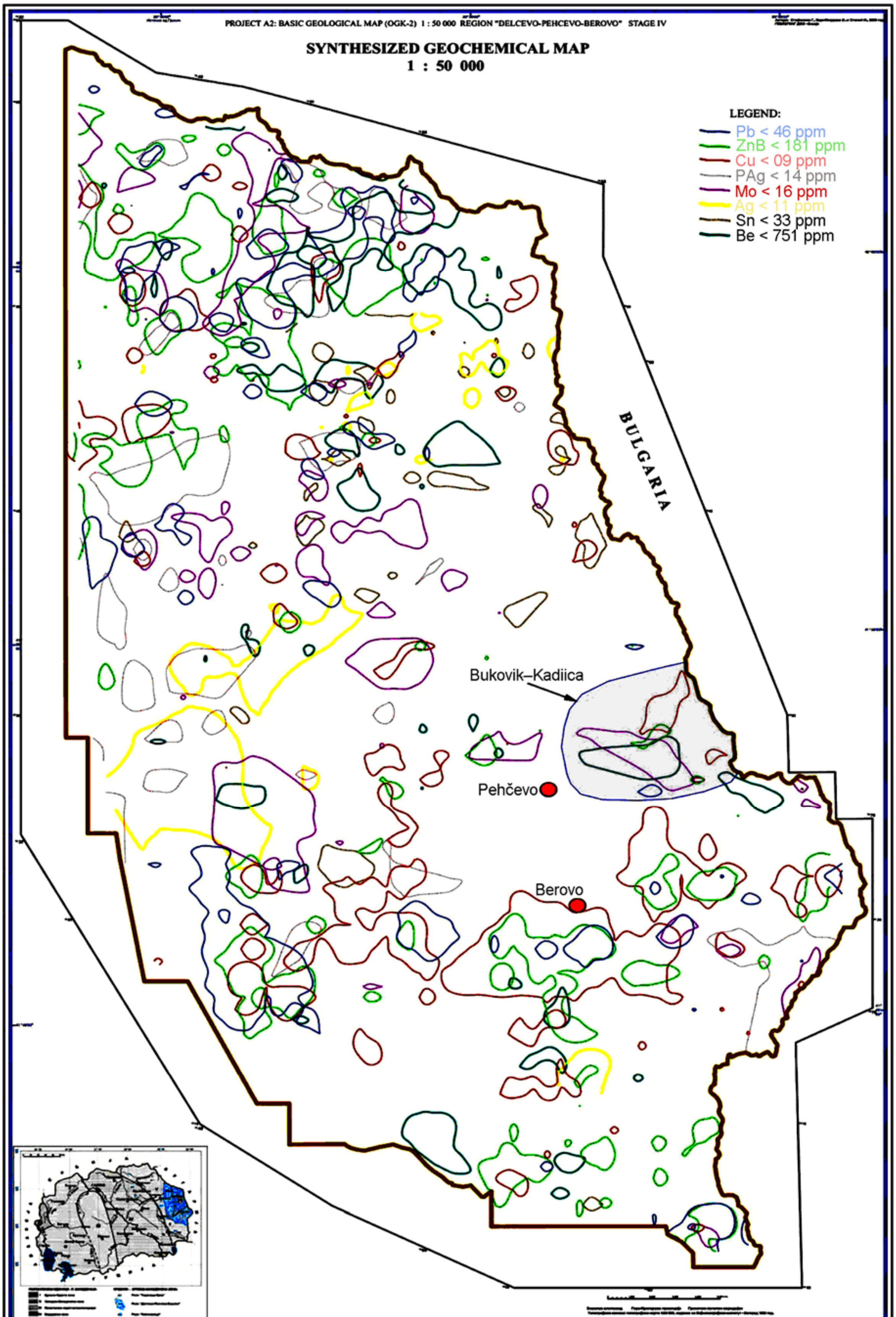


Fig. 1. Synthesized geochemical map of the ore-bearing region Delčevo–Pehčevo–Berovo (Hadži-Petrušev et al., 2008)

This locality has been studied a few times and there are serious indications of the discovery of ore deposit of polymetallic ores of economic significance. Those findings were also confirmed by the results from the geophysical studies conducted within this metallogenic field. Namely, the geomagnetic and aeromagnetic measuremens pointed to the presence of large masses characterized by magnetic susceptibility. Geophysical measurments of SP and IP pointed to an expressed electrical conductivity that spreads with the increase of the depth.

Geochemical interpretation of copper

Copper represents one of the main basic elements that were studied within the Delčevo–Pehčevo–Berovo area. Its presence was registered in most of the analyzed samples. In analyzed 12255 samples copper presence was registered within the 12143 samples. The copper concentrations ranged from 2 up to 2.000 ppm depending strongly on the lithological setting of the sampling location (Hadži-Petrušev et al., 2008).The copper concentrations all over the area of interest were of different values and intensities (Figure 2).

The most frequent bearers of the mineralization are volcanics and granitoids, while metamorphic rocks were the most suitable setting for mineralization deposition were. The statistical parameters such as mean value, standard deviation, and treshold of anomaly are pointing to the fact that the copper is present in enriched concentrations compared to the Clark values in similar lithological settings. Anomalous values were grouped in four categories. It was kept in mind that the samples with concentrations of least 250 ppm should ein the fourth category, which according o today's trends at World's copper markets represents a significant anomaly for initiating more detailed research. Of all the samples, 250 of them were with values higher than 250 ppm, which is a significant confirmation of the previously stated. For more illustrative view of the anomalous fields and zones a copper geochemical map was prepared over the topographic layer. Interpretations of the spatial setting of the anomalous fields and zones have been correlated to the geological composition of the studied region. Also, this kind of interpretation gives an idea about the most prospective and least prospective ones for further geochemical studies (Figure 2).

The biggest anomalous zone, composed of large number of anomalous fields has been registered in southern parts of the terrain (wide 8 km, long 25 km with E-W direction), while spatially it has been located in two different structural-lithological elements. The western parts of this zone were located in southern parts of the Plačkovica mountain, within the localities such as Laskov Čukar, Vaskov Čukar, Brankov Čukar, Zariski Rid, Sredni Rid, Mangovec and westward of Vladimirovo. These anomalous fields were located in the Plačkovica's granitoide complex, which is in direct connection to the gneiss-schists complex of the particular terrain. Anomalous fields have been generated within labile zones caused by faults of NW-SE and NE-SW direction.

The central and eastern parts of this zone were located at the area occupied by the Maleševo Mt. This part of the anomalous zone is composed of numerous anomalous field. The most representative ones are those at Vladimirovo, Rusinovo and Ratevo villages, southern, southeastern and eastern of Berovo up to the Macedonian–Bulgarian border. All of them, in general, have NW-SE direction and point to the cross-cutting knots between the NW-SE and NE-SW structural directions.

The second anomalous zone has been located in the northwestern part of the area and it is of lower intensity compared to the previous one. It has been located in contact parts between the Delčevo granitoide with meta-quartz keratophyres and meta-rhyolites. The most representative anomalous fields were located at the localities such as Kalankova Čuka, Bumbarci, Vitandžik and Kalinova Čuka. These anomalous fields are of NW-SE direction or at the cross-section knots of faults of NW-SE and NE-SW direction.

The third group of anomalous fields has been located in the eastern part of the area. From the spatial and lithological point of view they were located in two complexes. Anomalous fields around Pehčevo (Crnik, Ostri Rid and Bukovik) are located in metamorphic amphibolite-epidote complex intruded by dacite-andesite volcanics. Anomalous fields eastern of Delčevo were located around Virče, Grad and Dzvegor. From the lithological point view they were located at peripheral parts of the Delčevo granitoids intruded by younger dacite-andesites. The lowest anomalous fields were located in the southern parts of studied area. Located in the closest vicinity of Dvorište they represent direct consequence of younger dacite volcanism intruded in th gneiss complex of the Maleševo Mt. and northernmost parts of the Ogražden granitoide.

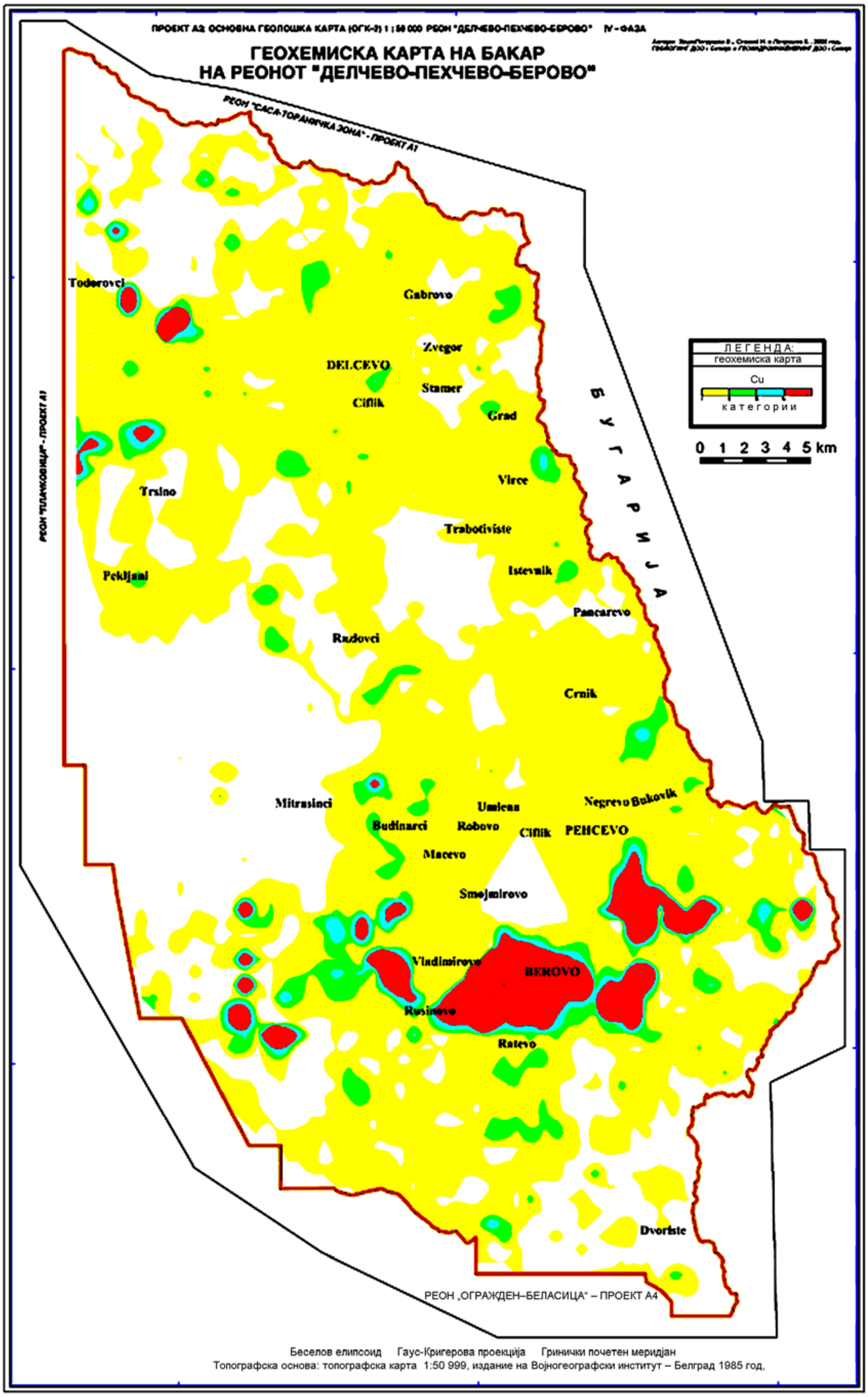


Fig. 2. Regional geochemical copper map of the studied area (Hadži-Petrušev et al., 2008)

DETAILED GEOCHEMICAL STUDIES OF THE BUKOVIK–KADIICA LOCALITY

Significant volume of detailed sampling of lithogeochemical, metalometric and stream sediments was performed during the detailed studies and geological mapping by the Geological Survey–Skopje, in the period 1981 up to 1985, as well as by the US company Phelps Dodge Exploration (through its subsidiary company here in Macedonia the Phelps Dodge Vardar) during the period 2002–2007. The first detailed studies performed by the Geological Survey have resulted with a few geochemical maps at scale 1 : 2 500, compatible with the detailed geological map 1 : 2 500, where alteration zones were shown and some of the mineralization occurrences. Especially interesting have been copper anomalies in the wider area between the Bukovik–Kadiica peaks, but interesting anomalies of Pb, Zn, Ag, Mo etc., also (Hadži-Petrušev, 1985) have been registered. These results served as a background to the further geochemical and mineralogical studies by the US based company Phelps Dodge Exploration, which during the few years period have preformed geochemical study programme combined with geophysical studies and exploration drilling (Aleksandrov and Bombol, 2007). In the text below we will focus in more detail to the results obtained by the Phelps Dodge Exploration.

Primary dissemination halos-lithogeochemistry

The geochemical sampling has been performed by the lithogeochemical method (rock samples). The total weight of the each separate sample was 2–3 kg, enough to be representative for the respective sampling point. All the occurrences of altered and/or stockwork rocks were sampled in order to determine the surface geochemistry features of the area. For better determination, some of the occurrences with complex geological composition have been represented by few samples. Particular small volcanic intrusions were sampled in a more detailed manner because of the possibility of presence of mineralization in them. In total at this stage 236 rock samples of altered rocks evenly distributed all over the area were sampled.

The preparation of rock samples was performed by crushing, grinding, pulverizing and shortening up to the weight of 150 g for each sample and providing a duplicate, also. Chemical analysis has been performed on an ICP-AES (35 elements) while AAS/FA has been used to determine Au, Cu, Mo and some other elements with increased concentrations.

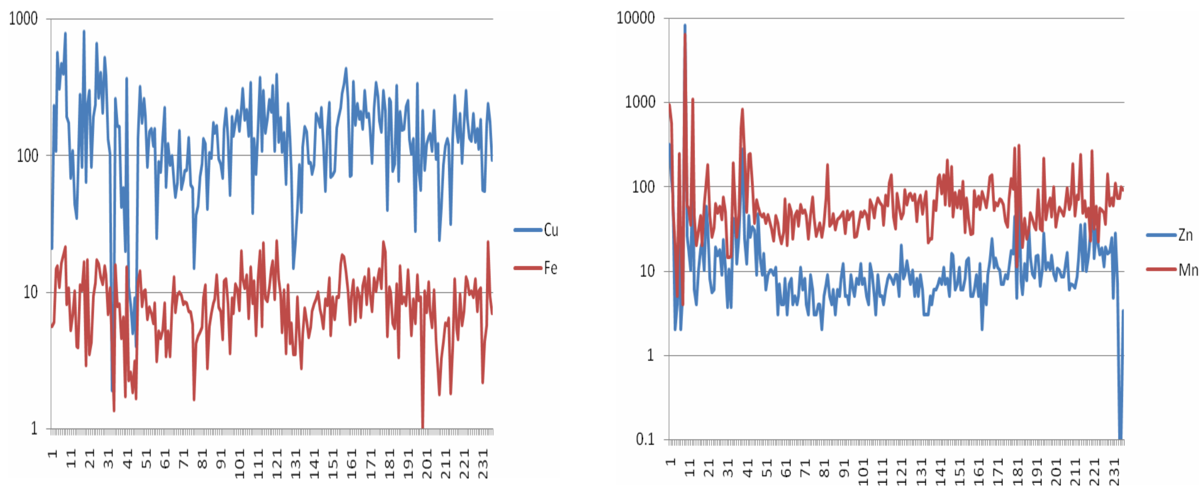
Obtained data have shown a whole array of different values for different elements. For example, values for particular elements were in the ranges as follows: 1.91÷809 ppm Cu, 1÷1447 ppm As, 2÷485 ppb Au, 0.441÷319 Mo, 1÷5012.33 ppm Pb, 0.1÷8120 ppm, 1÷23.47 % Fe, 0.052÷23.115 ppm Ag, 0.76013÷32 ppm Co, 8÷335.99 ppm Cr, 4–6400 ppm Mn, 1÷85 ppm Ni, 0.01÷3395 ppm Ti and 4÷364 ppm V. In our efforts for better understanding of the geochemical cycle and relations between certain elements we have performed an ANOVA statistical analysis (Table 1).

Table 1

Elemental correlation factors for lithogeochemical samples from the Bukovik–Kadiica locality

	Cu	Au	As	Mo	Pb	Zn	Fe	Ag	Co	Cr	Mn	Ni
Cu	1											
Au	0,190	1										
As	0,272	0,157	1									
Mo	–0,009	–0,109	0,380	1								
Pb	0,116	0,303	0,463	0,019	1							
Zn	0,011	0,633	0,093	–0,057	0,236	1						
Fe	0,719	0,158	0,305	0,022	0,143	–0,012	1					
Ag	–0,080	0,285	0,056	–0,094	0,191	0,331	–0,088	1				
Co	–0,021	0,299	0,006	–0,147	0,089	0,453	0,008	0,142	1			
Cr	0,280	0,187	0,089	–0,147	0,258	0,091	0,125	–0,105	0,304	1		
Mn	–0,028	0,607	0,066	–0,072	0,220	0,973	–0,039	0,322	0,560	0,123	1	
Ni	–0,188	0,033	–0,147	–0,034	–0,043	0,140	–0,289	–0,041	0,511	0,363	0,239	1

The outcomes of the statistical study are represented as correlation factors. The highest correlation factors in this media were achieved for the elemental pairs Zn–Mn with correlation factor of 0.973 and Cu-Fe with correlation factor of 0.719. In that direction we have proceeded with preparation of plots for more illustrative preview of those correlations (Figure 3).



a) *b)*

Fig. 3. Shape of the most representative plots of elements with highest correlation factors, Fe-Cu and Zn-Mn, Bukovik–Kadiica lithogeochemistry

As can be seen from the figure above the shape of one element almost ideally follows the shape of the other element with which it strongly correlates. Also, we would like to stress that elemental pairs such are Cu-Fe and Zn-Mn reflect their strong correlation in primary mineralizations as well as in hydrothermally related ones (Kroll et al., 2002). Detailed rock chip geochemistry around mineralization reveals that S and Cu show the highest geochemical contrast, with halos extending up to 0.5 km from mineralized zones. Of these two elements, S shows the more consistent pattern, which is very similar to those shown by Barnes (1997) and Deksissa and Koeberl (2004). Also, the dispersions of the lithophile elements (Rb, Sr, Ba, K, Ca, Na) are controlled "by type and intensity of wall-rock alteration, with halos extending slightly beyond ore zones but within the alteration envelope. Distribution of the femic elements (Zn, Mn, V, Ti, Ni, Co, Fe, Mg) is controlled principally by primary lithology.

Metallometry (horizon"B")

Sampling the secondary dissemination halos (soil sampling – horizon"*B*") has been performed in separate parts of the volcano-intrusive complex, estimated as the most promising ones based on the geological mapping, but without low extent occurrence at the surface. Sampling has been performed along profile lines of NS or EW direction, at mutual distance of 100 m, while the distance between the profiles for surface estimate was set to 200 m. For setting up the profiles the so called “heap chain” and GPS units of high accuracy were used. The mass of the sample used was around 500 g and with special tool was taken from the “B” soil horizon. 13 profile lines were sampled, long between 600 m and 2.1 km. In total, 181 samples including 7 blank samples were sampled. Parts of the area covered by network 200 × 100 m were located to the north and southwest of the Bukovik peak. Separate profiles characterize the area on the north of the Bukovik peak (profile X), as well as those to the south (southern part of the profile C) and southeast of the same area (eastern parts of the profile A and F). All the sampling profiles have been shown at Figure 4. Samples were dried at room temperature and sieved through the sieve of –80 mesh. From the sieved material by quatering material was separated with mass up to 70–80 g, which was later sent to analysis under the ICP for 30 elements and AAS for gold.

Obtained results have shown anomalous values for Cu, Mo, As, Au, Pb and partially for Ag. Based on these results geochemical maps for aforementioned elements were prepared. Few anomalies of copper were contoured (Figure 5).

The lowest limit for contour lines was determined at >100 ppm Cu. The most important anomaly has been located at W-SW of the main sheepfold at the Bukovik peak. It is long 800 m, 350–500 m wide and elongated in N-NW direction and separated at two parts in southern corner and with maximal value of 262 ppm Cu at the eastern part. Very characteristic were the anomalies determined at border parts of the area, below the level of 1400 m, covered by geochemical study of secondary halos.

The highest anomaly at the west is with the maximum value of 296 ppm Cu, while to the south the maximal value is 380 ppm Cu. Small anomalies (>100 ppm) were contoured at north and east near the end of the profile lines. This phenomenon could be described by the leaching of copper by the surface waters and its re-deposition close to the present water level, which overlaps with the existing wells.

Molybdenum anomalies have been contoured at values higher than 50 ppm. It has an irregular shape around the northern slope and almost overlaps the surface occurrences of the quartz-porphyry intrusion or lies below its occurrences. Maximal values toped up at 189 ppm Mo. At 20 ppm as the lowest limit values of the anomaly, the highest part of the Bukovik peak and its NW, N and NE slopes are within the anomaly with an exception of one small part to the north of the highest point. There is no correlation between Cu and Mo.

One gold anomaly has been determined with values higher than >80 ppb. It has been located on the high parts of the Bukovik peak close to the southern slope (Figure 6).

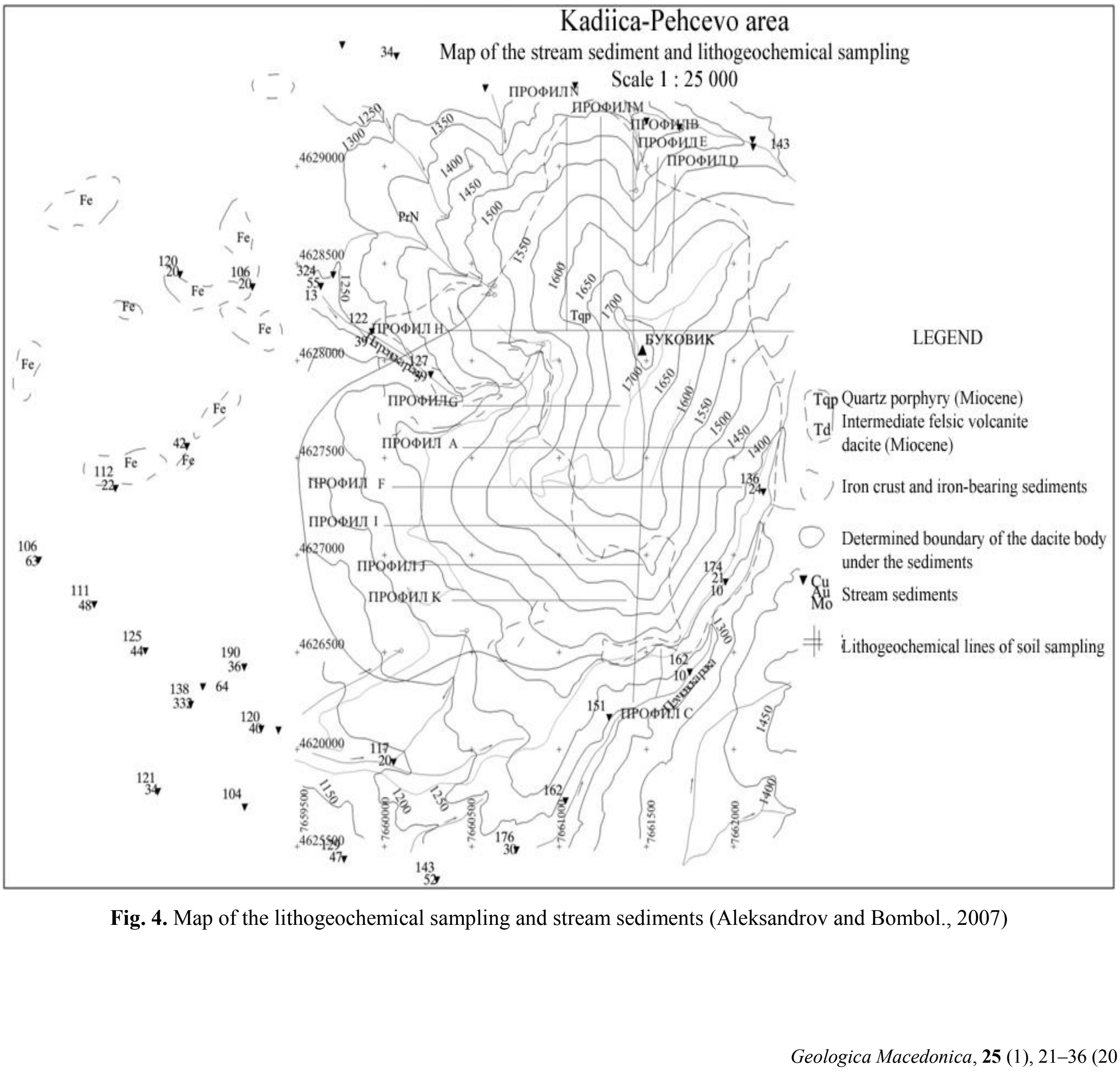


Fig. 4. Map of the lithogeochemical sampling and stream sediments (Aleksandrov and Bombol., 2007)

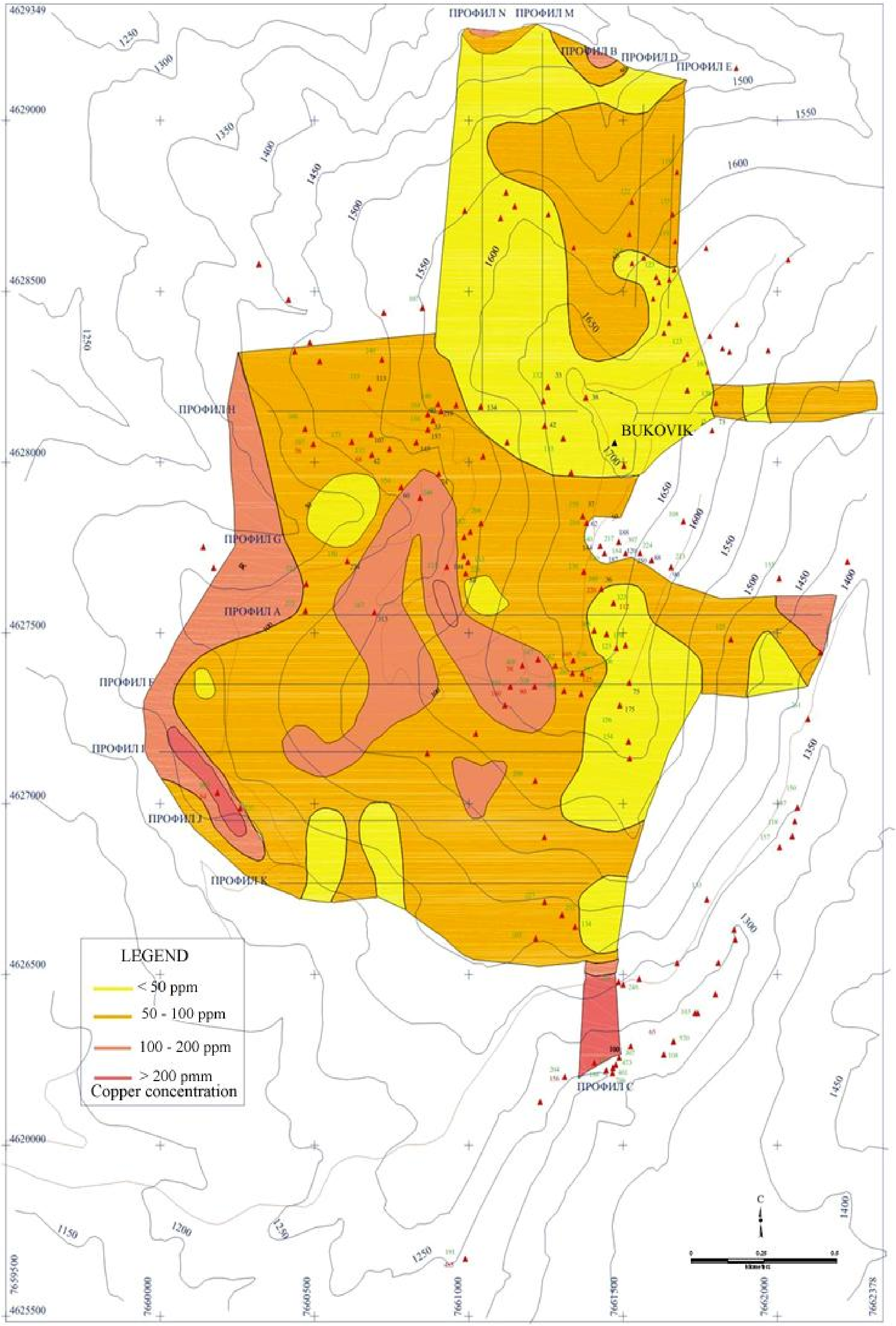


Fig. 5. Map of geochemical anomalies of Cu at the locality Bukovik–Kadiica (Aleksandrov and Bombol, 2007)

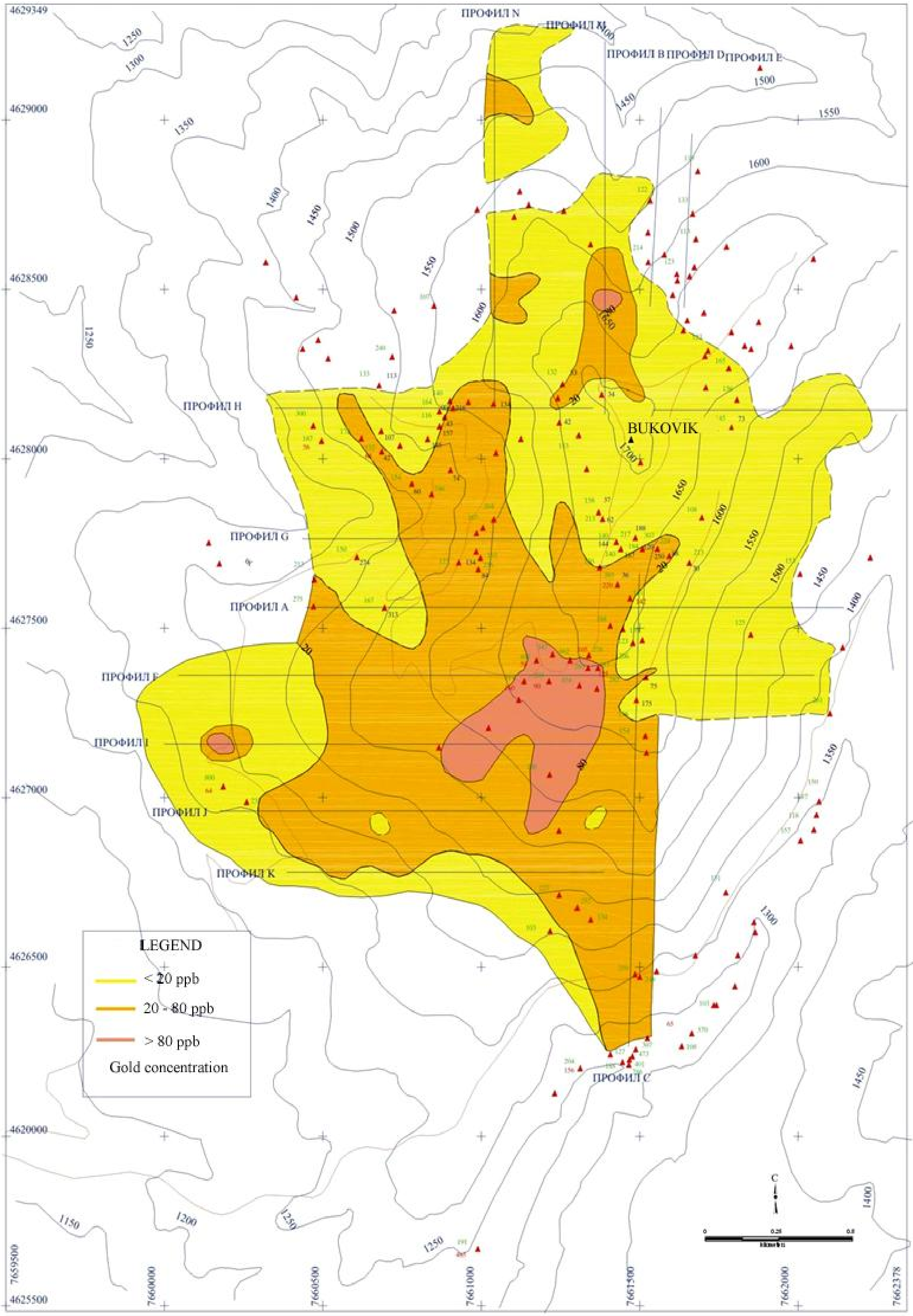


Fig. 6. Map of geochemical anomalies of Au at the locality Bukovik–Kadiica (Aleksandrov and Bombol, 2007)

The SW part of the anomaly has been divided into two parts. Northwestern part of the anomaly is with maximal value of 267 ppb and it overlaps with the SE part of the copper anomaly.

This anomaly is oval in shape with small elongation in NNE-SSW direction and it is long 500 m long and 350 m wide.

Wide arsenic anomaly was outlined at SW and S using lower limit concentration of 100 ppm As. The anomalies of second order, >200 ppmAs, were determined in two separate areas. One of them was with dimensions 500 × 400 m, while the other one was with 600 × 400 m, both with concentrations higher than 300 ppm As (max 475 ppm). The easternmost of these two anomalies overlaps with the formerly described Au anomaly.

For lead values above 90 ppm Pb were accepted as anomalous ones. In such case the lead anomalies almost overlap the As ones. This element anomaly covers the southern part of the mountain and it is open to its southernmost part.

The lowest limit concentration for cobalt was set to 190 ppm. Samples with higher concentrations than that have formed a narrow and elongated zone with N-S direction and maximal concentration of 600 ppm Co. Silver has shown only sporadical anomalous values.

In total, the obtained data have shown a whole array of different values for different elements. Values for particular elements were in the ranges as follows: 13÷433.3 ppm Cu, 2.3÷267 ppb Au, 0.5÷132 ppm Mo, 1.4÷11.8% Fe, 9.4÷600.1 ppm Pb, 7.7÷198.5 ppm Zn, 0.1÷58 ppm Ag, 3÷487.2 ppm As, 159÷15398 ppm Mg, 0.1÷2.3 ppm Cd, 1÷23.8 ppm Co, 5.2÷226.7 ppm Cr, 18.5÷1347.8 ppm Mn, 1.9÷47.4 ppm Ni, 151÷1100 ppm Ti and 17.9÷218.8 ppm V.

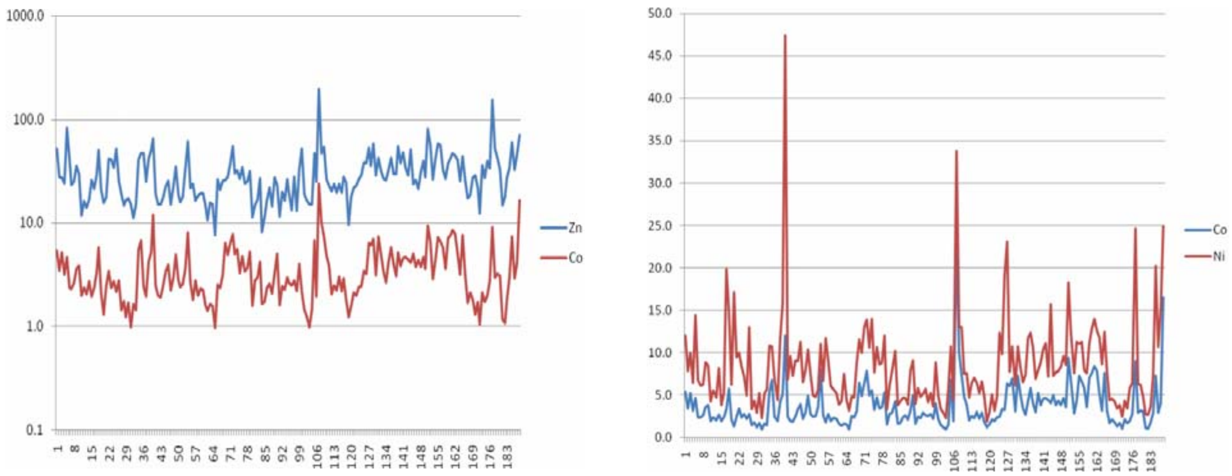
As well as for the lithogeochemical studies our efforts for better understanding of the geochemical cycle and relations between certain elements in soils resulted in an ANOVA statistical analysis (Table 2).

Table 2

Elemental correlation factors for soil samples from the Bukovik–Kadiica locality

	Cu	Au	Mo	Fe	Pb	Zn	Ag	As	Mg	Cd	Co	Cr	Mn	Ni
Cu	1													
Au	0,250	1												
Mo	–0,126	–0,079	1											
Fe	0,484	0,081	–0,358	1										
Pb	0,280	0,446	–0,387	0,292	1									
Zn	0,224	–0,026	–0,300	0,382	0,009	1								
Ag	0,684	0,090	0,015	0,079	0,074	–0,007	1							
As	0,352	0,603	–0,368	0,339	0,708	0,051	0,052	1						
Mg	0,097	–0,134	–0,273	0,417	–0,154	0,574	–0,057	–0,116	1					
Cd	0,154	0,180	–0,224	0,407	0,161	0,492	–0,096	0,340	0,321	1				
Co	0,206	–0,037	–0,377	0,402	0,107	0,811	–0,012	0,117	0,576	0,462	1			
Cr	0,206	–0,172	–0,236	0,505	–0,159	0,341	0,017	–0,158	0,796	0,219	0,340	1		
Mn	0,124	0,002	–0,373	0,172	0,245	0,530	–0,007	0,244	0,294	0,509	0,689	0,132	1	
Ni	0,186	–0,056	–0,363	0,405	0,014	0,702	0,003	0,052	0,822	0,340	0,787	0,604	0,516	1

The outcomes of the study are represented as correlation factors. The most representative correlation factors in this media were obtained for the elemental pairs Zn–Co wih correlation factor of 0.811 and Co-Ni with correlation factor of 0.787. In that direction we have proceeded with preparation of plots for more illustrative preview of those correlations (Figure 7).



a) *b)*

Fig. 7. Shape of the most representative plots of elements with most representative correlation factors, Zn-Co and Co-Ni, Bukovik–Kadiica metalometry-soils

As can be seen from the figure above the shape of one element almost ideally follows the shape of the other element with which it strongly correlates. Also, we would like to stress out that elemental pairs such as Zn-Co and Co-Ni reflect their strong correlation in primary mineralizations as well as in hydrothermally related ones. This is in strong correlation with the findings of the Barnes (1997) and Aliani et al. (2009).

Stream sediments sampling

For more precise estimate of the mineralization potential the method of stream sediments sampling has been performed. In dry conditions the sample with weight of 200–250 g was taken and sieved at place with sieve of –80 mesh. The wet ones were with weight of 5–10 kg, later on they were dried at room temperature, sieved and by quartering final sample with weight of 150 g was formed, as well as the duplicate sample with the same weight. The sampling always took part at modern river sediments and sample was taken perpendicular to the water flow along the whole width and maximal depth. For each sampling point was conducted a description of the geological setting of the stream-river, possible pollution, character of the river banks, etc. To be able to reach optimal coverage of the area of interest it was agreed that the distance between the samples should be 500 m. The 36 samples in total were sampled. Those samples alloweds to follow the drainage areas at the middle and lower part of the Pehčevska River until its entrance to the city of Pehčevo, Negrevska River from its source parts (Negrevo village) and all its left tributaries, Želevica River from its source parts up to the black road between the Crnik and Negrevo villages.

All the dry samples were quartered up to the mass of 150 g, making two identical samples, that were sent to a multielemental analysis (ICP) and for gold (AAS). The results of the most important elements are given in the Table 3.

Results from the river sediments sampling have confirmed findings of other types of research and studies. Copper anomalies (>100 ppm Cu) in drainage parts of the Pehčevska River Negrevska River, as well as in its left tributaries were with maximums of 324 ppm Cu in upper parts of the Negrevska River, whose sources are washing parts of proved anomaly of secondary halos of dispersion. Especially distinctive were the anomalies of Au in Negrevska River and its left tributaries that are constantly present, while at the Pehčevska River anomalies occur sporadically. The highest (anomalous) concentrations of Au occurred in the large left tributary of the Negrevska River, northern of Pehčevo, whose source parts have been located beneath the anomaly of secondary halos of Au. Maximal anomalous value for Au was obtained in the formerly mentioned stream and reached values of up to 332 ppb Au. Anomalous contents of molybdenum (>30 ppm Mo) were registered in upper parts of the Negrevska River, SW of the formerly mentioned secondary halos molybdenum anomaly, but molybdenum's absence in the stream of Želevica River is surprising. Zinc has shown interesting anomalies (>100 ppm Zn) along the margins of th volcanic body in Pehčevska River and Želevica River.

T a b l e 3

Results of chemical analysis (ICP) of samples from river sediments at the Bukovik–Kadiica locality (Aleksandrov and Bombol, 2007)

Sample No.	Cu ppm	Au ppb	Mo ppm	Fe %	Pb ppm	Zn ppm	Ba ppm	Ag ppm	As ppm	Sb ppm
SMK–001	67	3	1,5	6,29	100	52	79	0,3	138	8
E12102	117	20	0,9	4,45	1358	461	136	5	105	17
E12103	55	16	0,5	4,92	975	795	78	1,4	57	4
E12104	190	36	3,9	5,32	128	140	150	0,3	71	5
E12105	91	64	2,2	4,36	182	38	86	0,7	225	12
E12106	138	332	1,6	7,38	694	322	161	3,3	173	13
E12107	120	40	1,5	7,2	575	331	146	1,8	131	10
E12108	125	44	2,1	6,99	478	224	146	1,1	197	14
E12109	111	48	2,4	5,84	613	229	181	1,5	153	11
E12110	106	63	4,9	8,05	234	97	155	0,8	88	5
E12111	57	42	6,4	4,45	67	46	111	0,7	39	1
E12112	112	22	2,7	8,01	56	78	90	0,2	22	2
E12113	106	21	2,7	2,9	58	124	121	0,2	54	2
E12114	324	55	13	5,9	19	87	37	0,2	21	2
E12115	122	17	39	8,47	16	33	23	0,3	18	1
E12116	127	14	39	9,23	16	20	23	0,6	14	1
E12117	56	16	1,9	4,44	14	99	42	0,3	18	2
E12118	120	20	6,5	4,29	38	159	120	0,3	32	1
E12119	121	34	3,2	5,2	119	444	171	0,7	66	4
E12120	104	17	4	4,82	70	432	71	0,3	16	2
E12121	129	47	4	5,68	74	527	67	0,4	19	1
E12122	143	52	5,1	6,7	72	544	61	0,3	19	1
E12123	176	30	5,2	6,75	85	597	58	0,4	20	1
E12135	174	21	10	6,31	59	111	44	0,2	15	1
E12136	186	24	9,3	6,95	46	113	37	0,3	12	1
E12137	162	5	10	5,63	54	101	50	0,2	15	2
E12138	151	10	8,3	5,83	67	142	50	0,4	19	2
E12139	162	9	9	6,06	61	148	44	0,4	20	2
G13448	143	4	3,6	5,26	46	129	58	0,4	16	1
G13449	57	7	1	5,12	45	176	48	0,3	19	1
G13451	70	3	1,5	4,32	32	163	37	0,1	10	1
G13452	85	7	1,4	4,38	42	140	107	0,4	17	1
G13453	85	6	1,8	5,45	39	157	44	0,3	17	1
G13454	90	11	3,2	5,5	32	137	40	0,3	15	2
G13455	57	34	1,2	5,38	31	170	40	0,2	16	1
G13456	50	4	3,2	3,61	24	92	56	0,1	11	2

The absence of the Zn in drainages that wash away in the central part of the hydrosystem is a logical consequence. Its higher concentrations (up to ~600 ppm Zn) in lower parts of the sampled flow of the Pehčevska River are probably due to the presence of polymetallic veins and stockwork-impregnated occurrences uncovered by erosion processes. The absence of the anomalous concentrations of any other elements probably may be described by very fast flow of waters and steep relief and respectively fast change of the river sediments in the river beds and large dissemination along the river banks.

In total the obtained data have shown a whole array of different values for different elements. Values for particular elements were in the ranges as follows: 50÷324 ppm Cu, 3÷332 ppb Au, 0.5÷39 ppm Mo, 2.9÷9.23% Fe, 14÷1358 ppm Pb, 20÷795 ppm Zn, 0.1÷5 ppm Ag, 10÷225 ppm As, 1÷17 ppm Sb.

In order to get a more detailed insight about the relation between certain elements, similar to the lithogeochemical and metalometry programme, for stream sediments we have performed statistical analysis-correlation (Table 4).

The outcomes of the statistical study of stream sediments programme are represented as correlation factors. The most representative correlation factors in this media were obtained for the elemental pairs Pb-Ag wih correlation factor of 0.9099 and As-Sb with correlation factor of 0.9039. In that direction we have proceeded with preparation of plots for more illustrative preview of those correlations (Figure 8).

As can be seen from the figure above, the shape of one element almost ideally follows the shape of the other element with which it strongly correlates. Also, we would like to stress out that elemental pairs such are Pb-Ag and As-Sb reflect their strong correlation as it is in primary mineralization.

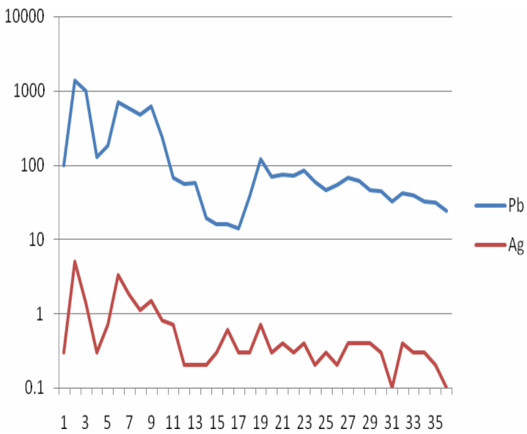
From all the aforementioned facts related to the conducted geochemical studies of the Bukovik–Kadiica locality we may to conclude that the geochemical associations of elements are very close to the ones given by Jankovic et al., (1995) for the Kadiica, as well as data for porphyry deposits Bučim (Čifliganec, 1987; Serafimovski, 1990) and Borov Dol (Tudzarov, 1993). Similar findings were also detected for numerous deposits and occurrence around the globe. Just to name few of them, Okote area in Ethiopia (Deksissa and Koeberl, 2004), Skouries deposit in Greece (Kroll et al., 2002), Tongshankou and Yinzu deposits in

China (Wang et al., 2004), Meiduk deposit in Iran (Aliani et al., 2009) etc.

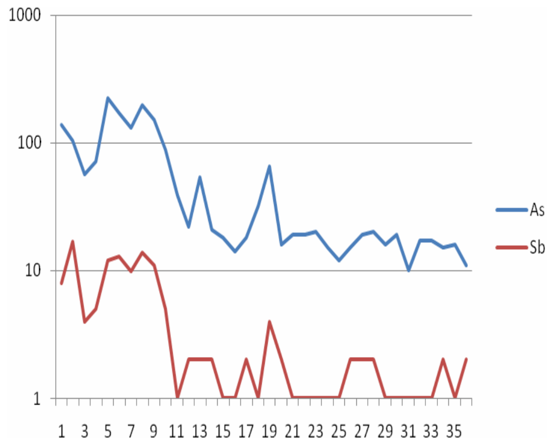
Table 4

Elemental correlation factors for stream sediments samples from the Bukovik–Kadiica locality

	Cu	Au	Mo	Fe	Pb	Zn	Ba	Ag	As	Sb
Cu	1									
Au	0,15400	1								
Mo	0,29079	–0,10854	1							
Fe	0,32261	0,25262	0,56464	1						
Pb	–0,09151	0,32622	–0,26346	0,00208	1					
Zn	–0,01765	0,14800	–0,31880	–0,06641	0,52324	1				
Ba	–0,06255	0,41612	–0,40494	–0,06175	0,53254	0,21153	1			
Ag	–0,02954	0,48423	–0,17336	0,05437	0,90995	0,37253	0,52237	1		
As	–0,08607	0,48614	–0,27443	0,08635	0,55936	0,04903	0,67156	0,53012	1	
Sb	–0,03762	0,44598	–0,28127	0,06690	0,78226	0,16024	0,65268	0,79150	0,90388	1



a)



b)

Fig. 8. Shape of the most representative plots of elements with the most representative correlation factors, Pb-Ag and As-Sb, Bukovik–Kadiica stream sediments sampling programme

CONCLUSION

With the realization of the extensive geochemical explorations and studies of the wider area of the Bukovik–Kadiica locality important information have been obtained in regard to the distribution of characteristic elements, which have been of high importance for the estimate of the potentiality of the studied area from the polymetallic mineralizations point of view. Namely, in the elemental association of the Bukovik–Kadiica deposit were determined: Cu, Fe, S, Mo, Au, Pb, Zn, Sn, As, Sb, Ti, V, Co etc. The group of major elements that constitute their own minerals or contribute significantly to the composition of other elements minerals stand out in this association. Such elements are: Cu, Fe, V, Sn, Sb, Pb, Zn, Ti, S, As etc. The rest of the elements occur in certain ore or rock forming minerals or hydrothermally altered zones and they appear asymmetrically without any consequential order.

The obtained data coincide with up to date information related to the geological, structural and mineralizing features of the Bukovik–Kadiica system. They would certainly be of interest during the planning of detailed mineral explorations for assessment of the ore-bearing potential of this very prospective locality.

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Р е з и м е

ГЕОХЕМИСКИ ПРОУЧУВАЊА НА МИНЕРАЛИЗИРАНИОТ СИСТЕМ БУКОВИК–КАДИИЦА, ИСТОЧНА МАКЕДОНИЈА

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Клучни зборови: примарни ореоли; стрим-седименти; металометрија; полиметални минерализации; локалитет Буковик–Кадиица

Во изведените регионални и детални геохемиски проучувања на стрим-седименти, почви и карпи во пошироката околина на локалитетот Буковик–Кадиица во близина на градот Пехчево, источна Македонија, беа детекти-

рани регионални и локални полиметалични аномалии на елементи како што се Cu, Fe, S, Mo, Au, Pb, Zn, Sn, As, Sb, Ti, V, Co и др. Со најстандардни вредности се појавија бакарот, молибденот, оловото и цинкот, што се совпаѓа со поранешните геохемиски проучувања. Овие податоци директно укажуваат на постоењето на бакарна минерализација во пошироката област, што исто така коинцидира со структурно-металогенетските карактеристики на областа Буковик–Кадиица. Деталните проучувања овозможија пресметка на корелационите фактори за најчестите елементи во областа од интерес. Особено изразени корелациони фактори беа одредени за парови елементи како што се Cu-Ag, Fe-Cu, Zn-Au, Pb-Ag and Pb-As.

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PETROLOGIC, MORPHOLOGIC AND FUNCTIONAL ANALYSES OF GROUND AND ABRASIVE STONE TOOLS FROM RUG BAIR, OVČE POLE VALLEY

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A b s t r a c t: This paper represents the results of the ground and abrasive stone tools analyses based on the finds collected during the excavation of Rug Bair undertaken in 1970s, and today stored in the Museum and Institute for Protection of Štip. The studies were made possible with the help from the Faculty of Natural and Technical Sciences, Štip, Republic of Macedonia. Through the stone material, an attempt was made a more comprehensive picture of the raw material, petrologic, technical and typological characteristics of the Neolithic stone industry at this site to be gained as well as its relationship with related simultaneously industries.

Key words: Neolithic; Rug Bair; Amzabegovo–Vršnik; Macedonia; row materials; ground; polished; abrasive; tools

LOCATION, EXCAVATION AND DATING OF RUG BAIR

The archaeological site of Rug Bair is located about 2 km south from the village of Gorobinci (Fig. 1), in the Saint Nicholas region, within the Ovče Pole valley. The location where the site is placed is a big naturally flatten terrace, in the middle a little concave recession, elongated in the direction east–west and with the dimension of 220 × 80 m (Археолошка карта, 1996).

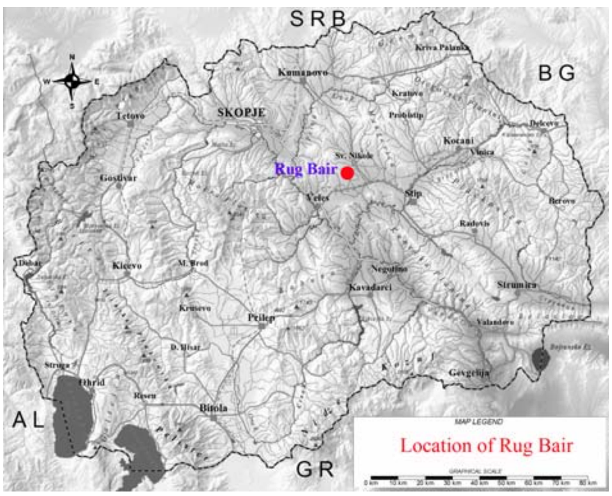

Fig. 1. Map of the Republic of Macedonia showing the location of Rug Bair

Natural conditions of the Ovče Pole valley, which is among the largest basins in the Republic of Macedonia, the geological structure of the environment, fertile land and river valleys of the Vardar and Pčinja are the topographic characteristics of this region that have contributed to the well-known Amzabegovo–Vršnik cultural group to develop a flat-type of settlements such as Rug Bair, morphologically different from Neolithic settlements such as "tumba", which can be found in the region of Pelagonia (Симоска, Санев, 1975). Today, except for one small spring, there are no water resources around the Rug Bair and the nearest river is located at a distance of 2 km. But during the Neolithic time, geomorphologic features were quite different. In a supporting of this paleoreconstruction, during the excavation in block G were detected river deposits suggesting that in the Neolithic period when the settlement lived, through one part of the site the river was flowing (Санев, 1975).

Unlike previous prospecting and excavation which has not been published (Saržoski, 1961), in the 1970s the City Museum of Štip undertook new excavation with a team from the Smithsonian Institute (Los Angeles, California) as part of a bilateral research project for exploring and studying of the Neolithic in eastern Macedonia. This excavation confirmed a multi-layer cultural settlement with a layer thickness of 1.40 m, in which the material remains were three times inhabited.

Rug Bair is a middle Neolithic settlement which belongs to the complex of Amzabegovo–Vršnik cultural group. The artifacts, especially ceramics founded in a large amount, according to the typology of forms, ornaments and the techniques used, as well as visual and other characteristics, are on the whole identical with the ceramics from middle Neolithic layers (II-IV) of the Barutnica site (in the literature known as Amzabegovo), but also with other settlements within Amzabegovo–Vršnik cultural group.

This archaeological excavation, followed later by zooarchaeological, archaeobotanical and palinological data in the frames of this region, showed a population which lived in warm and humid climatic conditions. Economic development was based on agriculture, cattle breeding and harvesting of wild plant species, some of them now cultivated in the territory of Macedonia. Fertile land allowed intensive farming, which was confirmed by a range of cereal grains found in archaeological excavations in this region. Nearby the site were mountain pastures dominated by low grasses and in the wider surroundings of the settlement there were mountains with extended forest that have enabled hunting and collecting of wood necessary for construction and fire. The vast amount and variety of ornamented pottery suggests that the craft was well-developed and technically accomplished. Ornamental imprints, found at the bottom of some vessel, indicate the existence of weaving crafts (Schwartz, 1976; Beug, 1976; Renfrew, 1976; Санев, 1975; Gruger, 1976; Димитровска, 2011).

The results obtained by processing the material from previous excavations at Rug Bair, were published in a sublimated article, originating exclusively from the trenches that were conducted by the ‘Yugoslav’ archaeologists (Санев, 1975).

For the purposes of this paper it is very important to emphasize that processed stone material derived from trench II and the squares F and H from trench III, which means that the material has not been published by now.

PETROLOGIC DETERMINATION OF THE RAW MATERIAL

Macroscopic determination of the raw material by a petrologist was performed for all artefacts from the site Rug Bair. Determination comprised the following categories: the type of the raw material, colour, structure, texture, varieties, mineral composition (examined macroscopically) and origin.

At the site of Rug Bair can be defined several types of rocks which are the base for the ground and abrasive stone tools made of: a group of metamorphic rocks types such as serpentinite, a group of volcanic rocks types such as andesite, a group of volcanic rocks types such as basalt, a group of sedimentary rocks types such as sandstones – in which the two subgroups differ (fine-grained and coarse-grained sandstones) and a group of residues of different origin (Fig. 2). The last group comprises a small piece of stone of different geological origin predominantly rich in silica, and there are also fragments of metamorphic rocks. Each artifact is made of a stone (rock or mineral) that has certain petrographic and technological attributes. Petrographic analysis of the raw materials used for making ground and abrasive tools from the Rug Bair was performed macroscopically and microscopically.

Raw material	Color	Structure	Texture	Varieties	Origin
Serpentinite	dark green	porphyritic	massive	fine-grained	local
Andesite	gray to dark gray	porphyritic	massive	coarse-grained	
Basalt	light gray to dark gray	porphyritic	massive amygdaloidal	coarse-grained	local
Sandstone	light gray to dark gray	psammite	massive	coarse-grained fine-grained	local
Miscellaneous	different	different		minerals (opal), metamorphic rocks	Local

Figure 2. Raw materials for ground and abrasive stone tools from Rug Bair

Serpentinite

Only one specimen of the dark green serpentinite was found. Macroscopically, the rock shows hardness, scratch and colour resemble nephrite. Because the artefacts made from nephrite are not yet confirmed on the prehistoric sites in the territory of Macedonia, for the purpose to define this raw material, a microscope preparation from the sample was made. The results showed that this is not a mineral, but artefact made of serpentinite, a specifically rock that belongs to the metamorphic rocks consisting mainly of serpentine minerals, which subsequently have been heavily modified. Serpentinite is a rock composed of one or more serpentinite group minerals, pyroxene and accessory minerals. In the alteration process pyroxene is transformed in chlorite group of minerals. The structure of the rocks is porphyroblastic. The base of the rock is fine-grained with the transformation of serpentine minerals in clay minerals. The team who processed the prospecting about the searching of 'Local resources of stone tools in Amzabegovo–Vršnik' was consisting of: Vasilka Dimitrovska (archaeologist), Biljana Garevska (paleontologist) and Stevče Donevski (local guide). During the prospecting, it was confirmed the local origin of serpentinite around the nearest area of Rug Bair, where exists deposits of this raw material by the banks of the Bregalnica river and its influents. The material is located on the surface in the form of small blocks.

Andesite

All specimens of andesite used in the manufacture of ground stone tools are gray to dark gray color. The structure is porphyritic, the texture is massive, and the varieties are coarse-grained. The ground mass is hypocrystaline and fenocrystals are represented by biotite, hornblende, and sanidine, but this interpretation needs more detailed microscopic examination of rocks. Hardness is not particularly emphasized. The origin is local in the vicinity of Rug Bair, where there are deposits of these rocks in the so called the Kratovo–Zletovo area.

Basalt

The samples of the basalts are of various colors, from light gray to dark gray shades. The structure is porphyritic, the texture is massive and amygdaloidal and the varieties are mostly coarse-grained. The samples that are amygdaloidal are also suitable for use because they have a hardness of basalt, which is a replacement for quartz sandstones in some regions (e.g. in Serbia) where they were used as an abrasive tools. The origin is local, from the vicinity of St. Nicholas, where there is a major occurrence of basalt 7–8 million years old.

Sandstone

The sandstones are of different colors, from light gray to dark grey. Despite the presence of quartz, the sandstones doesn't have high hardness, and their composition is generally consists of quartz, feldspar with a certain amount of mica. On the basis of macroscopic examination it is easy to determine whether the samples main mass is made of carbonate cement or silica. For that purpose, some specimens were treated with HCl acid to determine the presence of carbonate cement in the primary mass. The origin is local, and this type of sandstone is dominates in the flysch of the Vardar Zone.

Sandstones on the Rug Bair are categorized based on grain size, and thus recognize two groups: fine-grained sandstone (0.25 to 0.05 mm) and coarse-grained sandstones (2 to 0.5 mm). Since the Rug Bair is a site where it was first officially confirmed this type of raw materials through the petrologic analysis, the classification is made in order to follow the appearance of different varieties of sandstone in Neolithic sites in the territory of the Republic of Macedonia. This would determine whether there is some regularity in their use and make a connection and comparison of the materials.

A GROUP OF STONES WITH DIFFERENT GEOLOGICAL ORIGIN

In the collection there are several specimens determined in the category of miscellaneous. It is about a small pieces of stone with different geological origin predominantly rich in silica (one specimen can be included in opals), and there are also fragments of metamorphic rocks.

DISCUSSION ABOUT THE PROVENANCE OF THE RAW MATERIAL AT RUG BAIR

For all the artifacts of polished and abrasive stone, the petrologic determination of raw materials through the macroscopic examination was made. According to the results of the analysis, they revealed the presence of different types of raw materials.

Andesite is a volcanic rock and its presence in the territory of Macedonia is from the Tertiary age, including the samples from this assemblage. It belongs to a group of intermediate volcanic rocks that have relatively excess SiO_2 content (52–66%). It could successfully be used for tools of ground stone industry, but in our case the used for making abrasive tools is primarily due to its abrasive properties, which comes from the high content of quartz, as the prehistoric inhabitants of Rug Bair noted.

Basalt belongs to the group of basic igneous rocks, which have relatively low contents of SiO_2 (45–50%). Basalts are usually black in colour, depending on whether more or less the surface is altered with the climate impact. In the Ovče Pole region there are other phenomena of basalt that are significantly suitable for making tools because of finer (fine-grained) structure, as opposite to coarse-grained specimens suitable for abrasive tools found on the Rug Bair. Residents of Rug Bair chose specific basalt for this type of artefacts. For the reason which is still unknown, this Neolithic community has been using resources of basalt that were located further away from the site. This indicates that local resources may have been occupied by some other community or community that settled Rug Bair moved and may have acquired the habit to procure the raw material from resources that have been previously used, i.e. maybe they have not met the local resources of this raw material. The choice of this so called 'poor quality' variety of basalt maybe was conditioned, because this type of basalt has more abrasive ability of ‘better’ varieties of basalt that can be found around the site, and may have been deliberately chosen for manufacturing of abrasive tool. More specifically, it is a very high quality stone for abrasive tools (primarily the querns), and more compact basalts are not suitable for processing through the polishing because of its hardness. In relation to andesite, basalts have higher hardness and can be used as an abrasive, and a ground tools too. A large percentage of basalt in the collection indicates that the rock was one of the most frequent raw materials for abrasive tools of Rug Bair**.**

The sandstones are sedimentary rocks with a distinctive clastic structure, and polyvalent mineral composition. Rocks of this group represented a small number of tools at Rug Bair, and are mainly used for obtaining an abrasive type of tools such as the grindstones and whetstones, because of its highly abrasive properties.

In contrast to the basalt, which has been used exclusively for querns, both varieties of sandstone (fine-grained and coarse-grained) were the main raw material for grindstones and whetstones. However, it can be noticed that the grindstones are made of both varieties of sandstone, while for the whetstones was selected exclusively fine-grained sandstone, because purposes of these artefacts was their use mostly in processing and finishing primarily the artefacts from the bone.

The only archaeological site within Amzabegovo–Vršnik cultural group where the analysis of the raw material for making stone tools was processed very carefully is Barutnica (Fig. 3), the eponymous site of this culture. In the first excavation, definition of the origin of some raw materials for stone tools such as the hard materials – serpentinite and diorite, was made (Корошец, Корошец, 1973). Comment which can be attributed to the authors, who published this information without consulting a petrologist, is that serpentinite can be a tough material, unless it is not silicified. Later, when the trenches of the excavation extended, the publication (Gimbutas, 1976) revealed that the raw material used for the most of the ground stone industry consists of andesite (31%) and fine-grained to medium-grained sandstone (50%), and a small percent of basalt, quartz, metamorphic undefined rocks, limestone and quartzite. It was also pointed out that sources of these raw materials – sandstone and volcanic rocks – should be searched northwest of Saint Nicholas (in the vicinity of the site Rug Bair), since the prospecting did not gain any results about the sources of these rocks in the vicinity of Amzabegovo (Waide, 1976).

Most of the artifacts from the ground stone industry at Amzabegovo were made of the so-called green stone, which can be found north of the site in the slopes of Mt. Bogoslovec. Therefore the researchers concluded that the raw material for the typologically defined ground stone tools is of local origin. Color of the samples varies from light green to white and vice versa, to dark grey and black, with shades and transitions. The author of the article states that few tools are made of "real jade" (Smoor, 1976). The author by the term greenstone described the rocks which comprise few minerals in their composition, and the largest percentage belongs to the serpentinite and jadeite, with intrusions of asbestos. We must emphasize that the author of the article about the ground stone industry from Amzabegovo made a mistake in the determination of this green stone that apparently could be a green serpentinite or green shists (Smoor, 1976). Namely, serpentinite is a rock and jadeite is a mineral. Rocks such as serpentinites are also composed of several minerals, and one of them is the serpentine. An abundant source of these rocks ('green stone') is located 15 km south of the site Amzabegovo, where the population gathered on the northern and eastern slopes of the Mt. Bogoslovec. It is also stated by the same author that at that particular location can be found small nodules of jadeite.

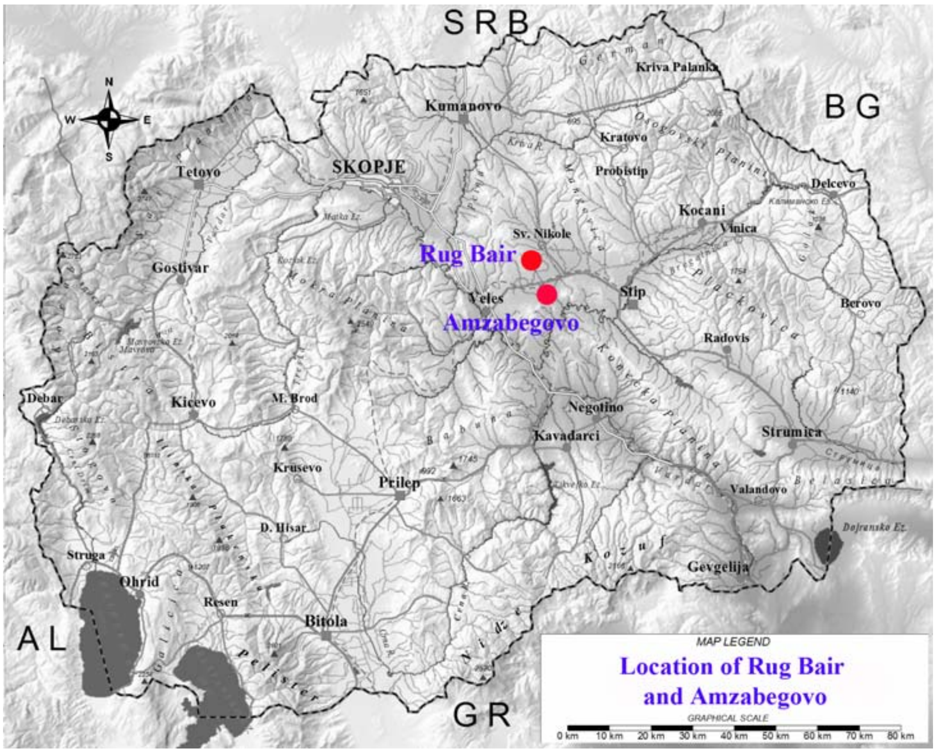

Fig. 3. Location of the archaeological site Amzabegovo, Republic of Macedonia

According to researchers, the ground and abrasive stone tools found at Rug Bair (axes, adzes, chisels, querns and mortars) are made of rocks with a Tertiary origin and of green sandy stone (Санев, 1975). Considering the lack of petrographic analysis of previously published material of ground stone industry, and the presence of only one tool (adze from serpentinite) in this collection, it is difficult to compare results in terms of whether they had used the same or similar raw materials. It also remains a mystery what the researchers meant by the term 'green stones' at Rug Bair and at Amzabegovo. Rug Bair is a village located 16 km north of Amzabegovo. In the assemblage was found an artifact of serpentinite, with the deposits of this raw material in the vicinity, while nephrite has not been confirmed in prehistoric Neolithic collections from the archaeological sites in the Republic of Macedonia. We can conclude that what was determined at the Rug Bair and Amzabegovo as a greenstone is not nephrite, but possibly serpentinite or green schist, although it is not disputed that some samples from Amzabegovo may have been made of nephrite that came through the import, trade or exchange of goods . There is also a possibility that nephrite could be from the local origin, which is a presumption that should be proved by further fieldwork.

According to papers from the congress held in Bratislava in 1999, it was established that the most frequent raw materials used in the Neolithic period on the territory of Europe for obtaining ground stone tools were: green schist, amphibolite, basalt, and to a lesser amount jadeite, eclogit, serpentinite, and others. (Težak-Gregl, 2001). Nephrite in the Neolithic Balkans was used as a decorative stone for luxury items (Antonović, Stojanović 2009, 183-191), and can be found in few places in Serbia, and much more in Bulgaria at the Neolithic sites by the river of Struma, with an attempt by the researchers to define the so-called nephrite culture of the Balkans (Kostov, 2005).

Existence of primary source for raw materials confirms that most of the artifacts on the Rug Bair are made of raw material with a local provenance that the population was able to gather around or near the site. A common feature of Rug Bair and Amzabegovo is the presence of serpentinite, volcanic rocks of andesite and basalt, and sandstones that creates the largest percentage of ground and abrasive stone industry at both sites. It is possible that the use of local resources was the same for these two Neolithic communities, because of their vicinity. The sources were accessible on the surface and this was the main reason why they came to the same place to collect the raw materials for their stone tools.

The geological material from which stone artifacts at Rug Bair were made is very diverse, but it is conditioned and limited to the amount of material originating from a single trench. In this regard there are analogies and parallels to Neolithic sites in Macedonia, where there is greater diversity in the raw materials used for ground and abrasive tools (like Tumba Madžari or Govrlevo), but unfortunately the material is not published yet.

Typological and technological analysis of the industry at Rug Bair

The main criteria for the classification of ground stone industry and abrasive tools were the morphology of artifacts and raw materials from which they were made of. However, we should pay attention to the definition of the terms "ground" and "abrasive." When we classify ground stone tools, then this primarily refers to a technique that was used for obtaining of these tools, while the term abrasive tools primarily refers to the raw material from which the artifacts were made of. All tools from Rug Bair were divided into two main groups: ground industry (polished stones) and abrasive tools (grinding industry).

This Neolithic collection have provided conditions to distinguish the manufacturing techniques of making objects from ground and abrasive stone, which generally includes: chipping and retouching, pecking and grinding (Антоновић, 1992).

Typological and technological analysis of the stone ground stone industry at Rug Bair

In order to reconstruct the technology of the tools, the analysis of ground stone included: the platform on which the tool was formed, the degree of preservation/fragmentation of artifact, morphometric characteristics, the processing stage (semi-finished / final product), processing technique, the morphology of the dorsal side, chemical/thermal damage (eg burning) and changes in materials, the presence of cortex and traces of use on the basis of the microscopic identification. During the processing of this type of tools, modified and adapted formulary was used (Антоновић, 1991).

Adze

Adzes are artifacts that belong to the group of ground stone industry, with the edge on the distal part of the tool (Fig. 4). The edge is not in the plane of symmetry, giving the tool an asymmetrical profile and thus morphologically in its typology is different from axes. The function of chiseling and trimming wood, used in making various wooden objects, is characterized by the use wear in the form of fine lines parallel with the longitudinal section of the tool (Антоновић, 1992; Antonović, 2003; Semenov, 1976).

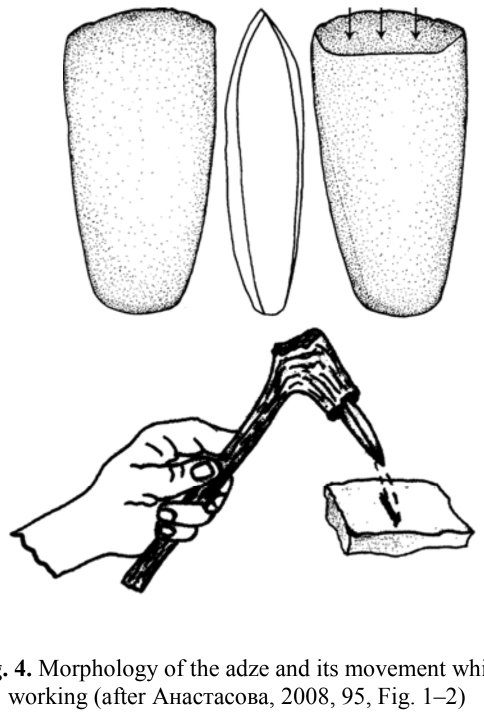

Fig. 4. Morphology of the adze and its movement while working (after Анастасова, 2008, 95, Fig. 1–2)

Only one fragmented adze from serpentinite (No. SII D13C) with preserved distal part was found at the site of Rug Bair. It is a final product that was obtained by polishing of the tool (T I/2). The specimen has defined edge in the distal part which is also broken. The analyses of the use wear traces on the surface of the artifact confirmed that the morphology of this type of tools such as adzes fits with its function (Fig. 5).

Fig. 5. Traces of use on the surface of the adze made of serpentinite × 40 magnifying (photo by authors)

Typological-technological analysis of the abrasive tools at Rug Bair

Abrasive tools are included in the archaeological finds, because they undoubtedly played an important role in the life of Neolithic people. Some types of artifacts in this group were used for millennia and remained morphologically unchanged to this day; resembling the form they had in prehistoric times. Abrasive tools include: grindstones, whetstones, pounders, querns and mortars (Антоновић, 2008).

Tools with abrasive characteristics from Rug Bair are represented with a small number of pieces. Their typology and function is given in summary, because this makes it easier to follow the analysis of this type of finds. The main basic feature of abrasive tools is the choice of raw materials which depends on the functions of the artifacts, while the shape of the tools is of secondary importance.

In the analysis of stone artifacts with the abrasive characteristics, analysis included: the dimensions of artifacts, the degree of preservation/fragmentation, physic-chemical and thermal damage as well as the changes in materials, the presence of cortex and traces of use on the basis of the microscopic identification.

The Rug Bair abrasive stone assemblage consists of 40 artifacts in total, which have been attributed to 4 main categories: grindstones, whetstones, pounders and querns.

Grindstones

The grindstones are artifacts belonging to the group of abrasive tools that were used for working and shaping of other solid materials (stone, bone, horn, ceramic, wood) by whetting and grinding. Depending on the work surface, the shape of the tools, and traces of use, different types (with subtypes) of grindstones can be distinguished, and according to the morphometric characteristics they can be classified into: manual (movable) and static grindstones, sometimes with large dimensions, with one or more work surfaces (Antonović, 2003; Антоновић, 2008).

Several types of grindstones can be found in the Rug Bair material. Except for one piece, the rest of the assemblage is fragmented. The grindstones from Rug Bair are classified into the following categories:

1. *Manual grindstones.* In total, 5 hand grindstones are found in the collection. Two pieces are small and were made of pebbles of coarse-grained sandstone (No. C2 SII; No. SII D2-1), partially fragmented, and with all sides polished (T II 2). The other two specimens from coarse-grained sandstone are fragmented, rectangular in cross section, with slightly convex work surfaces (No. FH3-1), and one (No. SIII F1-1) piece bearing also fragmented groove for modeling awls and needles (T I, 1). One manual grindstone of fine-grained sandstone was part of a larger tool, according to a depression located on the inside of the tool (No. SII E5). The artifact is polished on all sides and at the same time this is the only complete tool in the entire collection of ground and abrasive stones from Rug Bair (Fig. 6). The length of grindstone is between 40 mm and 69 mm, width ranges from 34 mm to 56 mm, and thickness is from 22 mm to 36 mm.

Fig. 6. Manual grindstone – the only complete tool in the assemblage (No. SII E5) (photo by authors)

2. Static grindstones. In the collection there are 2 fragmented pieces of static grindstones from fine-grained sandstone bearing at least one working surface. The preserved piece of the slightly flat and polished working surface in both cases indicates larger size grindstones.

a) No. SII C2-1 б) No. SII C2-2

Fig. 7. Static grindstones at Rug Bair (Photo by authors)

The first piece of static grindstone (No. SII C2-1) is a small triangular fragment with rectangular cross-section (83×63×20 mm). It looks like a plate with parallel sides and it can be recognized by one working surface which is polished by use, while the other parallel side to the surface is rough and without any traces of use (Fig. 7a).

The second piece of static grindstone (No. SII C2-2) is a massive four-side fragment with rectangular cross-section (102×82×51 mm) with preserved at least one work surface that is slightly polished and gradual. Fragmentation of the tool indicates that this sample comes from the grindstone of larger size and it is possible that had more than one working surface (Fig. 7b).

3. ***Double grindstones.*** This group includes the grindstones with two working surfaces. There are three fragmented examples of this type in the collection, made of fine-grained and coarse-grained sandstone. Two pieces are with parallel polished sides (No. SII F16; No. SIII FFH25-2) (T II, 3), and one is a fragment of a large static double grindstone (No. SII D7) which has a nice polished concave work surface (T II, 1).

Whetstones

Whetstones are included in the group of abrasive tools like the grindstones, but the difference is the small size and the type of raw material from which the products were made of. Whetstones are used for fine finishing of bone, bone needles and awls (Antonović, 2003; Антоновић, 2008).

Whetstones are artifacts made of material which could be used as a working surface from all sides of the tool (Fig. 8). The choice of materials for whetstone and their working surfaces are not related. Opposite of the grindstones made of rough materials and used for the grinding, whetstones were used on the way that would allow polishing all around the surface of the tool. They are classified primarily on the basis of rectangular shape in the form of small tablets with thin-section and a flat work surface.

Grinders are represented in the collection with four examples of fine-grained sandstone (No.SIII F40-1, No. SIII F40-2; No. SIII F42-1; No. SIII F42-2). The length of these artifacts is in the range from 31 mm to 70 mm, width of 22 mm to 59 mm, and a thickness of 6 mm to 13 mm (T I, 4, 5).

Fig. 8. The surface of whetstone from Rug Bair (No.SIII F40-1) – T XVIII No. 4 ×40 magnifying (photo by authors)

Querns

The quern as an abrasive tool is mostly characterized by massive specimens that have a flat or slightly concave working surface that was used for milling grains, pigments, ceramics... It consists of two parts, the lower (stationary) part of the quern and the upper (movable) part so called pounder. Querns could be used as universal tool for shaping the objects made from a hard material and it is sometimes difficult to distinguish the quern from the grindstone. The only way is according to traces of use wear of the working surface (Antonović, 2003; Антоновић, 2008).

The querns can have at least one, and sometimes more working surfaces. Since it was a multipurpose tool, when it is fragmented like some pieces from the Rug Bair (Fig. 9), then it is difficult to define how many working surfaces had this type of artifacts.

Fig. 9. Fragmented querns from Rug Bair (Photo by authors)

The Rug Bair querns, according to the shape, number and use wear of the work surface, are divided into:

1. Regular querns from basalt (No. SII C2-3; No. SII D2-2; No. SII F1; No. SII EA2-1; No. SII EA2-2; No. SII EA2-3; No. SIII F1-3; No. SIII F27; No. SIII F33-1; No. SIII F33-2; No. SIII H7; No. SIII FFH16-1; No.SIII FFH16-2; No. SIII FFH25-3) and andesite (No. SII H3; No. SIII H-5), fairly fragmented, where traces of use can be distinguished at least on one work surface.

2. Querns with two work surface – only one fragmented specimen from this type was found (No.SII D13-2) with recognizable two work surfaces.

3. Undefined fragments of grindstones – Due to the undefined shape, a fragmented piece of basalt (No. SIII F1-2) could be placed into two groups, as well as the grindstone without a work surface or as part of a quern. It is possible that this artifact belongs to the group of querns because it is made from basalt, opposite of grindstones which are usually made of sandstone.

Considering the fact that the quern was composed of two parts, all fragmented specimens belong to the lower or static part of the tool, while the upper, or movable parts of this tool on this site are represented in the form of pebbles. Based on the use wear traces of work surface that is more rough than polished, and the type of the raw material, we can conclude that these are the querns. The small fragments of these querns are preserved and only parts of at least one work surface, which is not enough for definition of their form. Work surfaces are mostly flat, sometimes concave from the use with a visible signs of previous treatment.

Pounder

The pounder is the last artifact included in abrasive tools, because it got its shape mostly by using. This group may include pebbles or rocks with a suitable shape without their moulding, and comfortable for holding in the hand. According to the use wear traces, the pounder was a multifunctional tool that was used as a retoucher, hammer, anvil, for crushing and grinding fruits, grains, pigments and others. This type of tool is a common artifact on the Neolithic sites often founded by the querns during the excavations (Antonović, 2003; Антоновић, 2008).

The Rug Bair collection comprises two fragmented pieces made of andesite (No.SII C1; No. SIII FH5) that were used in the function of pounders. Both implements are formed on pebbles suitable for comfortable holding in the hand. They were used on all sides, making the rough work surface (Fig. 10). The traces of intense burning can be recognized on one specimen with an ellipsoidal shape (T I, 3).

Fig. 10. The surface of a pounder (No. SII C1) ×40 magnifying (photo by authors)

Miscellaneous

This category includes specimens which could not be defined on the basis of their morphological characteristics. These include the waste of the raw materials rich in SiO_2 and a piece of opal. One specimen (No. F13 SIII) is a partly fragmented river pebble with elongated shape, made of quartz-feldspar metamorphic rock. Its interesting and nice shape resembles the retoucher, but on the surface there are no traces of use, so the purpose for its use by the local Neolithic community remains unknown. Perhaps it was a piece of raw material that was rejected, because it was not suitable for the the abrasive tools, nor for adzes or axes.

CONCLUSION

Analysis of the ground stone industry and abrasive tools found at Rug Bair confirmed the existence of the whole range of implements (Fig.11) which was established with the previous excavations of the site (Санев, 1975). The collection consists of 1 ground stone tool made from one raw material, 34 abrasive tools made form 4 raw materials, and 6 miscellaneous pieces without specific morphology and different geological origin.

Figure 11

The representation of types and tools of ground and abrasive tools from Rug Bair

Type of tool	Speci-mens	%	Com-plete tool	Raw material	Origin
Adze	1	2.4	/	Serpentinite	Local
Grindstone	11	26.9	1	Sandstone	Local
Whetstone	4	9.7		Sandstone	Local
Quern	15 2	41.5	/	Basalt Andesite	Local
Pounder	2	4.8	/	Andesite	Local
Miscellaneous	6	14.6	/	Raw material with SiO_2 Opal Metamorphic rocks	Local
Summary	41	99.9	1		

The Neolithic community at Rug Bair could collect the raw material used for obtaining the tool in the vicinity of the site. The selection of raw materials was determined due to their further usage. For grindstones and whetstones were used sandstones, for pounders – andesite, and for querns – basalt. Because of its abrasive properties and types of materials from which they were made of, the abrasive tools at Rug Bair are largely fragmented, except for one piece of the complete tool. We may assume that the abrasive tools are fragmented because the excavation included the garbage dump, e.g. a part of the site where the fragmented and unusable tools were thrown.

The ground stone industry at Rug Bair is represented with only one tool in the form of an adze from serpentinite, which can be found in many Neolithic sites in the Balkans and in Europe. The tool has fragmented distal part, obtaining of the implement was with chipping and retouching, and the final trimming wash with polishing which visually gave the adze shape of the tool (No. SII D13c).

The largest percentage of material from Rug Bair consists from tools with abrasive properties. This type of artifacts very rarely has an intentionally manufactured surface, because its shape is mostly obtained through usage, without the application of some of the techniques for making stone tools. Considering the fragmentation of the artifacts, it is difficult to determine specifically what technology has been used at the site for their obtaining.

According to the findings at the Rug Bair from other trenches that were published previously, ground and abrasive tools compared with the chipped stone assemblage are in a big amount and very heterogeneous (Санев, 1975), which is quite opposite case with the findings from this trench which is the subject of this paper. According to the researchers, they distinguished: axes, adzes, chisels, querns and mortars (Fig. 12, 13, 14, 15).

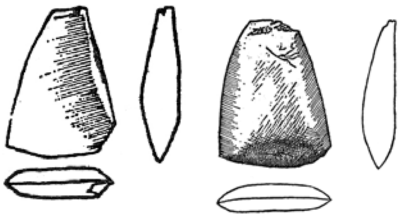

Fig. 12. Axes from Rug Bair (after Санев, 1975, T I, 1–2). No scale provided for the drawings.

Axes were not found in the processed material from Rug Bair. Based on the drawings and their description in a previous publication, there were more types and subtypes of axes with different longitudinal and transverse sections (Fig. 12). They were divided into axes with edges that are flat obtained with equal treatment of the bottom and top (Санев, 1975), i.e. with the parallel polishing of the dorsal and ventral side in the distal part of the tool.

Adzes were the most often found implements in the field. According to the reports of the excavators, they were divided on the basis of their form and section into several types and subtypes, and mainly described very descriptively (Fig. 13). Determination was made on the basis of the round edge grinded only from the bottom side (Санев, 1975). The latest research of Rug Bair found a piece of fragmented adze with the preserved distal part with an edge, and traces of use were confirmed the matching of the morphology of the tool with its function (Fig. 5; T I,2).

Chisels are a third category of edge tools at Rug Bair. In the observed assemblage, the chisels are lacking, and considering the fact that only one tool has been found in all trenches from previous excavation (Fig. 14), it is not possible to calculate the percentage of this type of tools in the settlement. The chisel has been described as an elongated tool whose upper side is rounded, while the edge is sharp, partly flat and oblique at one side (Санев, 1975). According to the typology, a chisel is a tool with an edge in the distal part, but the edge can be at both ends simultaneously. They are separated into a special category of tools due to the small size and the length of the edge that does not exceed 25 mm (Antonović, 2003). They can be recognized by the elongated form that is approximately equal to half the width (Anastasova, Pavuk, 2001; Anastasova, in press).

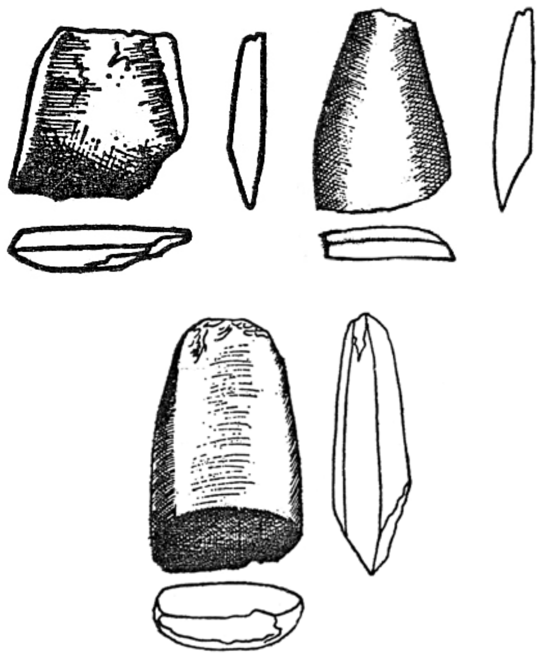

Fig. 13. Adzes from Rug Bair (after Санев, 1975, T I, 7–9). No scale provided for the drawings.

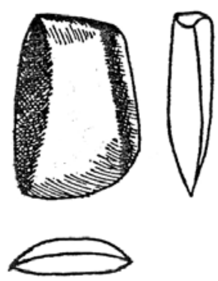

Fig. 14. The chisel from Rug Bair (after Санев, 1975, T I, 10). No scale provided for the drawing.

It should be noted that classical typology determines the types of tools by their morphology, and functional analysis determines the types according to their function. Ground tools with an edge in the distal part of the artefact, on the basis of the longitudinal section are divided into axes (with symmetrical) and adzes (asymmetrycal) cross-section. Considering the fact that published drawings are without any scale provided, what was previously identified as an axe could easily be a chisel, and vice versa, what is typologically defined as adze, after the use wear traces can be an axe. This is important because in the previously published material from Rug Bair some adzes have been classified as axes, and that which is determined by its morphology as a chisel could be also an ax, which depends on the use-wear traces on the surface of the tools whose analysis is not carried out by researchers.

Contrary to the previous publication which states the entire range of ground-edge tools, such as axes, adzes and chisels (Санев, 1975), it must be emphasized that in this assemblage from the site Rug Bair was found only one ground-edge tool, an adze. Axes, adzes and chisels are the tools that are related to woodworking (and possibly breaking bones) and can be found in the forested areas. The natural environment of the Neolithic community which settled the Rug Bair were the mountain pastures and mountains with forests and conditions for collecting the wood necessary for construction and fire. The absence of other ground-edge tools in this collection can be explained by the limited access to the material, which comes only from a single trench.

Typological and functional analysis of the processes assemblage indicates that the largest percentage of abrasive tools from Rug Bair belongs to the querns, and then to static and manual grindstones. Use wear traces, abrasion of the work surface and the type of raw material determine the type of tool. The special case is with fragmented querns and fragmented big massive static grindstones, which the researchers mostly classified all of them as a querns. Therefore, the static grindstones are not mentioned in the previously published collection of the Rug Bair that was processed in the 1970's, and within the group of the querns only complete specimens are described (Fig. 15). Also, it is stated that nearby the complete querns were found pebbles classified into pounders (Санев, 1975). Pounders, which were moving parts of the statically grindstones, are confirmed in this work too. Because pebbles were mainly used as a pounders, researchers often do not make much distinction between pounders and hand grindstone, which differ in form and traces of use.

Abrasive tools were used to process solid materials, as well as to carry out the preparation of food within the household. A large percentage of abrasive tools in the collection indicate that the inhabitants of this settlement carefully selected the raw material for implements of this type which had played a big role in the daily life of the population at Rug Bair.

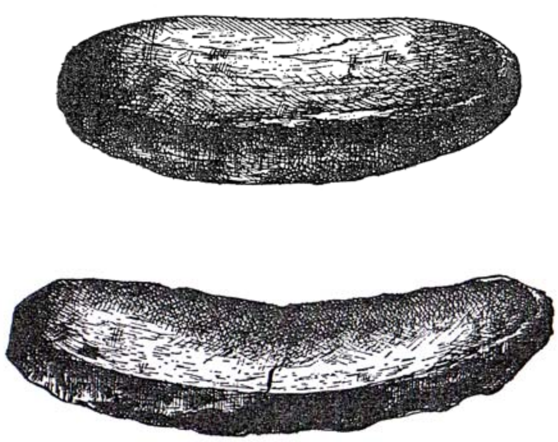

Fig. 15. Down (static) part of the quern from Rug Bair (after Санев, 1975, T II, 1–2). No scale provided for the drawings.

The ground-stone and abrasive tools from Rug Bair belong to the Middle Neolithic in the Republic of Macedonia. Although these artefacts are poorly indicative in terms of chronology, analysis of these industries within one archaeological site or in one region can show us the level of technology used while processing the stone, how these technologies developed during the time, and eventually lead us to remote but common Mesolithic roots, as tradition that is kept in some type of products.

Beside analogy with the contemporary Neolithic sites in Macedonia, these industries from Rug Bair can find its parallel in the published literature about Neolithic sites in the territory of the Balkans, primarily in Serbia such as Vinča (Антоновић, 1992), Donja Branjevina (Антоновић, 2002), Ilića Brdo (Антоновић, 1997), then Galabnik (Anastasova, Pavuk, 2001), Provadija (Anastassova, 2008a) and Dobroslavci (Anastassova, 2008b) in Bulgaria, or Makriyalos in Greece (Tsoraki, 2007).

The ground-stone and abrasive tools from Neolithic sites in the Republic of Macedonia have not been thoroughly analyzed in terms of raw materials. The absence of this analysis complicates the identification of the raw materials that were used by the Neolithic inhabitants within one culture or region, including their provenance and the geographical distribution area in which the residents were moving. They could point out to the ways the raw material was collected, whether it was imported or came via trade in the Neolithic communities whose lives depended on stone as primary material in their economics.

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Р е з и м е

ПЕТРОЛОШКИ, МОРФОЛОШКИ И ФУНКЦИОНАЛНИ АНАЛИЗИ НА ЗЕМЈЕНИ И АЛАТКИ ОД АБРАЗИВНИ КАРПИ ОД РУГ БАИР, ОВЧЕ ПОЛЕ

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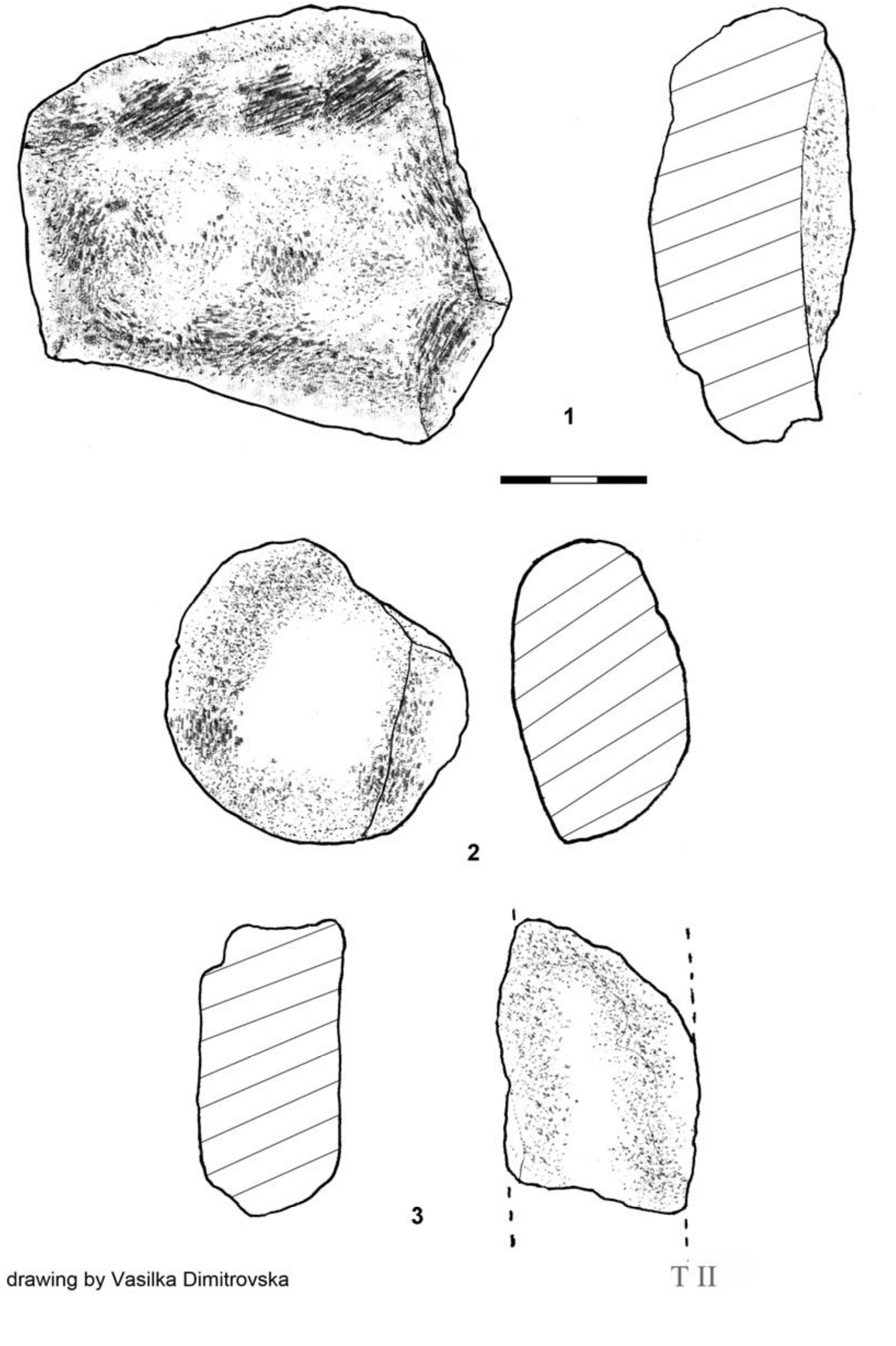
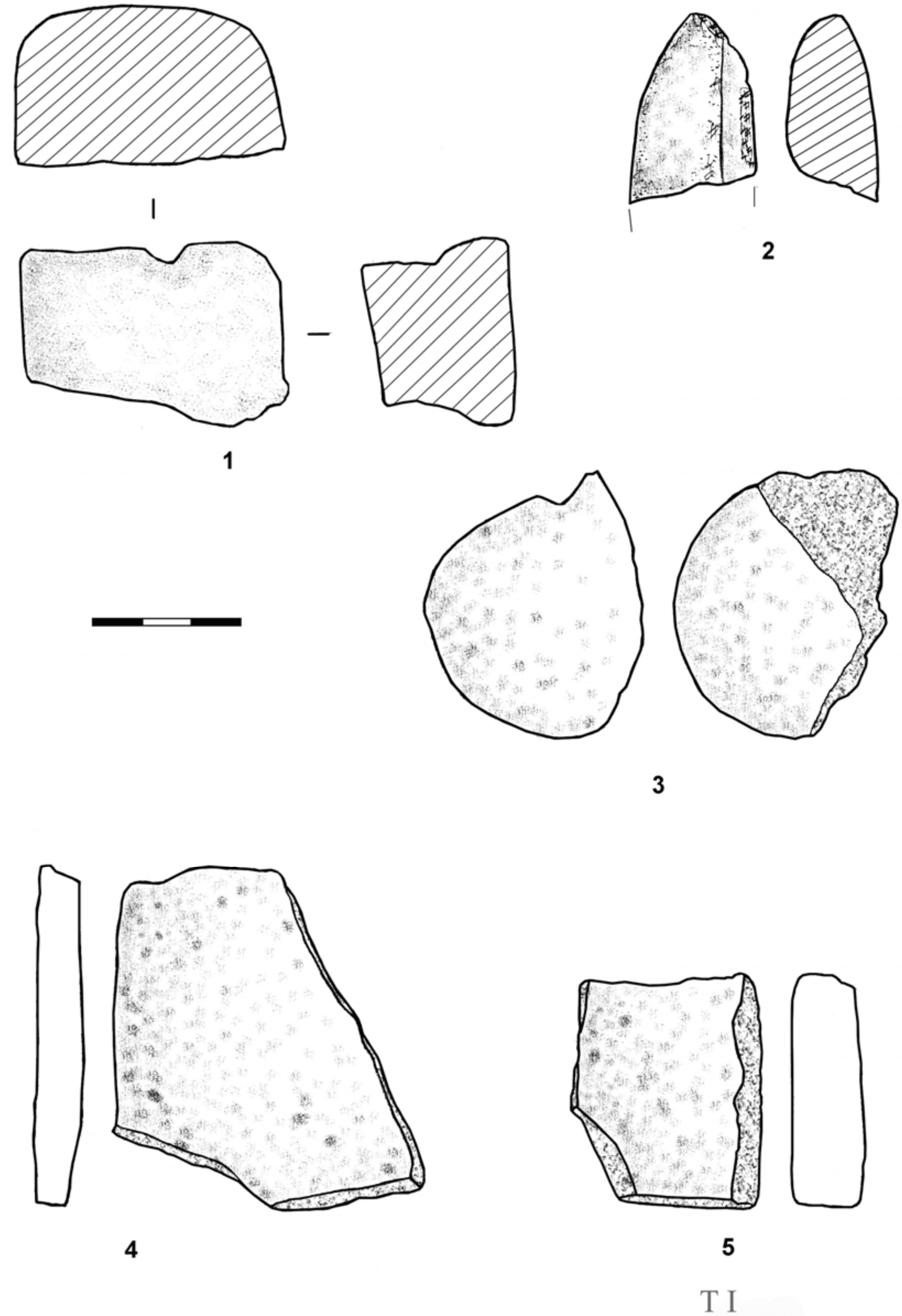
Клучни зборови: неолитски; Руг Баир; Амзабегово-Вршник; Македонија; суров материјал; земјени; полирани; абразивни; алати

Во овој труд се презентирани резултатите од анализите на земјени и алатки од абразивни карпи базирани на наодите собрани за време на ископувањата на Руг Баир во 1970-тите, а денес складирани во Музејот и Институтот за заштита во Штип. Проучувањата биле овозможени со помош на Факултетот за природни и технички науки во Штип, Република Македонија. Преку карпест материјал, направен е обид за добивање сеопфатна слика на суровиот материјал, петролошките, техничките и типолошките карактеристики на неолитската продукција од камен од овој локалитет, како и воспоставување на врската со паралелно поврзаните индустрии.



Appendix 1



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Appendix 2

GEOME 2
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GEOCHEMICAL ANALYSIS OF A BEAN SEED IN CERTAIN REGIONS IN THE REPUBLIC OF MACEDONIA

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A b s t r a c t: The presence of the macro-elements and elements in traces in the bean seed is determined by ICP-AES (atomic emission spectrometric with inductive plasma). The various bean seeds are taken out of five different types from some regions in the Republic of Macedonia. The results obtained refer to the analyses of 19 elements of the group of macro and micro-elements. There is a wide concentrated range in the samples from 30286,8 mg/kg for K in the test 9 to 0,15 mg/kg for Co in the test 8. More attention is devoted to the presence of Ca, Fe and Zn in the bean seed because it is a valuable source of these macro-elements and elements in traces which are important nutritive items for more that 2 bilion people in the world. Therefore, the biological importance of these elements in traces is perceived as well (their transfer and accumulation from the soil into the plants)

Key words: bean seed; geochemical analysis

INTRODUCTION

For more than 300 million people worldwide, beans are cheap food in the daily diet. Ordinary beans (Phaseous Vulgaris) in general are a source of Fe, Zn, Ca and other nutrients that the humans imbibe (Awadallah et al. 1986). The beans imbibibition is widespread in Central and South America, East Africa (Sherif et al. 1979) and most countries in Europe and Asia. Beans are a very important product in the nutrition in the Republic of Macedonia. Efforts to improve its nutritional content in terms of protein and minerals, especially Fe, Ca and Zn will be useful in the diet of many people. The analyses of various bio-components of the beans are more focused on the concentration of Fe, Ca and Zn. Much of the research on trace elements show that the average Fe concentration is about 55 mg/kg, but researchers have noted changes in the concentrations of Fe to 100 mg/kg and more.

The average concentration of Zn ranges from 20–60 mg/kg. Also the environment and the genotype influence the concentration of trace elements in the seeds of beans (Shaclette, 1972). Trace elements are extremely important for plant development and normal functioning of basic functions. Some trace elements (Fe, Zn, Ca, Mg, P, K and Cu) (Shaclette, 1980) are assumed as necessary for the development of plants in the capacity of food components in the past. In recent times various sensitive analytical methods (ICP-AES) have a different approach towards the determination of trace elements and therefore the significance of many of them is determined with greater confidence and greater success. If the result is well known that the wealth of trace elements significantly depends on the individual genotypes of beans, their generations, and the conditions for development in the environment.

The Enrichment Factor (EF) of 15 elements in the seeds of beans is estimated from the concentration of that element of the sample compared with the concentration of the same element in the soil of the region. The enrichment factor is calculated based on the known ability of transmission and accumulation of elements in the soil and into plant based on the biological activity of plants.

MATERIALS AND METHODS

The methodology applied to the analyses of the plant samples basically includes:

Samples of plants;

- Preparation of the samples;
- Identification of the presence of macro-elements and trace elements in the plants through the method ICP-AES;
- Interpretation of the obtained results.

Samples of plant origin

Taking the samples can be individual, if taken from one place of the lot or average, if more individual samples (10-25) from different places are taken. Basically it is much better to take an average of samples as in our case because the results are obtained with greater accuracy and provide a greater overview of the overall geochemical interpretation. While testing the material, whether trees, leaves, buds, roots, or, as in our case, the fruits of beans, special methodology is used, and also a special preparation of samples for analytical provision is made. Immediately before the analysis we indentified the type and variety of plants that are analyzed. The average is ten samples of beans from several places in the Republic of Macedonia: the willages Karbinci, Tri Češmi, Argulica (Štip), Žiganci (Kočani), Ratavica (Probištip), the Osojnica river (Vinica), Trabotivište (Delčevo); Tetovo; Capari (Resen) and Kavadarci (Bohula village). (Table 1).

Table 1

Location of the beans samples collected in the R. Macedonia

Test	Variety	Location
1.	Tetovec	Karbinci (Štip)
2.	Black-white	Ratavica (Probištip)
3.	Plitkar	Tri Češmi (Štip)
4.	Bounty	Osojnica (Vinica)
5.	Plitkar	Žiganci (Kočani)
6.	Tetovec	Tetovo
7.	Plitkar	Argulica (Štip)
8.	Plitkar	Trabotivište (Delčevo)
9.	Tetovec	Capari (Resen)
10.	Kavadarci	Bohula

Preparation of the samples

For obtaining more accurate results, the preparation of the samples was made with utmost precision and care. The samples for the analysis with ICP-AES method were prepared in three phases as follows:

- We dried the plant specimens in a special dryer.
- In porcelain dish and with grinding machine we pressed the samples in order to obtain a representative sample for laboratory analysis.
- We dissolved the samples in order to be able consequently to determine the elements of the ICP-AES instrument.

Drying the plant specimens

Fresh fruits of vegetables (beans) contain some moisture absorbed from the soil. Therefore, in order to eliminate moisture from the bean samples in the lab we dry them 48 hours in a special dryer at a temperature of 40 ^{o}C.

Milling and sowing

Once samples were dry, in the porcelain dishes and with a finely grinding machine we milled them until we got a dust form of samples. (The porcelain dishes are better for pressing the samples because thus the possible contaminations with the mills are avoided.) As a rule, samples need to be ground to sizes of particles of 150 μm and necessarily riddled through a sieve, size of openings smaller than 150 μm. In this way we received a laboratory sub-sample. For further analysis portions of the laboratory sub-sample are taken.

Dissolving

To determine the elements in the tested plant samples that are of interest for us, we dissolved them in a mixture of hydrogen peroxide and nitric acid. For this purpose of the analytical balance we needed to measure 5.0000 g of the lab sub-sample in a cup. Then, we wet the sample gradually with 5 ml HNO_3, and then slowly stir not to press another 5 ml H_2O_2. We covered the glass with watch glass and left it at room temperature until the reaction ceased to be turbulent, then heat edit until moisture salted. This procedure was repeated twice. After the third addition we added another 5 ml HNO_3 and finally by filtration through the filter paper with a white ribbon resulting solution is gathered in a measure flask of 100 ml. This resulting solution is used for the provision of physical elements that were of interest to us.

ICP-AAS methodology provision

These are the elements that can be analyzed and identified with the ICP-AES (Si, Al, Fe. Ca, Mg, Na, K, Ti, Mn), and most of the most common trace elements such as Be, Co, Cu, Mn, Ni, Pb, V, Zn. But certainly there are limited storage in terms of elements that can not be determined with satisfying certainty such a halogen elements, and inert gases, O, N, and C. Instruments of the emission analysis of elements with plasma atom often work at wavelengths of 180–900 nm, because with them non-metals such as S, P, N, C cannot be identified (their most intensive atomic lines lying on the lower wavelengths 180 nm). It is also hard to measure some trace elements that occur in very low concentrations (less than 1 μg/g) in geological samples. ICP-AES technique is not suitable for the provision of heavy alkal metals (Rb and Cs) content in traces, and the analysis of U, Th, W, Ta is usually below the level of detection for ICP-AES. For good analytical capabilities of ICP-AES, an explanation can be found only in the physical properties (temperature, chemical inertness and low emission electromagnetic radiation) of inductive ion plasma obtained by the tangentially introduced argon, which results in the widespread use of the same atomic spectrometry and the specific design of commercial instruments for ICP-AES.

INTERPRETATION OF THE OBTAINED RESULTS

Macro-elements and trace elements in samples of beans were determined using ICP-AES after the acid digestion. Analytical results for total concentration of 19 elements in samples of beans are given in Table 2, where concentrations of each item are determined by the dry weight of the base.

Table 2

Contents in mg/kg of tested elements in beans

	1	2	3	4	5	6	7	8	9	10
As	<3,31	<3,31	<3,31	<3,31	<3,31	<3,31	<3,31	<3,31	<3,31	<3,31
Ag	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18
Al	1,45	2,38	8,27	7,72	1,38	0,82	0,32	2,33	0,36	1,7
Sr	4,6	5,35	13,59	2,34	4,91	5,23	10,45	4,44	10,37	11,14
Ca	1600,99	1253	2636,85	1126,93	1399,83	2048,89	2367,84	2223,84	2918,85	2411,39
Ba	1,56	0,87	2,51	1,81	0,84	4,76	2,3	2,67	12,02	1,7
Ni	0,72	0,17	2,49	2,92	0,38	0,8	9,16	1,17	4,73	1,83
Mn	15	12,25	18,51	14,96	14,47	19,51	19,44	17,58	33,77	17,48
Fe	62,08	77,7	61,81	96,62	40,91	62,86	44,15	74,05	153,75	69,07
Cr	0,3	0,18	0,34	0,31	0,02	0,11	0,73	0,31	0,28	0,3
Mg	1472,39	1507,7	1557,7	1845,49	1172,51	1749,5	1789,73	1631,94	1856,07	1686,89
Na	27,07	25,39	32,5	25,44	19,92	54,82	50,81	22,26	29,25	68,18
P	4227,04	5730,37	3228,94	5522,39	3702,63	5537,56	4155,8	4470,96	5469,37	5029,23
Zn	44,66	39,98	38,52	39,69	35,51	41,44	69,97	33,95	54,66	51,79
Cu	12,55	12,46	10,91	8,76	4,93	7,59	11,91	9,98	9,79	12,22
Pb	<0,51	<0,51	<0,51	<0,51	0,69	<0,51	<0,51	<0,51	<0,51	<0,51
Cd	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18	<0,18
Co	<0,11	0,19	0,2	0,26	<0,11	<0,11	0,73	0,15	0,21	<0,11
K	24229,2	28441,6	25160,4	29699,7	18060,2	29043,7	25666,5	25972,5	30286,8	29861,7

Allowable levels of representation of nutritional minerals in traces in the seeds of beans are given in Table 3; these values can be used for proper comparison with results obtained for these 10 samples of beans and evaluation of their quality.

Table 3

Allowed nutritive concentration domains in elements of the beans
(J. B. Jones, Jr., B. Wolf, and H. A. Mils, 1991)

Elements	Contents
P (%)	0.25–0.75
K (%)	2.2–4.0
Ca (%)	1.5–3.0
Mg (%)	0.25–0.70
Fe (ppm)	50–300
Cu (ppm)	7–30
Zn (ppm)	20–60
Mn (ppm)	50–300

The concentration of various essential minerals in beans, in this research can be outlined as follows: K > P > Ca > Mg > Fe > Zn > Mn > Cu.

This is similar to the one determined by J. B. Jones, Jr., et al. (1991), only with the difference in the arrangement of Ca-P, Mn-Zn where Ca > P, Mn > Zn applies. It is known that the concentration of metals in the seeds of beans can be changed in accordance with the geographical origin of the beans and the factors associated with the treatment and the relationship of man to plants. In this study, seeds of beans are of similar cultivars, samples were taken in a relatively short period from different regions. Therefore, the statistical characteristics of important mineral content between different samples of beans may be prescribed to different geographic origins. Compared to the average mineral composition of seeds of beans, presented in Table 3, the beans from Macedonia have similar contents of K, P, Fe, Cu and Zn, a significantly reduced content of Mg, Ca, and a slightly reduced content of Mn (Morghan et al., 2002). Heavy and toxic metals such as Cr, Ni, Sr, Co are often associated with high pollution, because the variations of their levels in the seeds of beans from various regions are due to the location of the bean fields and their proximity or distance from roads. We can conclude that the level of heavy and toxic metals in the seeds of the bean varies. Macedonia has excellent conditions for the production of quality fresh food (vegetables and fruit) which has sufficient quality in view of nutritional elements and has a satisfactory low level of toxic elements at any time. Fresh food should be stored in warehouses in cold, dark places until its consumption. Due to the monitoring of the quality of fresh food and monitoring of the presence of mineral nutrients and harmful, hazardous and toxic heavy metals that are contained in it, in many countries around the world analyze these components during the 1, 3, 6, 9 and 12 month in one production year.

Genetic variability in the content of the macro-elements and trace elements

The first important issue because of which beans can be enriched with the content of the macro-elements and trace elements (Ca, Fe, Zn, etc.) is to determine the degree of association between genetic variability in the type and content of these same macro-elements and trace elements (Anderson et al., 1973). For this purpose, the content of the macro-elements and trace elements in the samples of beans is identified through ICP-AES technique. The representative samples show some variability in the contents of some macro-elements and trace elements in the different genotypes. The analysis of 10 samples of beans, where eight samples are of white grains, showed that the concentration of Zn ranged from 33.95–69.97 ppm with an average value of 46.3125 ppm, while the remaining samples of motley (pegav) bean the concentration of Zn was in the range from 39.69–39.93 ppm with an average of 39.81 ppm. A clear connection of the content of macro-elements and trace elements and the geographical origin was not been established, although plants that originate from several regions of the Republic of Macedonia (Kočani – vill. Žiganci, and vill. Argulica – Štip) show low concentrations of Fe content in comparison with the ones taken from some other regions. Also the analysis of samples of white beans, the concentration of Ca is in the range of 1339.83–2918.85 ppm with an average of 2201.06 ppm, unlike the samples of multicolored beans where the concentration of Ca ranges from 1126.93–1253 ppm with an average of 1189.965 ppm. Therefore we conclude that as in most developing countries thus also in the R. Macedonia there is a reduced content of Ca in the seed of beans, particularly in the genotypes of the darker color of grains. The important issue for increasing the content of macro-elements and trace elements and the extent of achieved this depends on how stable components are under certain conditions and processes in the environment (Beebe et al., 1999). In some cases the content of macro-elements and trace elements in the seeds of beans can be changed as a result of the effect of different types of soils and geochemical characteristics of the soil. In some experimental trials it was found that the lack of important macro-elements and trace elements in samples of beans is the result of the continuing process of impoverishment of the soil with the same components and the relationship of man to the overall environment. In these calculations, we noticed that a positive coefficient of correlation exists between several important macro-elements and trace elements. Between Fe and Zn the obtained coefficient of correlation is 0.09 between different genotypes, although in many other surveys of beans in the area of the Andes and North America the correlation coefficient is greater than 0,5 (Research on Trace Minerals in Common Bean). The values of the correlation coefficients of macro-elements in our samples of beans are presented in Table 4.

Table 4

Factor of correlation between the elements in the seeds of beans

	Mn	Zn	Ca	Mg	K	P
Fe	0.73	0.09	0.30	0.56	0.63	0.58
Mn		0.44	0.77	0.54	0.38	0.18
Zn			0.46	0.51	0.27	0.06
Ca				0.42	0.26	–0.21
Mg					0.85	0.54
K						0.78

The correlation coefficient (r) between the individual elements: Mn-Fe (r = 0.73), K-Fe (r = 0.63), Ca-Mn (r = 0.77), K-Mg (r = 0.85), PK (r = 0.78) is largely presented with high walues. The implication of these correlations are certain genetic factors, macro-elements and various trace elements and they are undivided, with increasing content of an element (e.g.: Fe) would result in an increase of content of another element (e.g.: Mn). These high values of correlation coefficient suggest that the physical and chemical factors of the element associations observed in bean seed may be essential for the distribution of elements in soil and plant (the root, stem, leaf and fruit). Some low values of the coefficient of correlation are determined only between: Zn-Fe (r = 0.09), P-Mn (r = 0.18), P-Zn (r = 0.06).

Evaluation of the enrichment factor for the analyzed elements in the beans samples

Generally, the plants most inorganic elements are derived from the soil and the elements are absorbed, transferred and accumulated in plants (root, stem, leaf, flower and fruit). Therefore, the concentration of elements in the seeds of beans affects the absorbtion and accumulative process. The comparison between the enrichment of elements in samples and soil is the basis for the introduction of the enrichment factor (*EF* – Enrichment factor) defined with the units frequently used index for geochemical analyses:

$$EF = \frac{[M]_{\text{specimen}} / [Al]_{\text{specimen}}}{[M]_{\text{soil}} / [Al]_{\text{soil}}}$$

where [*M*] sample and [*Al*] are the concentrations of sample analytical element and aluminium in the sample and [*M*] soil and [*Al*] soil concentrations of the analytical element and aluminium in the soil. The calculations of the enrichmentt factor (*EF*), and the concentrations of the analyzed elements are given in Table 2 and used the mean of the elements in ordinary soil (or earth's crust), where the concentration of Al in the sample and the soil (or bark) are used in normal analytical concentrations in them, because Al is one of many inactive elements of the geochemistry. According to the definition of *EF*, one can conclude that elements with *EF* > 1 are more accumulated in seeds of beans compared to the elements included in average soil (Fig. 1, a, b, c). These results suggest that important elements are absorbed from the soil and significantly accumulated in seeds of beans. On the other hand, the values of *EF* for Fe, Na and Cr are determined as the lowest compared with the values of *EF* for all other elements they suggest that Fe, Na and Cr are accumulated in beans. It should also be the case for the unimportant elements that are present here, such as Sr, Ba, Ni, and Cr, but the obtained values for EF are larger than one in every ten samples, which indicates active transmission of these elements in beans. This may depend primarily on the specific nature of the bean, although this feature cannot be explained here. Ten different samples of beans that are grown in different soils in different areas are analyzed in the presented analyses because it is difficult to discuss some basic characteristics of these elements to their primarily absorbing, accumulative and biological function. However, the enrichment factor can be used as one of the factors for determining the values of the kinetic behaviors of elements of interest to us, between plants and soil. Because of all this, the presented methods and the growing development in identical and different soils depend on the multi elementary basis.

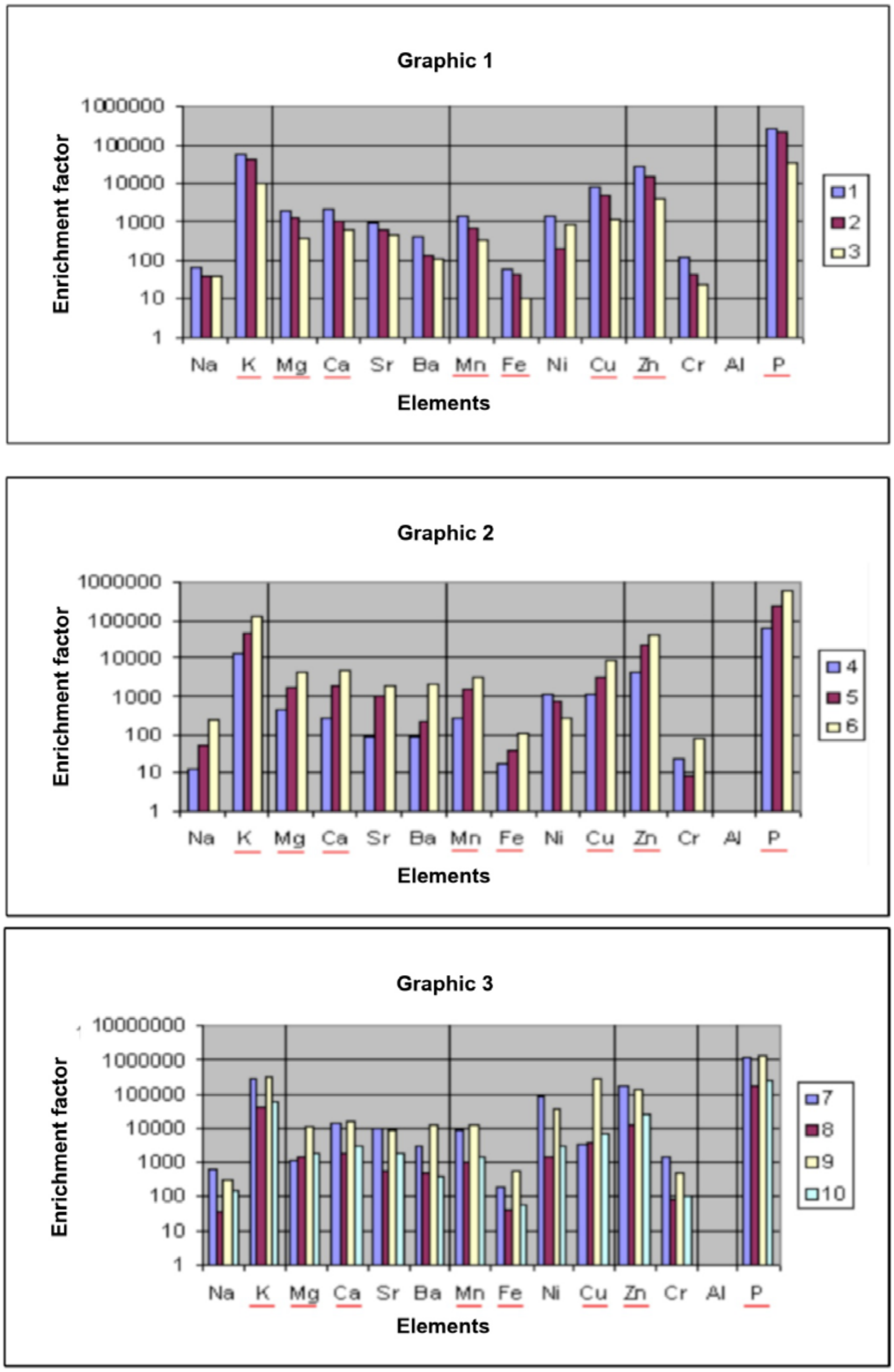

Fig. 1 (a,b,c). Graphic picture of the enrichment factor

CONCLUSION

Ten different samples of beans were analyzed by analytical method for multi element determination of the macro-elements and trace elements and also the results are precise and accurate in the digesting and analytical procedures for plant samples. The analytical results for the 19 items specified in the survey are presented in accordance with the values presented in previous research in this field worldwide. Because of all that, the presented analytical method is suitable for the provision of representation of the macro-elements and trace elements in samples of beans using ICP-AES. The content of important minerals (K, P, Mg, Ca, Na, Fe, Mn, Zn, Cu) in the beans in Macedonia is satisfactory in comparison with results from other countries, excluding the contents of Ca. The level of heavy and toxic metals (Co, Cr, Ni, Ba, Sr) in the seeds of beans in all the samples was satisfactory. The enrichment factor for the various analytical elements in the bean seed is determined in this study. It is concluded that all essential elements for plant growth, except Fe, were accumulated in sufficient copies of all beans. Therefore, the enrichment factor gives some important properties of the schedule for the kinetical behavior of elements in samples of beans absorbed by the soil.

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Р е з и м е

ГЕОХЕМИСКИ ИСТРАЖУВАЊА НА СЕМЕ ОД ГРАВ ОД ОДРЕДЕНИ РЕГИОНИ ВО РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: семе од грав; геохемиска анализа

Присуството на макро-елементите и елементите во траги во семетоод грав е одредено со ICP-AES (атомска емисиона спектрометрија со индуктивна плазма). Земени од пет разни видови семиња грав од неклку региони во Република Македонија. Добиените резултати се однесуваат на анализите на 19 елементи од групата на макро- и микро-елементи. Постои широк опсег на концентрации во примероците, од 30286,8 mg/kg за K во тестот 9 до 0,15 mg/kg за Co во тестот 8. Поголемо внимание е посветено на присуството на Ca, Fe и Zn во семето од грав, бидејќи гравот е значаен извор на овие макро-елементи и елементи во траги како важни нутриционистички состојки во исхраната на повеќе од 2 милијарди луѓе во светот. Затоа се земени предвид нивното биолошкото значење, како и трансферот и акумулацијата од почвите во растенијата.

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EARTHY–CRYPTOCRYSTALLINE VIVIANITE FROM THE TREPEL DEPOSITS NEAR THE SUVODOL VILLAGE, BITOLA, MACEDONIA

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A b s t r a c t: Within the frame of the trepel deposits (Fig. 1) near Suvodol village, Bitola city it was discovered (Lj. Petreski) an earthy-cryptocrystalline vivianite occurrence. The examined vivianite sample was confirmed by X-ray powder diffraction, chemical, SEM, DTA/TG, infra-red analyses. The treated vivianite sample actually represents a typical earthy-cryptocrystalline variety (Fig. 2) with a peculiar progressive oxidation state of Fe_2^+ to Fe_3^+ (FeO/Fe_2O_3 contents nearly 1:1). X-ray powder diffraction, DTA/TG-data are in quite good concordance with literature data.

Key words: earthy; cryptocrystalline vivianite

INTRODUCTION

According to the earlier examinations (Jelena D. Marković-Marjanović, 1956) vivianite (coarsely grained sample) was discovered in the area of the city brickkiln, Bitola. This vivianite occurrence was determined and elaborated only by means of the macroscopic characteristics of the treated mineral and description of it's geological environment. The new-discovered earthy-cryptocrystalline vivianite occurrence deserves a more complex elaboration by X-ray powder, SEM, chemical, DTA/TG, infra-red data.

EXPERIMENTS

Geological setting

The terrains around Bitola city, Suvodol village and the wider area belong to the Pelagonian depression composed of alluvial-delluvial as well as sediments of miocene-pliocene age which are superposed over the gneisses, micaschists (upper Precambrian age) of the Selečka mountain.

At the Suvodol village and the wider area there is an opened vertical cross section (starting from the surface to 150 m in depth) – daily excavation miner works according to the very intensive coal deposits exploitation. The mentioned vertical cross section actually represents a profile-line performed through a peculiar biogenetic-sedimentary formation composed as follows:

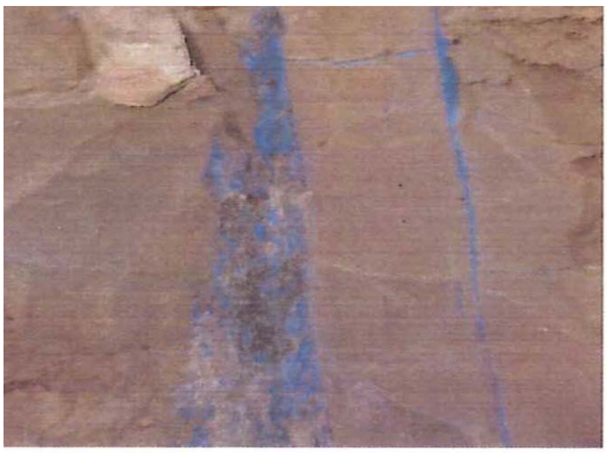


Fig. 1 Dark bluish earthy-cryptocrystalline vivianite enclosed in the surrounding trepel mass

The deepest part of the vertical cross section is composed of an alternating complex of coal layers (cca 1.0–39.0 m in thickness), sands, gravel etc.

The upper coal layer is about 1.5 m to 61.4 m in thickness.

The further layers of cca 10 m to cca 80 m in thickness belong to a typical biogenetic formation consisted of trepel sedimentary rocks.

The uppermost layers of cca 0.5–1.0 m in thickness belong to the redish-yelowish sands, gravels of alluvial-deluvial age.

In the frame of certain open fissures in the biogenetic trepel formation at Vranjevski part – microlocality 7 (Fig. 1) were discovered (Lj. Petreski) bluish earthy-cryptocrystalline masses of viviante representing a subject of our examination the results of which are given in this paper.

MINERALOGY

The examined vivianite actually represents very soft, earthy-cryptocrystalline sample with dark blue even marine bluish color (Fig. 1).

SEM–pictures (Fig. 2AB) show that vivianite crystals have plate-like forms (0.10) to cca 0.02 – 0.03 mm long and very intimately associated-enclosed in the typical micromass of the surrounding trepels sediments composed of micro fossils (alga Diatomeae).

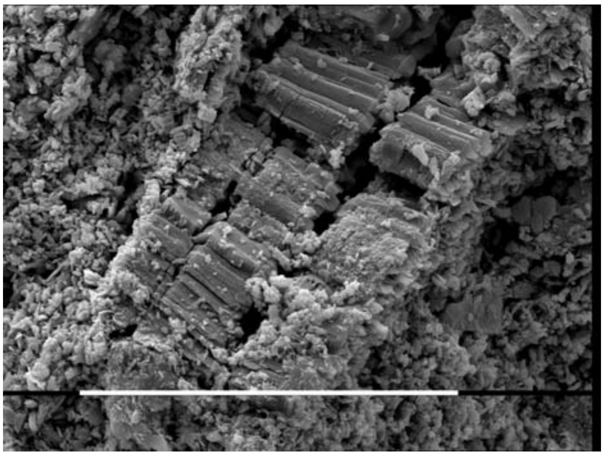


Fig. 2A. Superfine grained (0.02–0.03 mm) plate-like forms (010 of vivanite) in the surrounding trepel mass

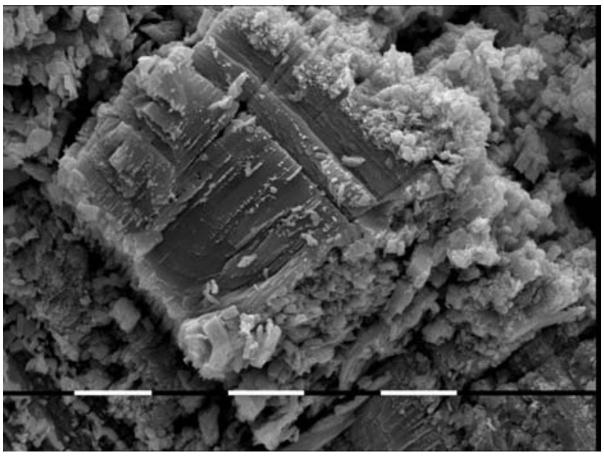


Fig. 2B. Superfine grained (cca 0.05 mm) plate-like forms (010 of vivanite) in the surrounding trepel mass

Recent X-ray powder diffraction examinations (CuKα/Ni; 36 kV; 18 mA) show that X-ray powder data of the treated vivianite sample are in quite good correlation (Tab. 1 and Fig. 3) with the compared earthy-cryptocrystalline vivianite samples from literature data.

Table 1

X-ray powder data of the treated earthy-cryptocrystalline vivianite sample compared with other cryptocrystalline vivianites from different microlocalities in the world (d – Å; I – intensities)

1	**2**	**3**	**4**	**5**	**I**
110	7,92	7,84	7,89	7,93	37
020	6,73	6,72	6,71	6,71	100
200	4,93	4,91	4,90	4,906	40
101	4,562	4,55	4,60	4,535	7
011	4,342	4,34	4,40	4,353	2
130	4,073	4,08	4,10	4,073	10
101	3,860	3,85	3,88	3,857	14
	–	–	–	3,636	5
	3,211	–	–	3,202	26
301	2,978	2,98	2,99	2,978	40
211	–	–	2,90	–	
240	–	–	2,83	–	
	2,773	–	–	2,768	4
231	2,728	2,72	2,73	2,718	19
141	2,716	–	2,68	2,700	17
330	2,634	2,64	–	2,639	10
141	2,586	2,54	2,54	2,592	2
	–	–	–	2,524	11
400	2,433	2,44	2,44	2,431	13
051	2,313	2,33	2,36	–	
002	–	2,30	2,33	–	
341	–	2,25	2,25	–	
251	2,194	2,20	2,20	–	
431;112	2,149	–	2,15	–	

1 – hkl values for vivianite (ASTM card – 30 – 0662).
2 – d-values for earthy-cryptocrystalline vivianite from Suvodol village.
3 – Earthy-cryptocrystalline vivianite, Wafotu, New Zealand. AU: 2473.
4 – Cryptocrystalline vivianite, Leadville, Colorado, USA, BM (NH): 1907, 115.
5 – Earthy (cryptocrystalline) vivianite, Humna, New Zealand. AU: 2408.
I – Intensities for vivianite sample – column 5.

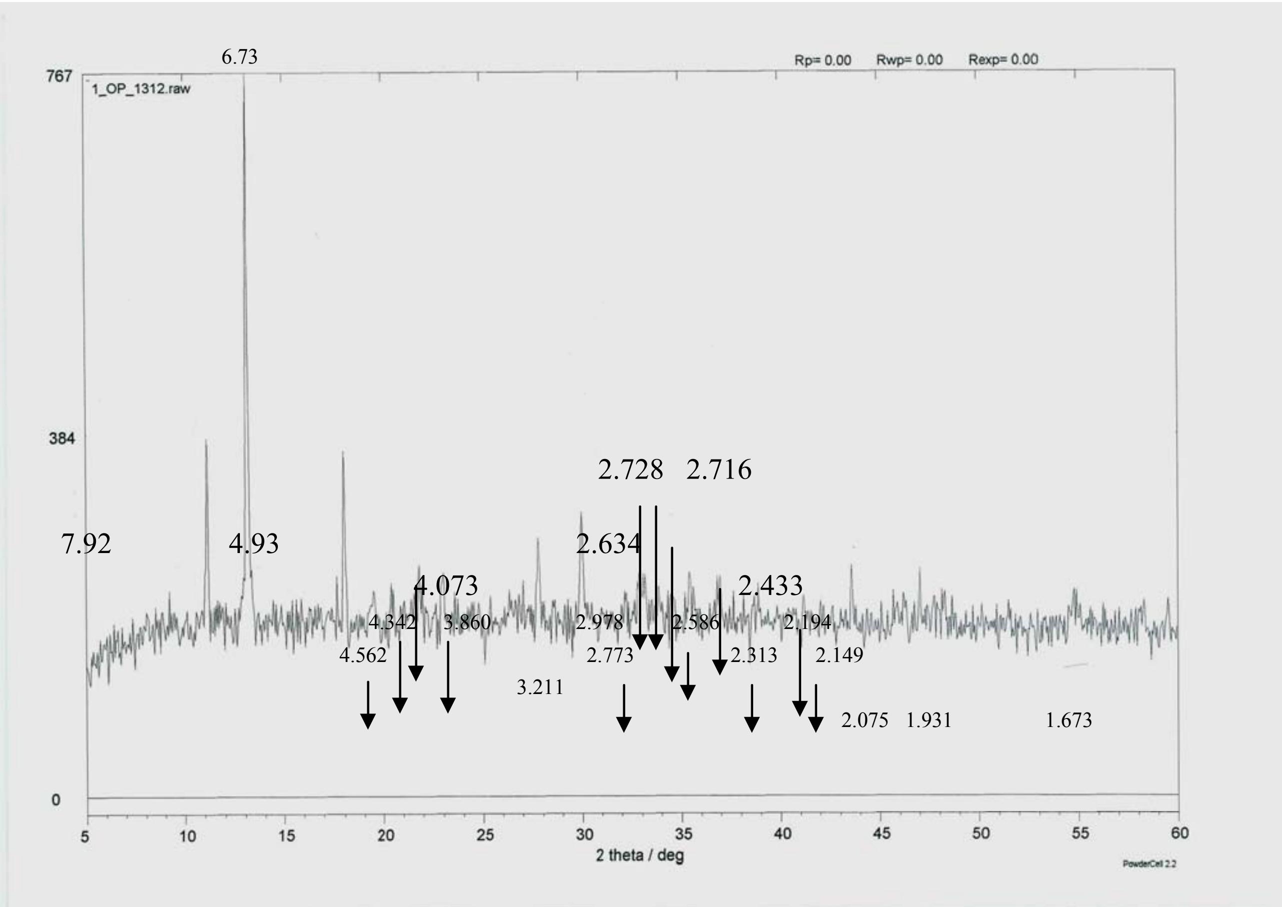


Fig. 3. X-ray powder diagram for vivianite from Suvodol village

DTA/TG-curve (Fig. 4) of the examined earthy-cryptocrystalline vivianite is very similar nearly identical with the same curves from literature date. The very big endo-peak at 160 °C is corresponding to the biggest water losses of cca 18% (visibly form the contributed TG-curve) while the other loss of weight of cca 6,3% is connected with OH^- groups.

The others thermal effects – egzo-peaks at 600 °C and 710 °C are probably connected with the oxidation changes of Fe^{2+} to Fe^{3+}.

The total weight loss of the examined vivianite amounts 24,3%.

The chemical analysis performed on a relatively pure monomineral (?) fraction by the classical wet chemical procedure shows results as follows:

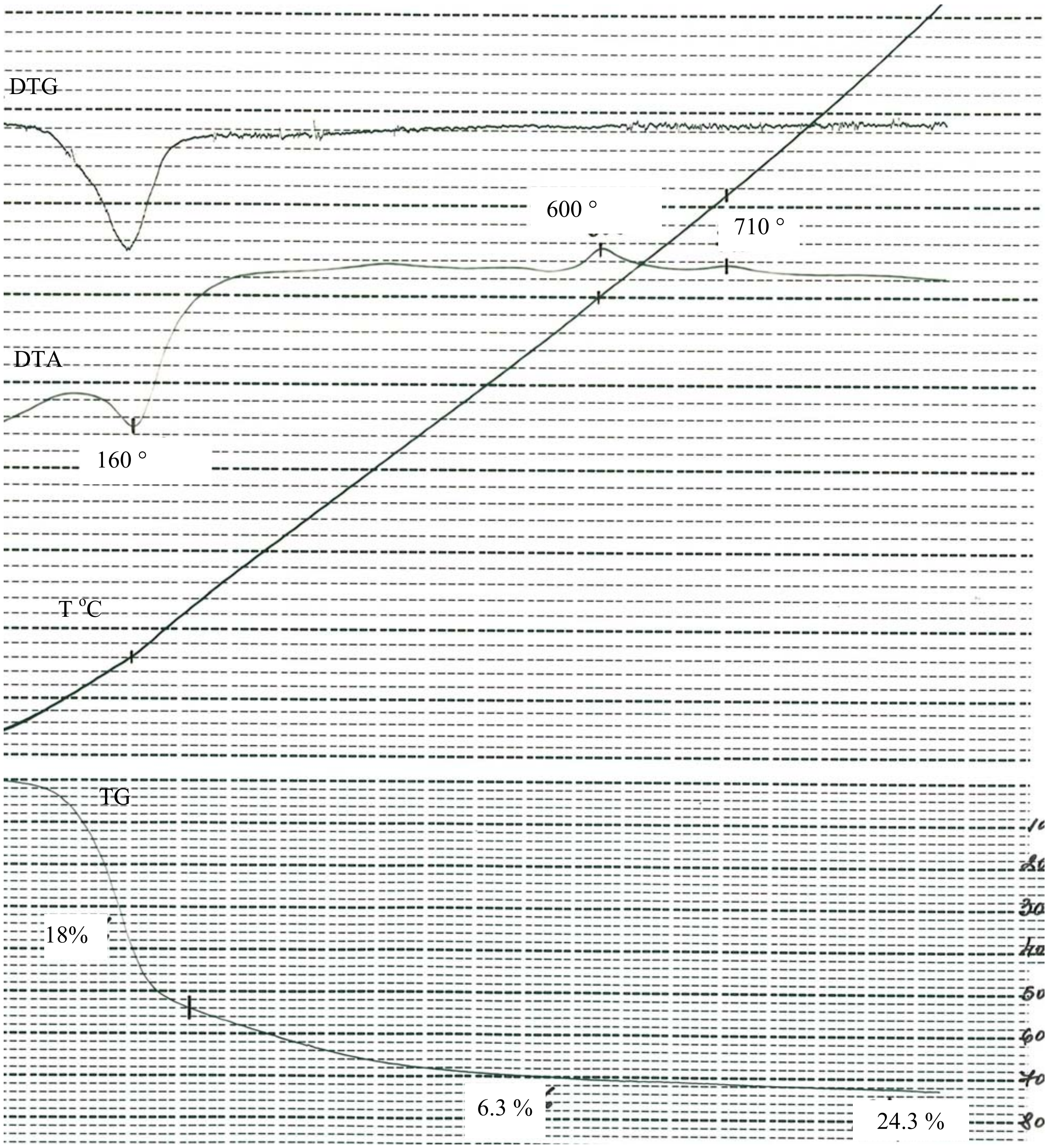
Table 2

Chemical analysis of vivianite (%)

FeO	23,17
Fe_2O_3	22,91
P_2O_5	29,22
CaO	0,37
MgO	0,12
Loss of igm.	24,10
Total	99,89

According to a classical geochemical procedure was calculated the formula of the examined vivianite sample as follows:

$$(Fe^{2+}_{1,6}\ Fe^{3+}_{1,4})_{3,0}\ (PO_4)_2\ (OH)_{1,4}\ 5H_2O$$



CONCLUSION

According to the geological prospecting activities, inside the area of the trepel sedimentary rock of biogenetic origin (of Pliocene age) at the Suvodol village, Bitola city, Macedonia, there was discovered earthy-cryptocrystalline vivianite with dark bluish color.

The mineral was examined by means of the complex mineralogical methods – X-ray powder diffraction, SEM, chemical, DTA/TG, infra-red analyses.

The examined earthy-cryptocrystalline vivianite sample – $(Fe^{2+}_{1,6}Fe^{3+}_{1,4})_{3,0}(PO_4)_2(OH)_{1,4}5H_2O$, reveals a structure type in which there is a progressive oxidation relation between Fe^{2+} to Fe^{3+} with consequently FeO/Fe_2O_3 contents nearly 1:1.

Infra-red analysis confirms that in the examined vivianite sample there are HOH molecules.

According to earlier examinations (by R. L Frost, W. Martens, P. A. Williams and J. T. Kloprogge) for vivianite was reported that the hydroxyl stretching vibrations are identified at 3460, 3281, 3104, 3012 cm^{-1}, while HOH bending was reported around 1660 cm^{-1}. Our IR-examinations are compatible with the mentioned literature data.

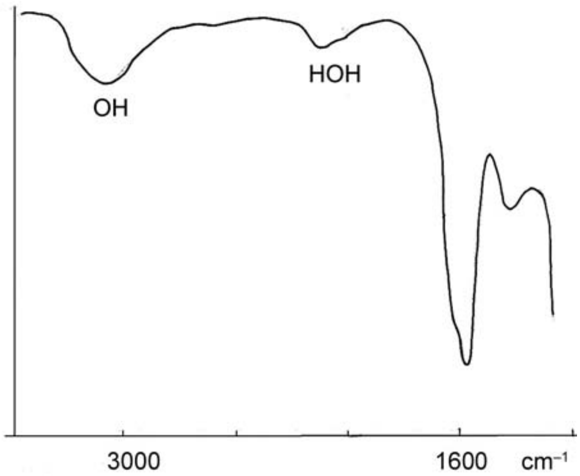


Fig. 5. Infra-red curve of vivianite

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Р е з и м е

ЗЕМЈАНО-КРИПТОКРИСТАЛЕН ВИВИЈАНИТ ОД НАОЃАЛИШТАТА НА ТРЕПЕЛ БЛИЗУ СЕЛОТО СУВОДОЛ, БИТОЛА, МАКЕДОНИЈА

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Клучни зборови: земјано-криптокристален вивијанит

Во трепелот од наоѓалиштето кај селото Суводол, Битола, беа откриени (Љ. Петрески) појави на земјано-криптокристален вивијанит (сл. 1). Испитуваниот вивијанит $(Fe^{2+}_{1,6}\ Fe^{3+}_{1,4})_{3,0}\ (PO_4)_2\ (OH)_{1,4}\ 5H_2O$ беше детерминиран со комплексни физичко-хемиски анализи (рендгенско-прашкаста, хемиска, SEM, DTA/TG, инфра-црвена). Овој земјано-криптокристален вивијанит се карактеризира со напреднат степен на оксидација на Fe^{2+} во Fe^{3+}, при што квантитативниот однос помеѓу FeO/Fe_2O_3 е приближно 1:1. Податоците од рендгенско-прашкастите (d-Å-вредности и DTA/TG анализи на испитуваниот вивијанит се многу добро компатибилни со податоците добиени за разни земјано-криптокристални вивијанити од други микролокалитети во светот.

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Original scientific paper

TREPEL – A PECULIAR SEDIMENTARY ROCK OF BIOGENETIC ORIGIN FROM THE SUVODOL VILLAGE, BITOLA, R. MACEDONIA

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A b s t r a c t: In the paper are shown results of the mineralogical-petrographical examinations of the trepel as a peculiar sedimentary rock of biogenetic origin from the Suvodol village near Bitola city, Republic of Macedonia. According to the microscopic (in polarizing translucent light), SEM, chemical, X-ray powder data was determined that examined trepel is composed mainly of opal (of biogenetic origin) as well as quartz, feldspars (plagioclases, K-feldspars), illite – hydromicas, chlorites of minor importance. Further examinations are in progress because the aforementioned results are based on one randomly selected trepel sample.

Key words: trepel; opal; biogenetic origin; alga Diatomeae

INTRODUCTION

The recent excavations of the coal deposits from the area of the Suvodol village, Bitola are forced to mining works of a thick hanginwall trepel layer, the thickness of which is even cca 50–70 m. So, the excavated trepel mass as a barren soil quantity reaches a huge ratio. In spite of the common trepel use in the world for the light brick, cement production etc., the excavated trepel mass from the mentioned microlocality actually still represents a potentially non-metallic raw material interesting for the further examinations.

According to the mentioned motive for trepel use in the non-metallic inorganic industry, induce an action for further mineralogical-petrographical examinations as primary and crucial task of major importance.

EXPERIMENTS

Geological setting

Treated trepel deposits were discovered in the Pelagonian depression, Macedonia, at the Suvodol, Brod-Gneotino villages and wider region, cca 15 km eastward from Bitola city (Fig. 1).

Fig. 1 Geographical situation of the Suvodol village and the wider region of Bitola city

According to the geological map (Fig. 2) for the Selečka mountain (characterized by very complex composition of gneisses, micaschists etc. of Precambrian age) can be seen that the geological-petrographical composition of the Suvodol village area is rather simplified as follows:

1. Within the frame of the Pelagonian depression at the Mojno, Suvodol, Vranjevci villages were discovered lakes sediments (of Upper Pliocene age) composed of sands, clay, marly clay, conglomerates (R. Stojanov, 1958).

2. According to the recent excavation mine works for coal exploitation at the Suvodol village a peculiar geological profile was opened as follows:

– the uppermost part is presented by agricultural soils etc. (of alluvial-deluvial age) the thickness of which is cca 0,5 – 1,0 m;

– the lower part belongs to a biogenetic formation composed of trepel sediments (the thickness of which is cca 50 – 70 m) and coal deposits at the bottom of the abovementioned open profile.

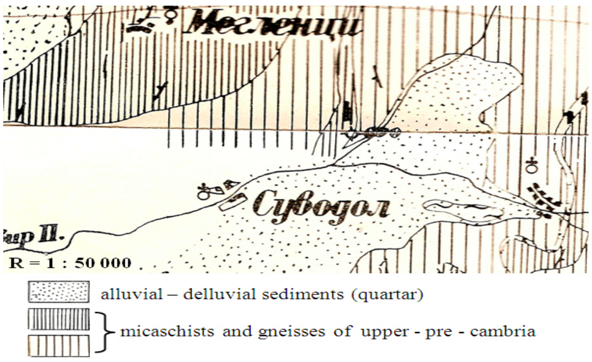

Fig. 2. Geological map of the Suvodol village area (R. Stojanov, 1958)

Macroscopic description

Examined trepel sample from the Suvodol village actually represents a sedimentary rock (of biogenetic origin) with grayish to grayish-white color, very light and soft (1–2 by Mohs), fine to superfine grained structure, porous, shell-like break, tongue sticky etc. (Fig. 3).

Fig. 3. Macroscopic figure of common trepel piece

The examination of the physical properties of the treated trepel sample gives data as follows:

– volume mass 0.60 – 0.70 g/cm^3
– water absorption 85 – 95 %
– open porosity 50 – 60 %
– total porosity 68 – 75 %
– density 2.41 g/cm^3.

Microscopic examinations

A) The microscopic examinations with the polarizing translucent light show that treated trepel sample is characterized with a micro-crypto-crystalline ground mass of optic isotropic nature. This groundmass is composed of opal inside of which there are very fine to superfinegrained quartz, feldspars, chlorites, illite-hydromica inclusions (Fig. 4).

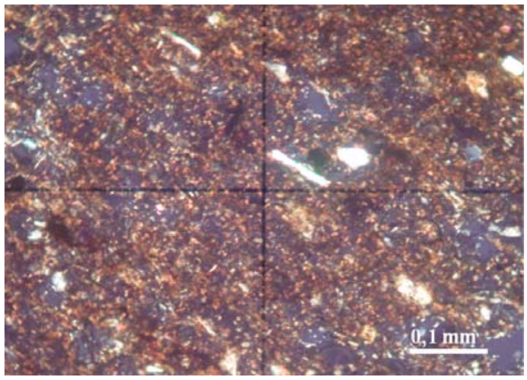

Fig. 4. Superfinegrained quartz, feldspars, illite, chlorite, (like spots and fibres) enclosed in the finegrained opal structure of biogenetic origin (N$^+$)

In the thin section there are rather completed or fragmented globular structures of opal (of vegetative origin) of major importance. The diameter of the mentioned opal globules amounts cca 0.05 – 0.1 mm (Fig. 5).

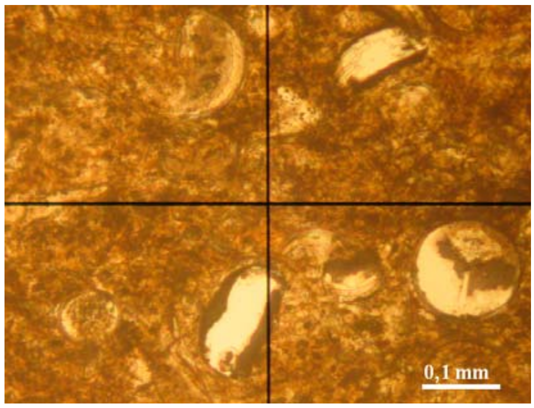

Fig. 5. Isotropic globular structure of trepel composed mainly of opal globules (N+)

In the opal groundmass fibres – pipes of opal vegetative products of alga Diatomeae long 0.1 – 0.3 mm can be rarely encountered (Fig. 6).

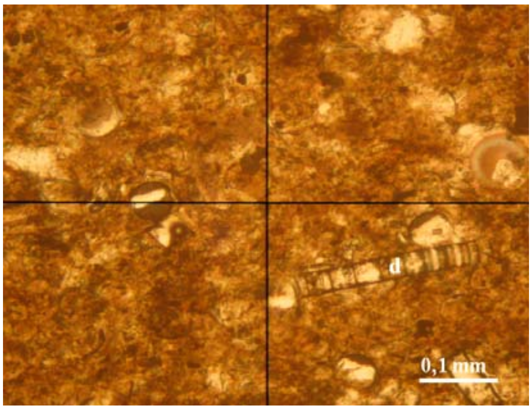

Fig. 6. A rare relics of alga Diatomeae (d) enclosed in trepel globular structure (N^+)

Very rarely biogenetic products of opal with forms of transversely cuttered cones can be seen in the section. These forms are not yet definitively determined (Fig. 7).

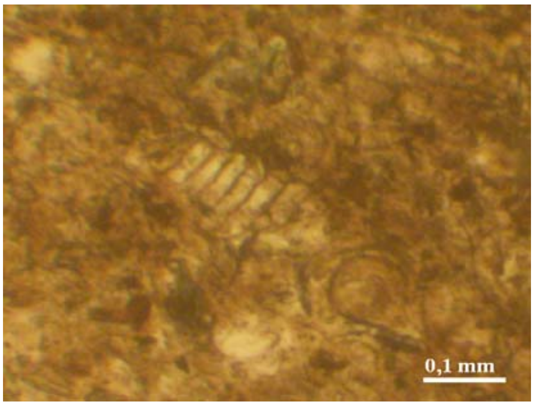

Fig. 7. Non yet determined microfossil of zoogenethic origin in the trepel mass (N^+)

Opal products with irregular fibrous forms remembering of roots of vegetative origin can be also rarely encountered in the thin section (Fig. 8).

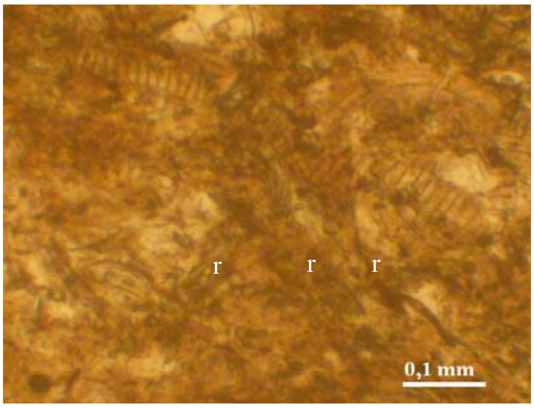

Fig. 8. Microfossils of vegetative origin resembling like roots (r) of microplants (N^+)

The globular structures (of vegetative origin) of opal are quantitatively predominant in the examined trepel sample. The rock structure is globular – isotropic, the texture is massive – homogenous.

B) The examinations by the SEM-method confirm the microscopic polarizing data especially from point of view that the globular structures have biogenetic nature. So, completed and fragmented globules of alga Diatomeae are shown on the SEM-pictures which disks resembling to disks of sunflower with or without peripheral ends.

It's evidently, that the globules of vegetative origin belong to two or more different types. These "sunflower" disks are completely perforated with discrete caverns, hollows along the total disk surface.

It's evident also that the trepel porosity is connected with the aforementioned caverns inside the surface of the globular structures. (Fig. 9, 10).

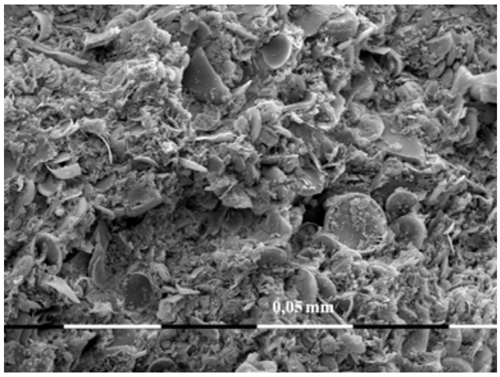

Fig. 9. SEM-photo of a common trepel mass composed of numerous microrelics – opal globules of biogenetic origin

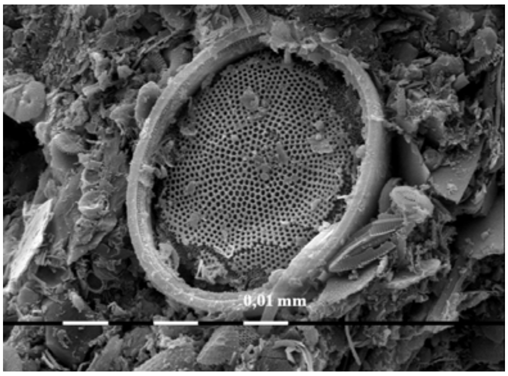

Fig. 10. Arachnoidiscus orantus – microfossil with a typical globular form

X-ray powder examinations

According to the X-ray powder examinations (DRON, 36 kV, 18 mA, CuKα/Ni) in the treated trepel sample were determined: opal, quartz, illite-hydromica structure type, feldspars (plagioclase, K-feldspars), chlorites (Fig. 11).

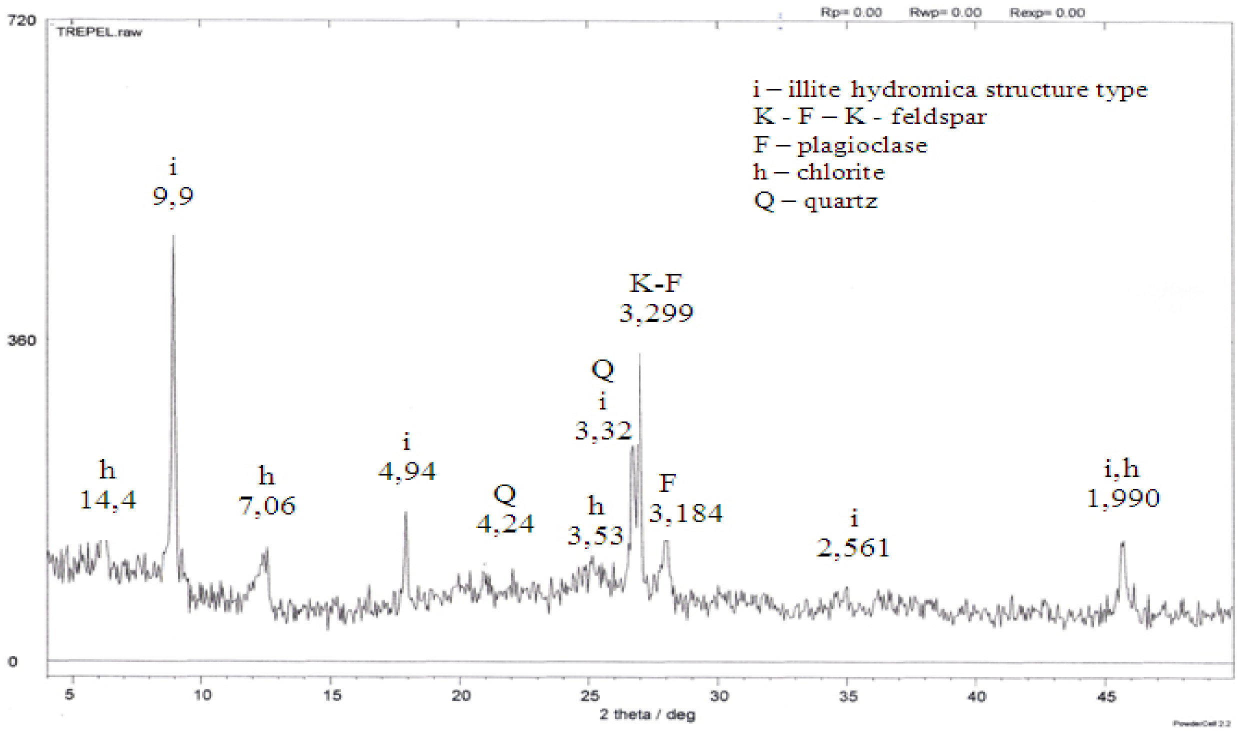

Fig. 11. X-ray diagram of examined trepelChemical examinations

A) A classical chemical - silicate procedure by the wett method was performed for the chemical examination of the treated trepel sample. Were determined results as follows:

Table 1

Chemical analysis, mass [%]

SiO_2	60.5
Al_2O_3	12.75
Fe_2O_3	6.57
CaO	2.60
MgO	2.16
K_2O	1.60
Na_2O	0.93
SO_3	0.95
loss of ign.	12.19
Total	99.80

Table. 2

ICPOES analysis of the microelements [ppm]

Ag	< 1	Mn	816
As	8	Mo	1
Ba	81	Ni	39
Bi	10	Pb	19
Cd	< 1	Sb	10
Co	17	Sn	10
Cr	37	Ti	54
Cu	51	Zn	81
Fe	39 371	Hg	< 1

– SiO_2, Al_2O_3, loss of weigh contents evidently indicate for the determined mineral phases - opal, illite, quartz, feldpars, chlorite in treated trepel sample.

– The total (Na_2O + K_2O) alkali oxide content of 2.53 % shows a feldspar containing about 16%.

– Indicated Fe_2O_3 (6.57%), MgO (2.16%) contents are compatible with the determined (Mg, Fe)-chlorites in this trepel sample.

– Rather low CaO content of 2,60% shows that determined plagioclase belong to an albite-oligoclase type.

B) In the treated trepel sample the contents of the microelements (by ICPOES method) were determined (after sample dissolution by mixture of different acids), as follows:

Determined microelements in very low contents represent probably another proof that treated trepels from Bitola city and wider region are not connected with the volcanic processes and emanations from the Kožuf area mountin.

On the contrary, the very low contents of the aforementioned microelements are another evidence for the biogenetic origin of the examined trepel.

DTA/TG results

DTA/TG results of the examined trepel sample are evidently compatible with the X-ray powder data. From DTA-curve obviously can be seen a very broad endo-peak starting of cca 80°C to 300°C with a minimum at 150°C corresponding for opal and minerals of illite-hydromica structure type. The other thermal effects are of minor importance.

TG-curve show a total loss weight of cca 17%, what's is compatible with the mineralogical composition – presence of crystalohydrate minerals (opal, illite) in contents of cca 50 – 70%.

Genesis

A semi-quantitative evaluation of the examined trepel sample from the Bitola area show that it's composed approximatively as follows:

– opal cca 30 – 40 %
– K feldspars + plagioclases cca 10 – 16 %
– illite 20 – 30 %
– quartz cca 15 %
– (Mg, Fe)-chlorites cca 15 %.

The quantitatively predomination of opal (of biogenetic sources – approved by SEM-method) over the aforementioned silicate minerals indicates that treated trepel has a typical biogenetic and common treatment compatible with the literature data. There are certain hypothetic indications that in the treated trepels there is probably opal of chemogenetic origin.

CONCLUSION

– The trepels from the Suvodol village, Bitola city, actually represent typical sedimentary rocks of biogenetic origin, due to the numerous vegetative evidences in forms of very discrete globules – microfossils Arachnoidiscus orantus, alga Diatomeae etc. The opal forms of zoogenetic origin are not excluded in the examined trepel.

– The aforementioned genesis of the examined trepel is completely compatible with the common genetically treatment of these sedimentary rocks from different microlocalities in the world.

– Examined trepel from the Suvodol village is actually an evidence for the continuity of the living micro-organisms after the sedimentation of the former vegetation – main contributor for the creation of the coal deposits in the former lake basin of Miocen-pliocen age. The finegrained vegetative relics, which were sedimented together with quartz, illite, feldspars, chlorites, over the former vegetation products actually represent a special type of stopper preserving reductive conditions useful in the carbonization process for the creation of the coal deposits.

– The mineralogical and chemical composition of the examined trepel evidently offer different possibilities for the development of a complex inorganic technological industry for production for example for light bricks, cements etc.

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Р е з и м е

ТРЕПЕЛ – ПОСЕБНА СЕДИМЕНТНА КАРПА ОД БИОГЕНО ПОТЕКЛО ОД СЕЛОТО СУВОДОЛ, БИТОЛА, Р. МАКЕДОНИЈА

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Клучни зборови: трепел; опал; биогено потекло; алги Дијатомеи

Трепелите од с. Суводол, Битола, претставуваат типични слабо врзани седиментни карпи од биогено потекло што е потврдено со бројни докази (од фитогено потекло) во форма на многу дискретни микрофосили од редот на алги Диатомеи.

Наведената генеза на испитуваниот трепел е комплетно во согласност со општиот генетски третман на овие карпи од разни микролокалитети во светот.

Испитуваниот трепел од с. Суводол е вистински доказ за континуитетот на живите микроорганизми (од фитогено потекло) по седиментацијата на растителни продукти одговорни за создавањето на наслојките од јаглен во поранешниот езерски басен од миоцен–плиоцен. Овој седиментен комплекс, составен од трепели и јаглени, де факто претставува една биогено-седиментна формација.

Финозрните фитогени реликти во трепелот, кои беа седиментирани заедно со суперфинозрнестита тиња од кварц, илит, фелдспати, хлорити врз растителните продукти, претставуваат еден специјален заштитен чеп кој обезбедил редукциони услови корисни во процесот на карбонизација на растителни продукти од кои настанале денешните јагленови наслојки.

Минералошкиот и хемискиот состав на испитуваниот трепел евидентно нуди разни можности за развиток на комплексна неорганска технолошка индустрија за производство на лесни тули, цементи итн.

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Original scientific paper

THE POSSIBILITIES OF USING THE GRANODIORITE OF KOSOVSKA RIVER, VILLAGE OF ČANIŠTE (WESTERN MACEDONIA), AS AN ARCHITECTURAL STONE

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A b s t r a c t: The granodiorite of the Kosovska River, western Macedonia, has been examined in order to determine the possibility to be used as an architectural stone. The analyses themselves as well as the laboratory testings have been done on samples of granodiorite. The samples were taken from the surface parts, and the results from their physical and mechanical examination have shown that rock mass itself satisfies all requirements form the use as architectural stone according to the state standards of R. Macedonia. Also the quality of the stone is greater in the deeper parts of the terrain where the influences from the outside have a very small effect. This stone does not have highly decorative features but it has a very fine granual structure which has a positive effect for the technical characteristics and for the being a subject for processing.

Key words: granodiorite; Kosovska River; architectural stone; mineralogic-petrographic content; structural-textural characteristics; basic minerals

INTRODUCTION

The granodiorite of Kosovska river is located about 0.5 km north-west from the Čanište village and about 6 km south-east from the village of Kruševica, in the series of gneisses which has been broken through with granite and granodiorite as part of the metamorphic complex of the Pelagon. This area is geographically close to Selečka Mountain as an eminent orthographic unit in this part of Macedonia. The largest water artery in this part of the terrain is Čaniška river which has Lozjanska river, Kruševiška river and Kosovska river as its confluents.

In the past period, up to now, in search of good quality granite, many other regions have been researched on many occasions in the area of Mariovo, but no significant results have been received.

Stojanov (1958 and 1960) has researched these terrains and distinguished many varieties of gneisses, mica schists, amphibolite and granitoid rocks. In the doctoral dissertation Stojanov stated some conclusions which concern the entire Pelagon and believes that in the beginning of the Algonquian orogenic movements a progressive metamorphosis has been done in the lower precambrian complex and towards the end of the orogenic movements granodiorite-adamelite masses have taken root.

In the period of making the Basic Geologic map of SFRY the authors of the leave Vitolište (Dumurdžanov, Hristov 1976) and Prilep (Rakičević, Stojanov, Arsovski, 1965) processed the leave content of the rocks of the leave Vitolište where the granodiorite Kosovska river belongs.

The Kosovska river granodiorite has been researched in detail by Spasovski (2010) when for the first time its mineralogic-petrographic and chemical content is determined.

RESEARCH METHODS USED

The mineralogic-petrographic research have been done on the Faculty of Natural and Technical Sciences in Štip by the author of this paper, while the chemical content of the granodiorite is determined in the chemical laboratory in Železara in Skopje.

The research of the physical-chemical characteristics was performed in the laboratory at the Faculty of Civil Engineering in Skopje. The examinations were performed during 2010. Because the rock masses are not well disposed, the samples were taken from the surface of the terrain. As a consequence in the samples themselves there are some cracks which is a result from the great influence of the atmosphere. However the examinations of the samples have shown credible values of their physical-mechanical characteristics. It is certain that the samples from the greater depths would give much better results.

GEOLOGIC CHARACTERISTICS

In the geologic structure of the area that is included in our observation and research there are three types of rocks that included: muscovite gneisses, granodiorite and quartz diorite (Fig. 1, 2).

The muscovite gneisses are outspread in the northern and north-eastern part of the researched area. They are characterized with grey colour with glittering radiance from the leaves of muscovite which can clearly be noticed. They are characterized with slightly distinguished parallel schistose texture. The structure of the gneisses is grano-lepidoblastic with slightly distinguished striped texture. The main minerals in the rock are: quartz, feldspar and mica. The participation of salic and femic minerals is approximately equal in quantity, i.e. the salic are slightly more present. The quartz is found in xenomorphic crystals as well as in feldspars. The feldspar is K-feldspar – orthoclase and plagioclase. The orthoclase is fairly clayed while the plagioclase is more strongly clayed. The plagioclase is albite to intermediate plagioclase. It is rare to find some larger xenomorphic crystals of orthoclase, as porphyroblastic. The mica is represented with muscovite and biotite and they are found in not clearly distinguished lines. It is typical for the biotite that it is bleached – baritised, so it has a fairly weak brownish interference. The secondary minerals are the epidote, ortite, rarely granite and mining mineral in irregular shapes. The epidote is quite common in long crystals andis regularly associated with mica lines. The apatite and the zircon are accessory minerals.

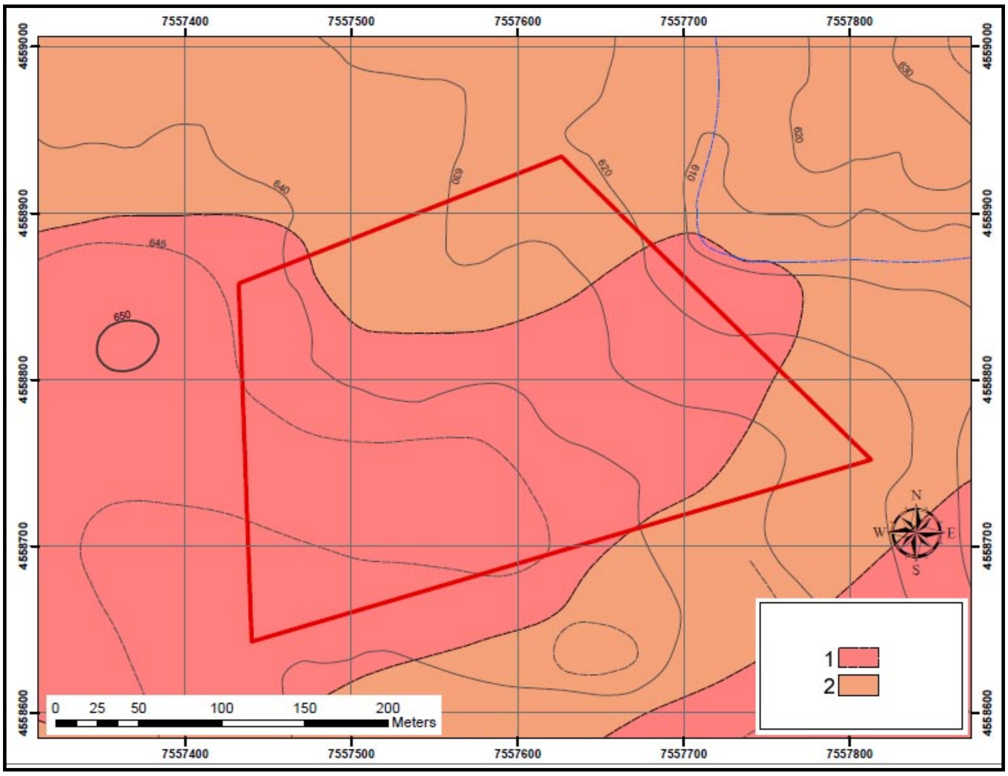


Fig. 1. Geological map of the locality Kosovska river (Spasovski, 2010)
1. granodiorite, 2. muscovite gneiss.

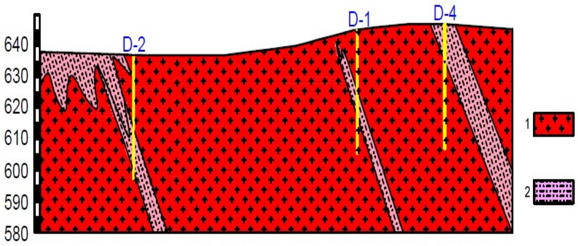


Fig. 2. Geological cross-section of Kosovska river
1. granodiorite, 2. muscovite gneiss

The amphibolic quartzite is characterized with grey-greenish to dark grey-greenish colour. The minerals are present in granules with medium size with a particular slightly distinguished oriented striped texture. It is a very hard rock with massive – oriented texture. As main minerals, the quartz, the amphibole, biotite, plagioclase and not so often K-feldspar, are noticed. When the quantity is concerned, the coloured minerals (amphibole, biotite and epidote) are slightly more common that the salic. The rock is additionally metasomatically-faldsparized. Na-feldspar is present in big irregular crystals with inclusions and crystals from epidote–coesite and amphibole. K-feldspar is less present and mostly in a shape of xenomorphic crystals. The quartz is xenomorphic with standardized size of the grains and they most often fill the interspace of the remaining minerals. The amphibole is present in big square crystals and it can rarely be found in a type of small leave crystals mixed with biotite and big crystals of the epidote. The biotite is also present in bigger and smaller leaves (liski) with different orientation. The secondary minerals are the ortite and the coesite while the accessory minerals that are present are apatite and the zircon.

The granodiorites are most commonly found and mostly constitute the middle part of the researched area. (Fig. 2). They are characterized with middle to large-grained content and light grey-pink colour equally present in the entire sample. The mineral grains are with the size of 5 mm, and rarely slightly bigger ones with 1 cm. With a microscope it can be spotted that they have hypodiomorphic grain structure. The main minerals are: quartz, plagioclase, orthoclase and biotite. The plagioclase is strongly metamorphic and the products are the epidote and the coesite and also a certain zonal allotment of the plagioclase is present. Separate crystals of the plagioclase have completely turned epidote with larger crystals of the epidote. The orthoclase is xenomorphic fresh and completely weakly clayed, and regularly poikilitic incorporates smaller crystals in the plagioclase and the biotite. The biotite is found in big square leaves and smaller rectangular leaves outspread – separate and in places grouped in small clumps. The biotite contains idiomorphic spires – microlites of the coesite and on the edges there are also crystals of the epidote and the apatite. The quartz is found in the interspace with smaller xenomorphic grains. The rock is quite strong, with slight cracks on it, i.e. with slight mechanic deformations which can be seen with the slightly distinguished undulose darkening of the quartz as well as the slightly present micro-cracks at the orthoclase.

PETROGRAPHIC-MINERALOGIC CHARACTERISTICS

There were some representative samples from the locality Kosovska river selected for the mineralogic-petrographic examinations. 5 petrographic slides are made which were examined with a polarized microscope with transmitted light brand Leitz, Wetzlar, Germany.

The mineralogic-petrographic examinations were performed at the Faculty of Natural and Technical Sciences at the Institute for geology by the author of the paper.

The granodiorite is characterized with medium to large grained content and light grey-pink colour equally present throughout the entire sample. The mineral grains are most common with the size of 4 to 5 mm, but there are also grains with the size of 1 cm.

With a microscope it can be seen that they have hypodiomorphic grain structure (Figs. 3 and 4). The main minerals are: quartz, plagioclase, orthoclase and biotite. The plagioclase is clearly defined and is present in hypodiomorphic and irregular crystals, lengthened and wider rectangular shapes. The plagioclase is strongly made metamorphic, and the products are the epidote and the coesite, but also there is a certain zonal allotment in the plagioclase, a more intense alterisation of the plagioclase in the middle parts. The plagioclase is in quantity more present that the orthoclase and the quartz, some separate crystals of the plagioclase are completely made epidote with larger crystals of the epidote. According to the altered products and the weak zonal allotment, the plagioclase are a type of intermediate plagioclase, i.e. andesine-labradorite weakly acid.

The orthoclase is xenomorphic fresh and completely weakly clayed, and regularly poikilitic incorporates smaller crystals in the plagioclase and the biotite. The orthoclase is weakly microclined at separate crystals.

The biotite is found in big square leaves and smaller rectangular leaves outspread – separate and in places grouped in small clumps. It has clear brown pleochroism. The biotite contains idiomorphic spires-microlites on the coesite, and on the edges there are also crystals of the epidote and the apatite.

The quartz is found in the interspace with smaller xenomorphic grains. It is slightly undulose darkened which points to the fact that it has slight mechanic deformations. Allanite and zircon are accessory minerals.

The rock is quite strong, with slight cracks on it, i.e. with slight mechanic deformations which can be seen with the slightly distinguished undulose darkening of the quartz as well as the slightly present micro-cracks at the orthoclase.

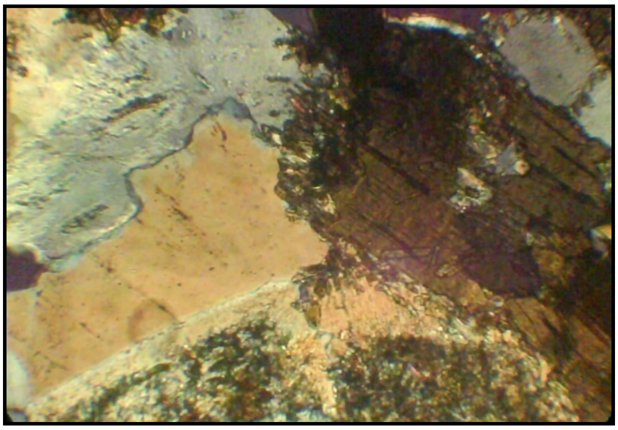


Fig. 3. Microphotography of the granodiorite of the Kosovska river locality. Crosswise nicols, magnified 10×.

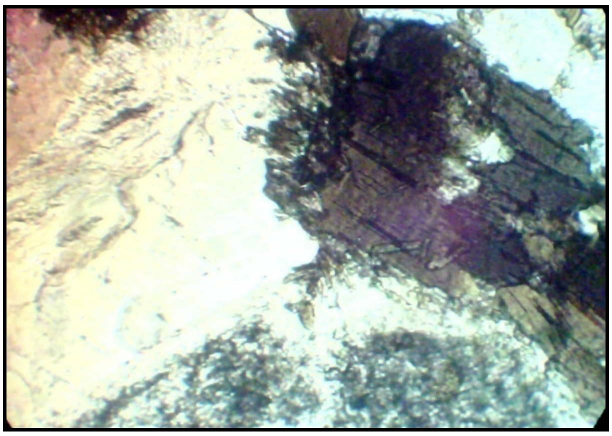


Fig. 4. Microphotography of the granodiorite of the Kosovska river locality. Parallel nicols, magnified 10×.

Quartzdiorite is characterized with dark grey-greenish color, medium grain size content with a particular slightly distinguished oriented striped texture. The hard rock is with massive oriented texture. The rock is constituted of quartz, amphibole, biotite, plagioclase and not so often K-feldspar, which are the main minerals. When the quantity is concerned, the coloured minerals (amphibole, biotite and epidote) are slightly more common that the salic. The rock is most possibly additionally metasomatic feldspatized. Na-feldspar is present in big irregular crystals which include many inclusions and crystals from epidote–coesite and amphibole. With separate albites, some polysynthetic lamellas can be seen. K-feldspar is less present and mostly in a shape of xenomorphic crystals. The quartz is present in xenomorphic standardized size of the grains in the interspace of the remaining minerals. It is clearly evident that the coloured minerals are present in irregular size of the crystals with different orientation, i.e. the crystals of the amphibole and the biotite are presented vertically and sidelong with a given slightly distinguished oriented texture (Figs. 5, 6, 7 and 8). This points out that the rock apart from the metasomatic processes has gone under metamorphism from regional – retrograded metamorphism.

The amphibole is found in big square crystals and with little leave-like crystals, stretched about shapes and densely mixed with biotite and big crystals of the epidote. The amphibole is weakly alkaline hornblende. The biotite is also present in larger and smaller leaves with different orientation. The secondary minerals are the allanite, coesite and mining mineral (oxide mineral), and the apatite and the zircon are accessory minerals

Fig 5. Microphotography of the amphibolic quartzdiorite of the Kosovska river locality. Crosswise nicols, magnified 10×.

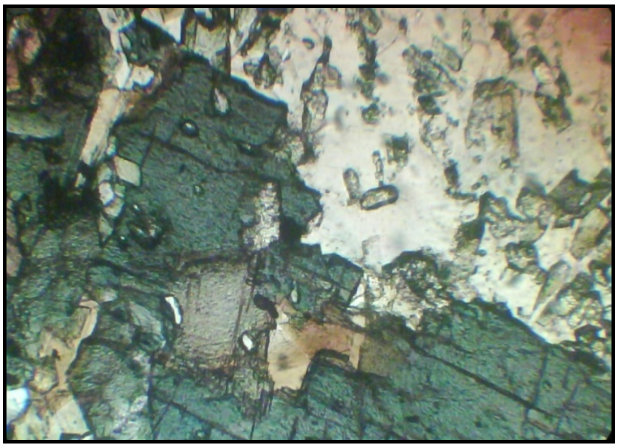
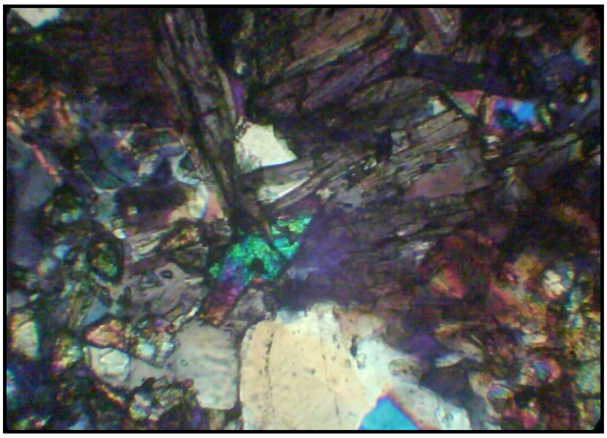


Fig. 6. Microphotography of the amphibolic quartzdiorite of the Kosovska river locality. Parallel nicols, magnified 10×.



Fig, 7. Microphotography of the amphibolic quartzdiorite of the Kosovska river locality. Crosswise nicols, magnified 10×.

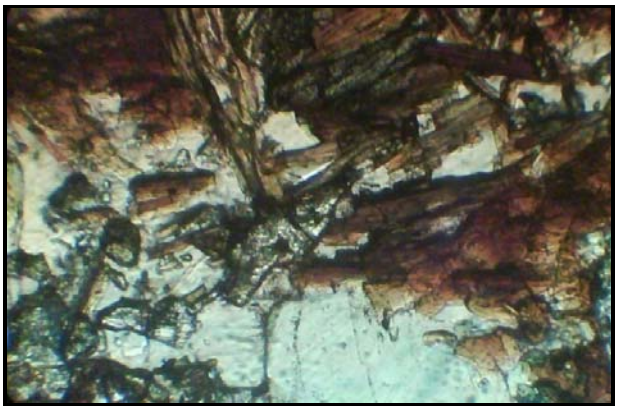


Fig. 8. Microphotography of the amphibolic quartzdiorite of the Kosovska river locality. Parallel nicols, magnified 10×.

Striped muscovite gneiss has grey color with glittering radiance from the leaves of muscovite which can clearly be noticed. They are characterized with medium grained contentand slightly distinguished parallel schistose texture. The regular pattern of minerals throughout the sample can be seen.

With a microscope the grano-lepidoblastic structure with slightly distinguished striped texture can be observed (Figs. 9 and 10).

Fig. 9. Microphotography of the thin striped muscovite gneiss of the Kosovska river locality. Crosswise nicols, magnified 10×.

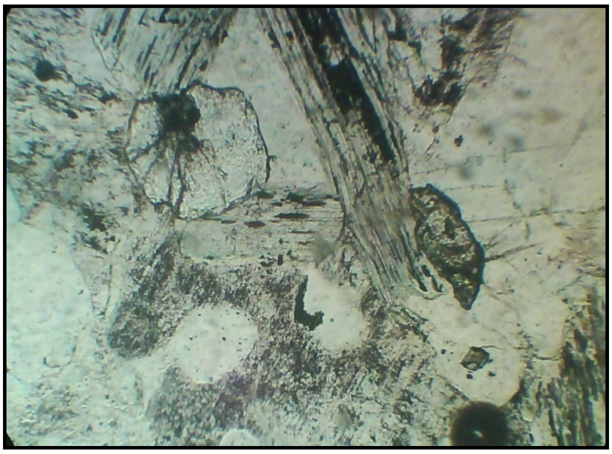


Fig. 10. Microphotography of the thin striped muscovite gneiss of the Kosovska river locality. Parallel nicols, magnified 10×

The main minerals in the rock are: quartz, feldspar and mica. The participation of salic and femic minerals is approximately equal in quantity, i.e. the salic are slightly more present.

The quartz is found in xenomorphic crystals as well as in feldspars. The feldspar is K-feldspar – orthoclase and plagioclase so the plagioclase is more present. The orthoclase is fairly clayed while the plagioclase is more strongly clayed.

The plagioclase is albite to intermediate plagioclase. It is rare to find some larger xenomorphic crystals of orthoclase, as porphyroblastic.

The mica is represented with muscovite and biotite and they are found in not clearly distinguished lines. It is typical for the biotite that it is bleached – baritised, so it has a fairly weak brownish interference. There is an impression that it is muscovite with separated Fe-component with thicker irregular shapes at the leaves themselves. It is possible that it is mica-phengite.

The secondary minerals are the epidote, ortite, rarely granite and mining mineral in irregular shapes. The epidote is quite common in long crystals and is regularly associated with mica lines.

The apatite and the zircon are accessory minerals.

It is a metamorphic rock which has pointed and not well defined striped texture. The quartz is undulose darkening while the feldspar are with cracks and altered.

CHEMICAL EXAMINATIONS

The chemical characteristics of the granitoide rocks from the Kosovska river locality, Čanište, respresent a contribution to the broadening of the knowledge for this massive on the territory of the Republic of Macedonia. This massif is evidently different from the surrounding rocks by its content, structural-tectonic features, color and the manner of its origination.

Basically, granodiorite is characterized with homogeneous – solid to compact texture, which locally turns to porphyroide. With such arrangement and intergrowth of the mineral components, a beige to greenish basic color spotted with biotite of black color is formed in the mineral aggregate.

For more detailed presentation of the chemical content of the granodiorites from the Kosovska river locality, five representative samples were taken from the granodiorites and one sample from a light grey rock with great compactness. The examinations of the taken samples were performed at the Faculty of Natural and Technical Sciences with the instrument AES-ICP. The chemical content of the analyzed samples are presented in Table 1.

From the table presented it can be stated that the analyzed samples are characterized with a constant chemical content which can be seen in the content of SiO_2 which is in range of 58.88 to 73.74. These rocks are distinguished as granodiorite, gneiss and amphibolite quartz-diorite. From the analyzed samples it can be spotted that there is a slight increase of Al, Ca, K, Fe and Mg, but especially Al which is probably due to the additional secondary processes which the analyzed samples were influenced by.

Table 1

Chemical content of the analyzed samples from the Kosovska river locality (%)

Components	Symbol of the sample					
	Kr-1	Kr -2	Kr 3	Kr -4	Kr -5	Kr -6
SiO_2	68.42	69.14	69.10	58.88	58.58	73.74
TiO_2	0.12	0.12	0.334	0.28	0.32	0.069
Al_2O_3	12.94	12.96	14.24	15.20	15.40	12.45
Fe_2o_3	3.20	3.10	2.08	8.30	8.20	2.07
MgO	1.02	1.02	0.31	2.03	2.13	0.30
CaO	4.05	4.15	2.09	6.95	6.95	2.35
Na_2O	4.82	4.79	3.94	4.06	3.99	3.90
K_2O	3.10	3.11	4.58	1.50	1.50	2.80
P_2O_5	0.80	0.78	0.51	1.20	1.20	0.48
Humidity110° OH^-	0.077	0.076	0.07	0.043	0.043	0.037
Humidity1000°OH^+	0.70	0.70	0.50	0.73	0.73	0.80
Total:	99.25	99.88		99.20	99.04	99.02

Note: The analyses 1, 2 and 3 are granodiorite and 4 and 5 represent the amphybolite - quartz-diorite, 6 gneiss.

PHYSICAL-MECHANICAL CHARACTERISTICS

The purpose of this research is to determine the physical-mechanical characteristics of the stone and to determine the eligibility of the material for its application in the civil engineering for the production of fractioned broken stone aggregate for concrete and asphalt compositions and for other applications in the trade in accordance with MKS standards.

The performed analyses are in accordance with the valid standards: MKS, B.B2.009, MKS B.B8.003, MKS S.E9.021, MKS U.E9.028, MKS SE4.014, MKS B.B8.045.

The received results for the physical-mechanical characteristics of the granodite are presented in Table 2.

Table 2

Results from the physical-mechanical characteristics

N°	Analysis	Method according to MKS	Unit	Symbol	Results from the analysis	Conditions for quality: BET.MKS B.B2.009 BNS/MKS U.E9.021/028 AB/MKS U.E9.028
1	Pressure strength in dry conditions	B.B8.012	MPa	$\sigma_p$min $\sigma_p$max $\sigma_p$sred	114.90 154.40 136.10	BET/min. (80;160) BHS/min (100) AB/min. (120;140;160) Tampon/min.(100;120)
2	Pressure strength in water satiation condition	B.B8.012	MPa	$\sigma_p$min $\sigma_p$max $\sigma_p$sred	110.80 122.93 118.45	BET/min. (64;128) BHS/min (100) AB/min. (120;140;160) Tampon/min.(100;120)
3	Pressure strength after 25 ice cycles	B.B8.010	MPa	$\sigma_p$min $\sigma_p$max $\sigma_p$sred	93.50 108.00 103.80	/
4	Water absorption	B.B8.010	% (m/m)	*U*		BET/min. (1.0) AB/min. (0.75;1.0) Tampon/min.(1.0)
5	Resistance to destruction and scraping	B.B8.015	$cm^3/50\ cm^2$	*Ab*		BET/min. (35.0) AB/min. (12.0;18.0;35.0)
6	Volume capacity with cavities and cracks	B.B8.032	kg/m^3	γ_r		(2000–3000) kg/m^3
7	Volume capacity without cavities and cracks	B.B8.032	kg/m^3	γ_z		(2000-3000) kg/m3
8	Degree of density	B.B8.032	% (mm)/	*G*		/
9	Porosity	B.B8.032	% (m/m)	*P*		/
10	Consistency to ice exposure	B.B8.001	Damage and loss (g)	*M*	No loss of the weight, damage and cracks	BET/min. (5.0) AB/min. (5.0) Tampon/min.(10.0;12.0)

After the performed analysis of the received results it can be concluded that for a stone material of high strength to pressure, rock breakage, high resistance to destruction and scraping, low absorption of water, compact to high transmission mass and constant to the ice exposure.

According to the determined physical-mechanical characteristics, the examined stone from the rock of the locality 'v. Čanište' is a eligible stone and it can be applicable in various fields as well as in civil engineering, as the following:

– production of concrete mixtures,
– production of bitumen layer,
– production of road metal.

CONCLUSION

The samples were taken from the surface parts of the terrain where the influences from the outside are quite intense. In the deeper layers of the ground, the rock mass is found as blocks and less affected by the atmospheric influence which enables a better quality. Based on the received results from the analyses it can be concluded that it can be used as an architectural stone.

The rock mass is medium-granular which makes the granodiorite from Kosovska river to give valid the physical-mechanical characteristics and eligibility for processing (cutting, polishing, etc.). The absence of pyrite enables endurance from the influences from the atmosphere.

The weaknesses of this stone are the following: it has average decorative values, heterogeneous appearance. These rocks masses are almost an easy subject to erosion in the surface parts, but they have decorative possibilities in the deeper parts.

According to the mineral-petrographic content, structural-textural characteristics the granodiorite is quite solid and can be widely used in the civil engineering primarily as architectural stone for production of tiles for interior and exterior use for tiling walls. The remaining part after the cutting can be used as technical stone for aggregate with different granulation for the use of concrete and asphalt mixtures, as well as for other building needs.

According to the mineral-petrographic content, structural-textural characteristics the amphibolite quartz-diorite can be widely used in the civil engineering. It can be used as architectural stone, as technical stone for stone blocks and separated aggregate for asphalt and concrete mixtures, as well as for other building needs.

Due to the great quantity of phyllo-silicates – micas it is expected the striped muscovite gneiss to have low strength characteristics and for that reason it is not recommended for use as technical stone. The feldspars are also significantly clayed so the stone would have weak resistance from the atmospheric influences. Generally the striped muscovite gneiss from its mineral-petrographic aspect and structural-textural characteristics is not suitable for building purposes. It can only be found useful as electroinsulation material where the mica content is requested.

With the received values for the mineral-petrographic features of the granodiorite from the Kosovska river locality, it can be concluded that it satisfies all criteria for an architectural-building stone, even some parameters are even higher that the requested ones.

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Р е з и м е

МОЖНОСТИ ЗА КОРИСТЕЊЕ НА ГРАНОДИОРИТОТ ОД КОСОВСКА РЕКА, С. ЧАНИШТЕ (ЗАПАДНА МАКЕДОНИЈА), КАКО АРХИТЕКТОНСКИ КАМЕН

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Клучни зборови: гранодиорит; Косовска Река; архитектонски камен; минералошко-петрографски состав; структурно-текстурни карактеристики; главни минерали.

Гранодиоритот од Кошарска Река, западна Македонија, е испитуван со цел да се утврди можноста за негово користење како архитектонски камен. Самите анализирања, како и лабораториските испитувања, беа извршени на примероци од гранодиоритот. Примероците се земени од површинските делови. Резултатите од нивните физичко-механички испитувања покажаа дека карпестата маса ги исполнува сите барања за употреба како архитектонски камен согласно со државните стандарди на Македонија. Исто така, квалитетот на каменот е повисок во подлабоките делови на теренот, каде што надворешните влијание имаа многу мал ефект. Овој камен нема високи декоративни својства, но има ситно зрнеста структура која претставува позитивен ефект за техничките карактеристики и подложеност на обработка.

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