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## CHEMICAL AND GEOCHEMICAL CHARACTERISTICS OF THE MAJOR MINERALS IN THE ORE DEPOSIT MITRAŠINCI (EASTERN MACEDONIA)

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**A b s t r a c t:** The chemical examinations of individual grains as well as monomineral fractions of magnets are made towards possible concentrations of major and element impurity and for that purpose the magnets from the Mitrašinci vicinity are embraced. The results of these examinations made on partial individuals as well as separated monomineral fractions of the magnetite, give basic data for the concentration of the major and elemental impurity in examined magnets in the Mitrašinci vicinity. Together with the examinations that are made on the magnets of the Mitrašinci vicinity, it is posited that some element impurity are concentrated constant in them, during some elements are concentrated occasionally. From the element impurity in the crystal structure of the magnets from the Mitrašinci vicinity there are: Cr, Ti, V, Mn, Ni, Co, Zn, Mg and Al. Si and Ca are also incorporated. In these paper the results from the latest examinations of partial individual and monomineral testing of the magnetite will be shown, and they are referring on the element impurity presence of the above mentioned minerals.

**Key words:** Mitrašinci vicinity; element impurity; major elements; magnetite; titanomagnetite; ilmenite

### INTRODUCTION

In Eastern part of Macedonia, on the wider area of village Mitrašinci – Berovo, in the complex of Precambrian metamorphic rocks, there is well developed horizon of amphibolite rocks in which iron-titan mineralization (ilmenite, titan-magnetite and magnetite) appears.

The data for concentration of the major and element impurity in the magnets allows, among the other examinations, complete explanation of crystal-chemical nature of this very wide spread mineral in the geological creation. The results for the concentration of major and element impurity in the magnets also give significant information's necessary for seeing certain typogenetic characteristics of the magnets, concerning explanation of complex process of its formation.

Element impurity in the magnets, most often are isomorphic, in crystal structure of the magnetite they are replacing  $Fe^{2+}$ , or  $Fe^{3+}$ .

The presence of the isomorphic element impurity affects directly on the morphological-structural characteristic of the magnetic individuals, they regulate the dimension and the grade of the dispersion of the microsolidness, dimension and grade of the dispersion of the parameters of the elementary cell, as well as other attributes that are in function from the inner structure of the mineral.

As isomorphic elemental impurity in the crystal structure of the magnetite  $Fe^{2+}$  is replaced with Mn, Mg, Ni, Co, Zn and Ca, until  $Fe^{3+}$  is replaced with Ti, V, Cr, Al and Si.

Data according to the presence and contents of the elemental impurity in the magnets from Mitrašinci field can only be found in the work of Spasovski (1993, 1994, 1997, 1998, 2001), Serafimovski and Spasovski (1994).

### APPLIED METHODOLOGY

For achieving the designated goal there are field research done and there are modern laboratory methods of research made.

As basis for field research basic geological maps of Republic of Macedonia 1:100 000, 1:25 000, 1:10 000 and available literature and funds are

used. When taking the samples there was taken care, so they can be taken from bigger number of litological environments which will give illustrative informations for the mineral composition and geochemical characteristics of the individual rocks and minerals.

Along several-year investigations on the field, there were large amount of laboratory investigations needed, whereupon laboratories in several European institutions were used such as: Ivan Rilsky – Central Science Investigation Laboratory, Geochemistry – Sofia, RGF – Štip, Mines for Pumbum and Zinc Sasa, etc.

## RESULTS AND DISCUSSION

The character of allocation of rear and ore elements in the magnetite is widely used for explanation of the genetic connection of the fields with different intrusive rocks. On the comparison basis of the chemical composition of the ore constitutive magnetite with the magnetite with intrusive complexes with different formation type, it is proved that the characteristics of initial magma, inherit the post magma ore constitution.

The legislation of the allocation of the element impurity in the magnetite in certain format can be used for validating the connection between ore making and intrusives.

In geochemical view, special attention is given to the data for the allocation of vanadium, chrome, aluminium and other elements impurity in the ore phases. In the magnetite, titan magnetite and ilmenite from Fe-Ti ore making, there are Fe, Ti, V, Cr, Al, Mn, Mg and Ni analyzed.

The analysis shows that Cr, V and Mg are concentrated in the magnetic phase, Mn is only

concentrated in the ilmenite phase, and Al is showing constant concentration in both, in magnetite and ilmenite. At titan-magnetite we have decreasing of the contents of Al and Cr, and increasing of the contents of Ti and Mn.

The chemical content of the magnetite is designated by electronic micro-drill, and the results are given in Table 1.

The structure of the magnetite is allowing isomorphic replacement of Fe with bigger number of elements, primarily with Ti, V, Cr, Mn, Mg, Al, Ni, Co, etc.

Most common elements, especially their concentrations in the magnets, depend from the type of the magma and from their ore-regenerating processes. From that aspect magnetite can be used as information for explaining the formation belonging of magmatic complex, as well as for appraisalment of the ore.

Table 1

*Quantitative X-ray spectral microanalyses of magnetite from the Mitrašinci vicinity (in %)*

Elements	Mt-1	Mt-2	Mt-3	Mt-4	Mt-5	Mt-6	Mt-7	Mt-8
Fe	74.29	71.99	72.63	70.46	70.70	72.40	71.15	73.40
Ti	0.11	0.00	0.39	0.45	0.55	0.21	0.20	0.05
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
Mg	0.00	0.00	0.00	0.00	0.33	0.00	0.20	0.00
Al	0.00	0.00	0.00	0.00	0.44	0.40	0.45	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.39	0.32	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V	0.17	0.20	0.21	0.28	0.28	0.00	0.15	0.36
Cr	0.00	0.00	0.00	0.05	0.06	0.00	0.00	0.04
O	25.36	27.81	26.77	28.76	27.65	26.58	27.53	26.14
Σ	100.01	99.99	99.99	100.00	99.99	99.98	100.00	99.99

**Note :** The analyses are worked in the laboratory for geochemical examinations AD in Sofia under the supervision of H. Stančev.

According to the data given in Table 1 it can be noticed that magnetite has relatively equal chemical content which can be seen in the contents of the Fe from about 70.46 %, rarely and 74.29%. As impurities in very small amounts it consist Ti 0.05–0.55%, Ni 0.32–0.39%, Cr 0.04–0.06 %, V

0.15–0.36, etc. The magnets are constantly accompanied with low concentrations of Al, Mg, and Mn.

In the titanomagnetite we always meet concentrations of Mn that are moving in the borders from 0.22 to 1.43%, but without concentration of Cr, Mg, and V, and in totally small amounts and occasionally there are Al and Co (Tab. 2).

Table 2

*Quantitative X-ray spectral microanalyses of the titanomagnetite from the Mitrašinci vicinity (in %)*

Elements	Tm-1	Tm-2	Tm-3	Tm-4	Tm-5
Fe	47.36	52.60	54.97	63.71	64.44
Ti	20.55	14.22	12.63	8.06	8.25
Mn	1.43	1.20	1.09	0.56	0.22
Mg	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.18	0.33	0.30	0.31
Ni	0.00	0.25	0.35	0.45	0.36
Co	0.00	0.00	0.00	0.06	0.06
V	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00
O	30.57	31.54	29.65	26.44	26.36
Σ	99.91	99.99	99.02	99.58	100.00

**Note:** The analyses are done in the laboratory for geochemical examinations AD in Sofia under the supervision of H. Stančev.

In Table 3 is given the chemical composition of one magnetite grain in which the distribution of the element impurity is examined, going from the periphery towards the center.

From the above mentioned Table 3, it can be seen that in the analyzed magnetite grain, we have constant appearance of Co and V, Mn is appearing only in the central part and in two analyses, near the center of the analyzed grain. Chrome is appearing in the center and in two analyses in the periphery, titan is appearing only in one analysis, and the nickel and the zinc are not present at all in the analyzed magnetite grain. Also from the same table it can be seen that the analyzed magnetite is characterized with consistence in its chemical composition that can be seen in the contents of Fe that are moving in the borders from 71.41% to 73.32% and that highest contents from 73.32% Fe are noted in the center of the analyzed grain.

The chemical composition of the magnetite in the Mitrašinci field is plotted on FeO–Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> diagram after Buddington & Lindsley and in the series of thick dilutions magnetite-ulvospinel, ilmenite-hematite and pseudobrucite (Fig. 1).

From the diagram shown in the Figure 1 it can be seen that all of the analyses are plotting about one spot near the FeO–Fe<sub>2</sub>O<sub>3</sub>, line and some of the analyses are laying on the line it self. This position of the analyzed magnetite only confirms the establishment of pure magnetite, concerning magnetite poor with element impurities.

The composition of the ilmenite is very complexed, but the analysis shows close values of Fe and Ti, although ilmenite is characterized with wide temperature interval of crystallization.

In Table 4 is given the chemical composition of ilmenite (under the cloak of lemel and/or alotri-morph homogeny grains) accurated on electronic micro-drill.

From Table 4 it can be seen that the ilmenites from this field are pure and the same are characterized with about equal chemical composition. In the ilmenite there is constant presence of Mn it contents that are moving in the borders of 1.61 % to 2.21 %. In the ilmenite occasionally are concentrated Mg (0.23 – 0.26%), Al (0.19 – 0.34 %) and Ni (0.08 – 0.29 %), until it is not established concentrations of Cr, Co and V.

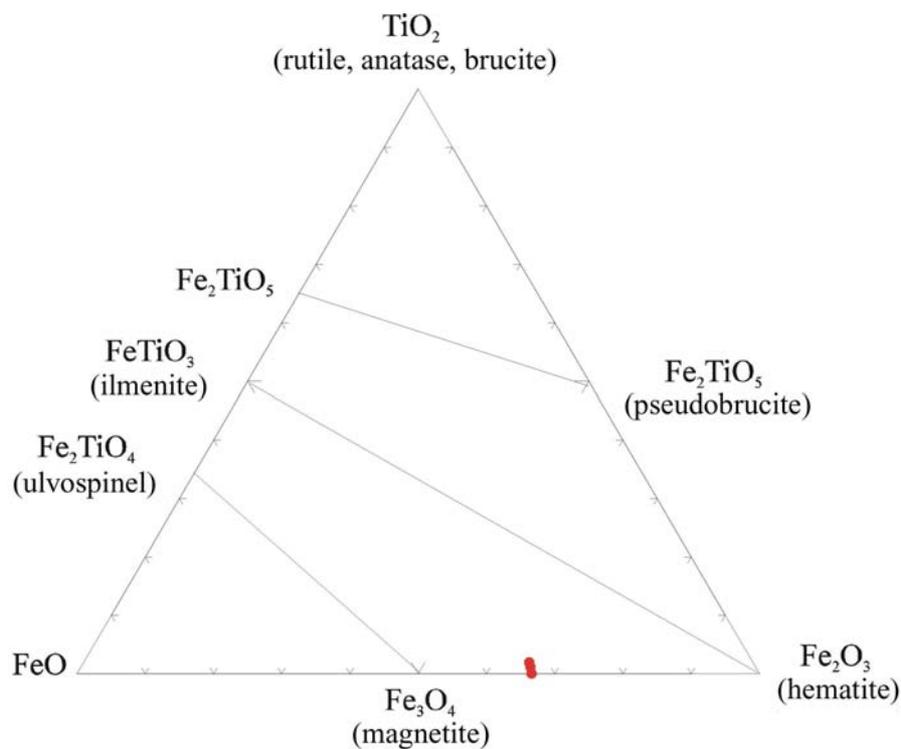
T a b l e 3.

*Quantitative X-ray spectral microanalyses of magnetite grains from the Mitrašinci vicinity (in %).*

Elements	Mt-1	Mt-2	Mt-3	Mt-4	Mt-5	Mt-6	Mt-7
Fe	72.83	72.84	73.32	72.72	72.26	71.69	71.41
Ti	0.00	0.00	0.00	0.00	0.00	0.08	0.00
Mn	0.00	0.00	0.07	0.14	0.17	0.00	0.00
Cr	0.00	0.00	0.04	0.00	0.00	0.05	0.06
V	0.08	0.15	0.12	0.10	0.16	0.12	0.11
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.53	0.65	0.47	0.48	0.75	0.48	0.59
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O	26.56	27.35	25.98	26.57	26.66	27.57	27.83
$\Sigma$	100.00	99.99	100.00	100.01	100.00	99.99	100.00

**Note:** Analysis 1, 6 and 7 are in the periphery, analyses 2, 4 and 5 are in the medial part, and analysis 3 is in the centre of the magnetite grain.

The analyses are done in the laboratory for geochemical examinations AD in Sofia under the supervision of H. Stančev.



**Fig. 1.** Projection of the magnetite in the Mitrašinci field of FeO–Fe<sub>2</sub>O–TiO diagram in the series of thick dilutions magnetite-ulvospinel, ilmenit-chematite and pseudobrucite (Fe<sub>2</sub>TiO<sub>5</sub>) after Buddington & Lindsley

T a b l e 4

*Quantitative X-ray spectral microanalysis of the ilmenite from the Mitrašinci field (in %).*

Elements	Ilm-1	Ilm-2	Ilm-3	Ilm-4	Ilm-5	Ilm-6	Ilm-7	Ilm-8
Fe	33.81	33.36	32.28	35.22	33.95	34.64	35.30	34.42
Ti	32.25	32.60	32.50	27.51	29.57	27.59	30.81	32.03
Mn	1.79	1.61	1.79	1.78	2.21	1.74	1.76	1.68
Mg	0.00	0.23	0.36	0.00	0.00	0.00	0.25	0.00
Al	0.00	0.00	0.34	0.23	0.34	0.23	0.19	0.00
Ni	0.00	0.00	0.00	0.29	0.19	0.08	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O	32.19	32.21	32.68	34.90	33.73	35.50	31.69	31.87
$\Sigma$	100.04	100.01	99.95	99.93	99.91	99.93	100.00	100.00

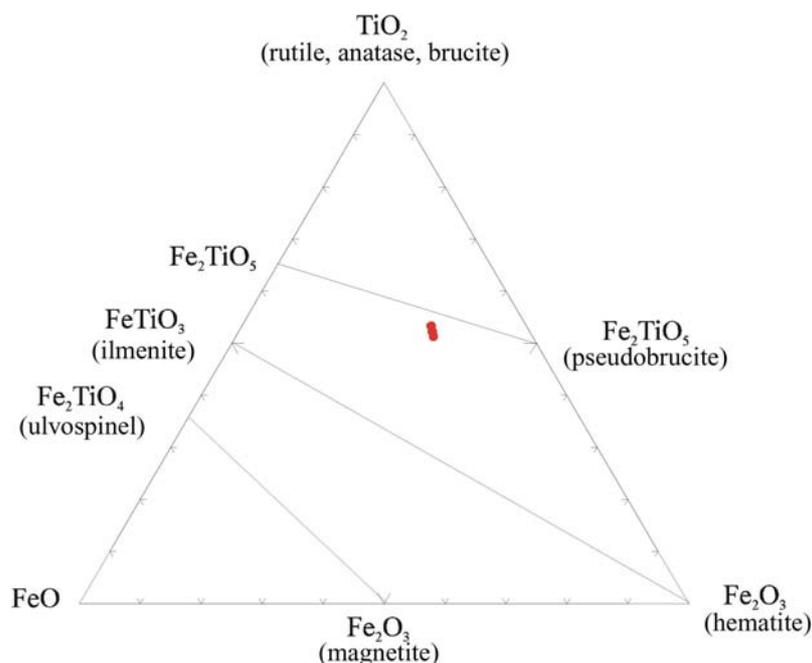
Note: Analysis 1, 2, 3 and 4 are allotrymoph grains of ilmenite, and analyses 5, 6, 7 and 8 are ilmenite lamellas in the magnetite.

The analysis is done in the laboratory for geochemical examinations AD in Sofija under the supervision of H. Stančev.

Some ilmenite aggregates are showing corrugated darkening, that shows certain increased pressures that probably are the indicator of these deformations. The chemical composition of the ilmenite from the Mitrašinci field is plotted on FeO–Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> diagram after Buddington & Lindsley in the series of hard dilutions magnetite – ul-

vospinel, ilmenite – hematite and pseudobrucite (Fig. 2).

From the diagram shown bellow on Figure 2 it can be seen that all the analyses are falling almost in one spot in the field between the series of ilmenite – hematite and pseudobrucite.



**Fig. 2.** Projection of ilmenite from Mitrašinci field of FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> diagram in the series of hard dilutions magnetite – ulvospinel, ilmenite – hematite and pseudobrucite /Fe<sub>2</sub>TiO<sub>5</sub>/ after Buddington & Lindsley.

This position of the analyzed ilmenite shows on their minimal enrichment with  $\text{TiO}_2$  component, probably as a consequence of starting processes of their transformation into rutil or sfen (anatas, brukit). Geochemical characteristics of magnetite in certain measurement can be seen and on the basis of the content of the element impurities. Here, special attention deserves elements from the group of iron, in the first row titan, vanadium, cobalt, nickel, chrome, manganese, aluminum and magnesium. For complete perceiving of the geochemical characteristics from the Mitrašinci field, except analyses of the electronic micro-drill there are five analyses of monomineral magnetite made, with the method of atomic absorption (in the mines Sasa), and three analyses with the method AES-ICP (RGF in Štip) (Table 4).

From Table 4 it can be seen that the contents of MN varies from 201 to 1001 g/t, the contents of Ni from 11 to 19 g/t, the contents of Cu are moving in the borders from 23.18 to 56 g/t, Cr from 2.94 to 7.09 g/t, Ag from 1.34 to 3 g/t, the content of Cu are between 10 and 42.35 g/t. Special attention deserves the contents of vanadium who are moving in one brief interval from 540.2 to 725.4 g/t. From these data it is clear that the bigger variations are present in the contents of Mn, during all the other elements are in one brief interval. Basic reason for this kind of arrangement of the elements is probably based on the change of physical chemical conditions of ore delusions; in first line the temperature and the concentration of the ore delusions.

T a b l e 4

*Content of the major and element impurities in the magnetite from the Mitrašinci field (in g/t)*

Elements	1	2	3	4	5	6	7	8
Fe	64.34	64.11	61.38	61.81	60.38	64.54	64.04	60.45
Ti	–	–	–	–	–	549.3	241.9	224
Mn	201	570	862	832	1001	578	575	579
Ni	11	19	15	12	17	7.60	12.03	12.39
Co	56	54	52	55	53	23.41	23.18	24.12
Cr	–	–	–	–	–	5.63	2.94	7.09
Cu	10	13	28	20	19	13.73	17.34	42.35
Pb	42	67	36	45	51	35.86	84.6	21.34
Zn	59	88	80	79	78	102.2	89.6	82.1
Ag	2	3	2	2	2	1.34	1.64	2.10
V	–	–	–	–	–	693.9	725.4	540.2
Cd	6	6	6	6	6	3.66	2.17	3.12

**Note:** Analyses from 1 to 5 are done in the laboratory of the Sasa mines, analyses 7, 8 and 9 are done in the laboratory of RGF in Štip.

## CONCLUSION

The results of the chemical analysis, made as well as on individuals, and on separated monomineral fractions of magnetite, are showing that studied magnetite are poor with element impurities, although bigger number of elements are showing constant appearance, but their concentrations are low and they don't have any significant influence on the typomorph and typogenetic characteristics of the magnetite.

From the element impurities in the crystal structure of the magnetite from the Mitrašinci field there are: Cr, Ti, V, Mn, Ni, Co, Zn, Mg and Al. Si and Ca are included in this group.

Element impurities that in the crystal structure of the magnetite are mixed, and covered as isomorphic substitutions of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ , most often in the magnetic individuals and are regularly arranged not bringing on inhomogeneity in the crystal structure.

The element impurities in the magnets are often present as isomorphic element impurities, which in the crystal structure replace  $\text{Fe}^{2+}$ , or rarely  $\text{Fe}^{3+}$ . In the crystal structure of the magnetite  $\text{Fe}^{2+}$  is replaced Mn, Mg, Ni, Co, Zn, as well as Ca, until  $\text{Fe}^{3+}$  in smaller amount is replaced with Ti, V, Cr, Al and Si.

The concentration of isomorphic element impurities in the examined magnetite's from Mitrašinci vicinity and the ore appearances, and especially Cr, Ti, V, Ni and Co, are carrying typomorph

geneticall characteristics and developing approval of the genetically connection of the ore delusions with the magma with different petrochemical composition, as well as obtaining detailed informations for the genesis of the ore metals.

The element impurities are allowing complete perception of material composition, in fact the nature of the crystallization environment because the magnetites during their genesis are absorbing detailed typomorph element impurities from the environment it self.

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## Резиме

### ХЕМИСКИ И ГЕОХЕМИСКИ КАРАКТЕРИСТИКИ НА ГЛАВНИТЕ МИНЕРАЛИ ОД НАОЃАЛИШТЕТО МИТРАШИНЦИ (ИСТОЧНА МАКЕДОНИЈА)

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**Клучни зборови:** наоѓалиште Митрашинци; елементи примеси; главни елементи; магнетит; титаномагнетит; илменит

Извршени се хемиски испитувања на индивидуални зрна, како и на мономинерални фракции на магнетитите за да се утврдат можните концентрации на главните елементи и на елементите примеси, за која намена се опфатени магнетитите од наоѓалиштето Митрашинци. Резултатите од овие испитувања, извршени како на поединечни зрна така и на издвоени мономинерални фракции на магнетитот, даваат основни податоци за концентрацијата на главните елементи и на елементите примеси во испитуваните магнетити.

Со извршените испитувања на магнетитите од наоѓалиштето Митрашинци е утврдено дека некои од елементите примеси константно се концентрираат во нив, додека некои елементи се концентрираат само повремено.

Од елементите примеси во кристалната структура на магнетитите од наоѓалиштето Митрашинци се јавуваат: Cr, Ti, V, Mn, Ni, Co, Zn, Mg и Al. Кон оваа група се приклучуваат и Si и Ca.

## MINERALOGICAL AND CHEMICAL CHARACTERISTICS OF MARBLE OF BELA POLA DEPOSIT

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**A b s t r a c t:** This paper presents mineralogical characteristics of marbles from the Bela Pola deposit. We have made mineralogical-chemical analyses of marbles and associated minerals in them. The investigation was carried out at the Faculty of natural and technical sciences – Štip. Marbles from Bela Pola are dolomite and dolomite-calcite types. Microscope investigations have shown that marbles from Bela Pola have granoblastic structure but at some places it can be found with porphyroblastic structures. Percentage on calcite and dolomite is: 94.08% dolomite, 6.25% is calcite in white marbles. On the other hand calcite is present with 93% in gray marbles. Except dolomite and calcite also appear the following accessory minerals: quartz, fluorite, corundum and paragonite. In general, after summarizing all the facts, which have resulted from this research we could say that, the Bela Pola marbles are massive, compact and white with high quality. In accordance to all formerly mentioned features, this marbles can be classified in the commercial group of marbles suitable for external application or internal design.

**Key words:** marble, calcite, corundum, fluorite

### INTRODUCTION

The Bela Pola locality is situated near the village of Nebregovo at 19 km from Prilep. It is situated at the base of the Babuna mountain massive in north part on Prilep.

This locality has good infrastructure connected with Prilep across locally road Prilep–Nebregovo and Prilep–Sivec mine.

Bela Pola marble belongs to the Pelagonian marble mass. This marble mass is situated between Prilep anticline on the south–west and intensively folded mountain mass Mukos on north–east. (Fig. 1) Marble mass is sinking to the north–west under Pliocene sediments on periphery at the Pelagonian basin. It also appears near Cave locality and Kozjak syncline (Marik 1940; Stojanov 1958, 1960).

Lithostratigraphic and tectonic characteristics of this mass are pointing out to multistage process of sedimentation, regional metamorphism and late tectonics deformation.

White small grains dolomite marbles are appearing on the south–western part of the marble mass, but calcite marbles are situated on the north–east higher parts of the marble mass.

Hydrogeological characteristics of marble deposit have shown presence of few smaller water sources. All of them are situated at 910 – 930 m above sea level.

The presence of the water is very important element, because technology of marble exploitation is impossible without water.

### RESULTS AND DISCUSSION

Microscopic investigations have shown that these marbles have small grains structure and porphyroblastic structure at some places. In the crushing zones were determined cataclastic and mylonitic structures. Dolomites grains are 0.1–0.5 mm

in size. They are rounded and have pronounced cleavage. Accessory minerals like, fluorite, corundum and paragonite are appearing in the crushed system in marble mass.

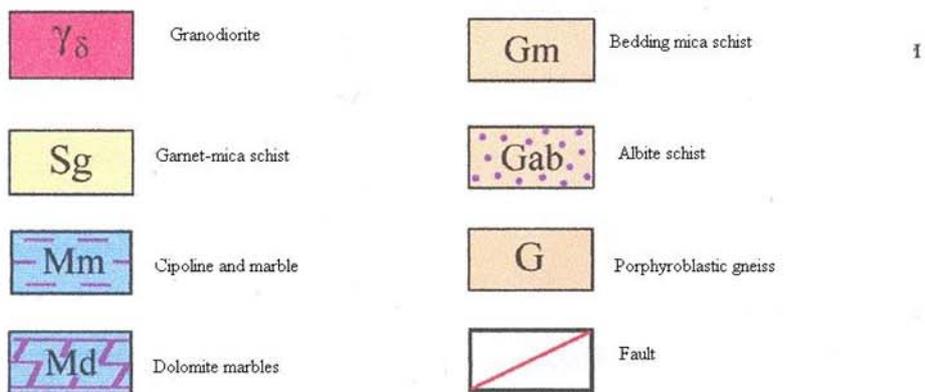
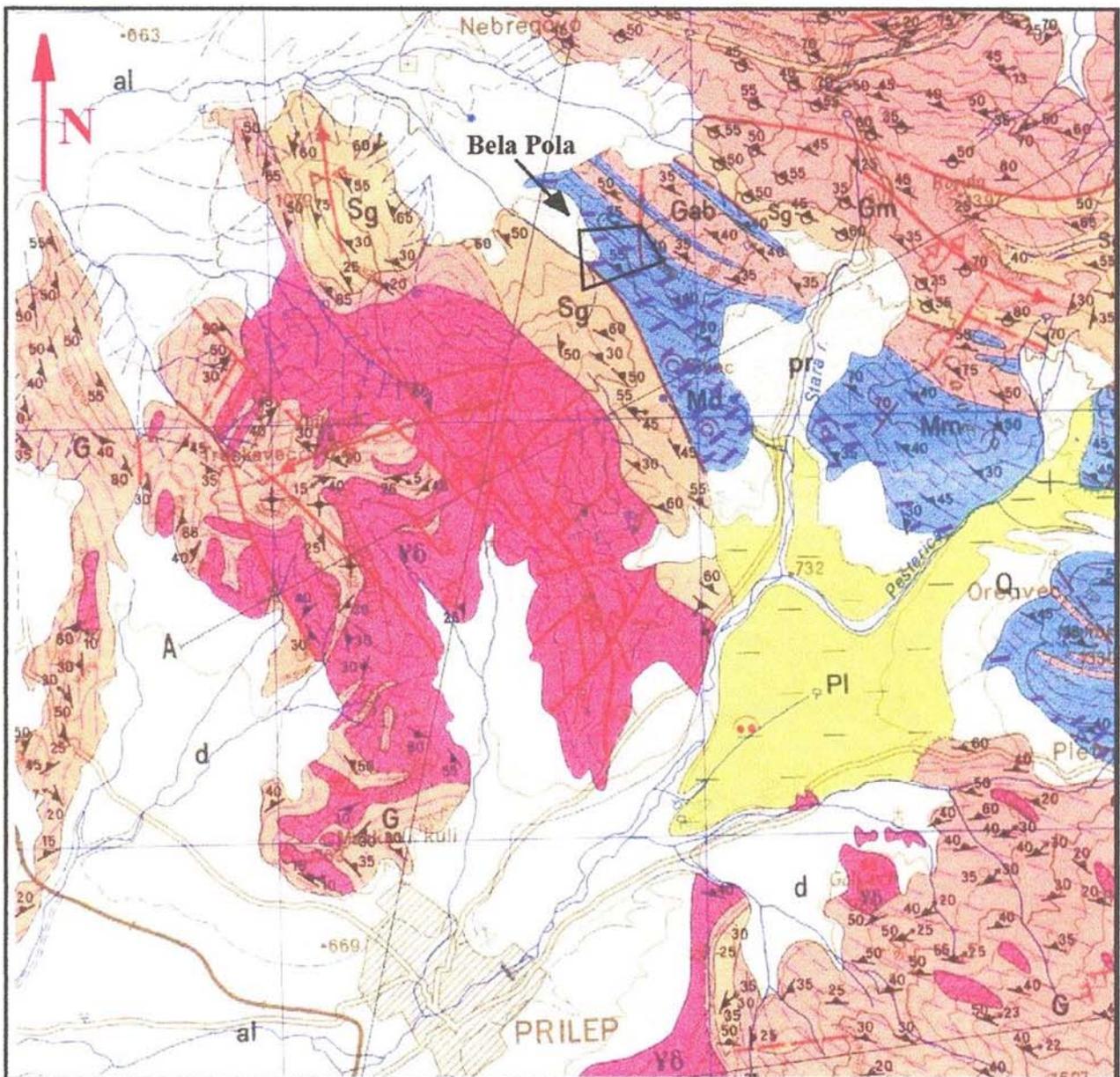


Fig. 2. Detal geological map on Bela Pola marble deposit

Marble mass has been classified in few categories based on: appearance form, system of the crushing, degree of compactness and crushing.

I. Massive marbles with low degree of crushing. They are relatively compact, white, saccharose, poorly stratified with or without presence of calcite. On some places, which are exposed on erosion, were formed dolomites gravels thick above 1 m.

II. Marbles with bank form – were classified as the second category and extends in form of stripes width from 75 to 100 meters. Those are saccharose white marbles with or without calcite. The crushed of marble mass is slightly larger than the previous, which gives the impression that it is of worse quality.

III. Plate slaty – clear stratify marble. Thin layers white marbles are occupying the north-eastern parts with expressed foliation which is on distance between 10 and 30 cm. This category still does not represent interest.

IV. Crushed marble without clear stratification. These marbles are found around marbles of I

and II category. These marbles are not interesting for exploitation.

Beside the classification of marbles towards the degree of compactness and crushing, for the white marble of the zone of Bela Pola–Sivec mineralogical composition and its impurities, or color are important. Also, on the basis results of previous studies, exploitation and set aside blocks of marble there are three categories of marbles:

– Bela Pola extra white category – pure white saccharoid dolomite marbles without presence of calcite. Their spatial determination of surface-based mapping is impossible to define. It was made only by the results of exploration drilling.

– Bela Pola white category – white marbles with saccharoid dolomites and calcite occurrences that are chaotically arranged in the mass and not very common.

– Bela Pola gray saccharoid dolomite marbles with more frequent runs of calcite occurrences. High presence of calcite in this type of marble gives gray-white color.(Fig. 2).



Fig. 1. Bela Pola deposit

#### *Physico-mechanical characteristics*

Physico-mechanical characteristics on marbles are:

Strength of the pressure in the dry state –  $P_{sr} = 148.20$  MPa

Strength of the pressure condition –  $P_{sr} = 132.10$  MPa

Strength of the pressure after freezing and thawing 25 cycles

–  $P_{sr} = 117.60$  MPa

Water absorption

–  $\sigma = 0.0792$  %

Volume mass

–  $\gamma = 2845$  kg/m<sup>3</sup>

Resistance against wear by scraping

–  $A = 31.2$  cm<sup>3</sup>/50 cm

### Chemical characteristics of the Bela Pola marbles

For chemical investigations samples were taken of white and gray marbles from the Bela Pola. Chemical analyses were made with ICP-AES method. Major and trace elements were determined. The results are shown on table 1

Table 1

#### Chemical analyses of white and gray marble

	White marble	Gray marble
	%	
CaO	31.89	54.23
MgO	20.56	1.70
Al <sub>2</sub> O <sub>3</sub>	0.00	0.02
Na <sub>2</sub> O	0.01	0.05
K <sub>2</sub> O	0.12	0.12
	mg/kg	
As	<5	<5
Ag	0.85	<0.5
Ti	1.70	0.95
Sr	82.72	172.03
Ba	1.30	2.49
Ni	<1	1.89
Mn	9.22	11.57
Fe	128.10	61.24
Cr	1.69	0.57
V	5.40	4.38
P	<5	14.39
Zn	5.11	8.26
Cu	14.02	128.15
Pb	0.02	1.83
Cd	<0.5	<0.5
Co	<1	1.97
Mo	1.62	<1
W	1.24	2.41

The results in table 1 and diagram on (Fig. 3) shows that gray marbles contains high concentration of CaO, but white marbles contain high concentration of the MgO.

We made analyses of percentage ratio on dolomite and calcite in white and gray marbles.

These results have shown that white sample is dolomite marble. Percentage of calcite and dolomite are: 6.25% and 94.08% respectively.

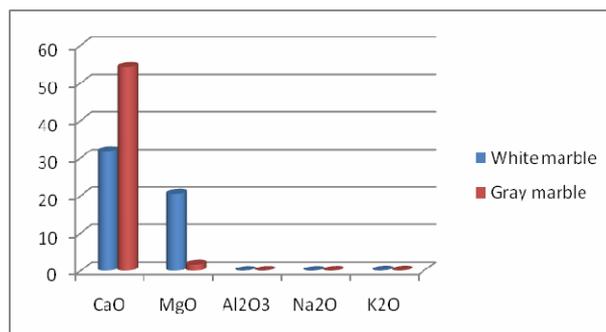


Fig. 3. Concentration of major elements in white and gray marble of the Bela Pola

On the other side results show that gray marble is calcite marble. Calcite is present up to 93%.

Concentration of trace elements is shown on the (Fig 4). Gray marble contains high concentration of Sr and Cu. Concentration of Fe is high in white marble.

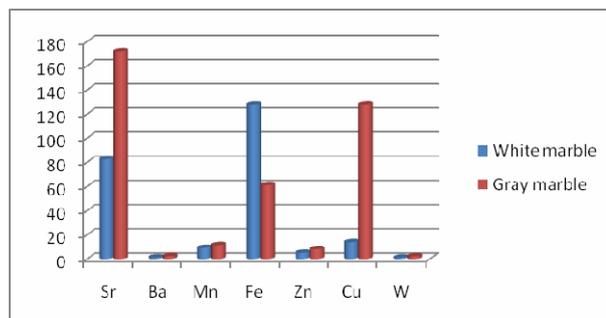


Fig. 4. Concentration of trace elements in white and gray marble of the Bela Pola

Proportional dependence between trace elements in white and gray marbles of Bela Pola is shown of (Fig. 5).

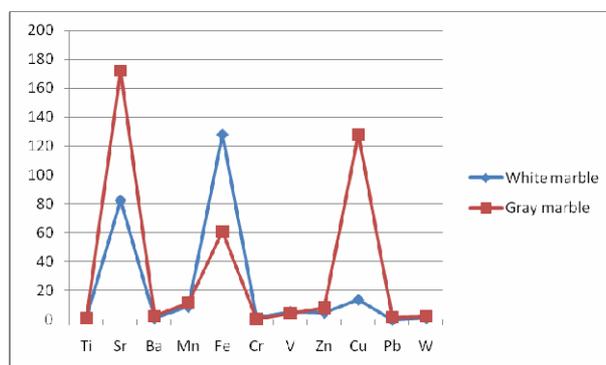


Fig. 5. Proportional dependence between trace elements in white and gray marble of the Bela Pola

In crushed marble mass system, are present individual crystals of calcite fluorite, and corundum.

Calcite (CaCO<sub>3</sub>)

Individual crystals of calcite are 2–3cm in size (Fig. 6). They are also distinguished with regular growth crystal form. Calcite is discolored (Fig.7a), but it can be found as yellow ones (Fig 7b). Cleavage is clear (1010). Crystallize hexagonally, 3m. Hardness 3, specific gravity 2.71. g/cm.



Fig. 6. Calcite crystal from Bela Pola



Fig. 7. Form on appearance on calcite from Bela Pola

Table 2

Chemical analyses of calcite

	Calcite 1	Calcite 2	Calcite 3
	%		
CaO	55.56	54.22	55.74
MgO	0.39	1.626	0.182
Al <sub>2</sub> O <sub>3</sub>	0.01	0.0076	0.013
Na <sub>2</sub> O	0.01	0.0094	0.009
K <sub>2</sub> O	0.03	0.115	0.012
	mg/kg		
As	<5	<5	<5
Ag	<0.5	<0.5	<0.5
Ti	0.78	0.44	0.64
Sr	29.30	107.52	61.62
Ba	5.32	3.61	4.07
Ni	2.22	3.04	1.74
Mn	1.96	3.50	10.35
Fe	14.73	504.10	24.00
Cr	0.74	0.59	0.85
V	1.48	2.97	1.80
P	<5	<5	<5
Zn	6.17	8.17	9.62
Cu	7.41	6.01	16.39
Pb	7.44	3.80	8.93
Cd	0.70	1.24	0.87
Co	<1	,1	<1
Mo	1.13	<1	<1
W	2.52	1.45	1.57

The results in table 2 have shown that the concentrations on CaO in sample 1 nad 3 are similar. In sample 2 concentration of CaO is smaller as a result of the higher MgO concentration. (Fig. 8) shows proportional dependence between Ba, Cu and Pb. Also, there is proportional dependence between V, Cd, Ni and Ti (Fig. 9).

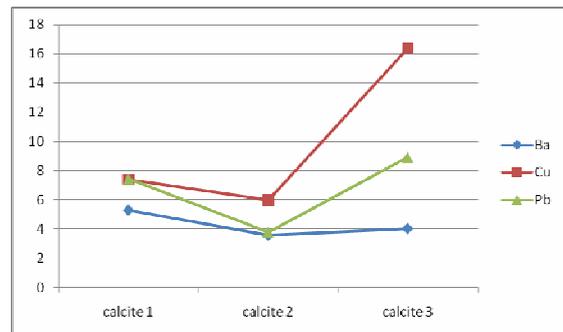


Fig. 8. Proportional dependence between Ba, Cu, Pb

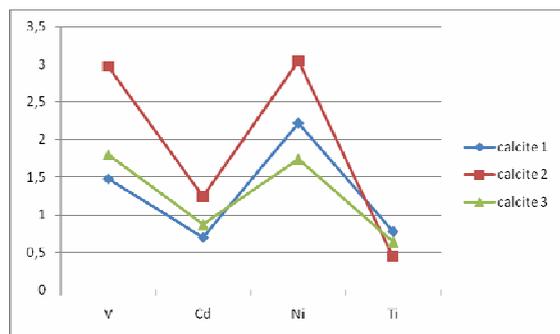


Fig. 9. Proportional dependence between V, Cd, Ni and Ti

### Corundum ( $Al_2O_3$ )

Corundum occurs in thin plate crystals or rounded grain. Grains are 1 – 2 cm in size. Ideal crystal form is very rare. Pure sample has vitreous lustre and irregular fracture. Colour is pink in the different hues (Fig. 10, 11) Pink colouring derives from chromium impurities. The content of  $Cr^{+3}$  is 10.11ppm. It is shown in table 3. Specific gravity is 4 – 4.01  $g/cm^3$ , optical is anisotropic, pleochromatic colour is blue-dark purple. Interference colour is gray first order, Ne – 1.768, No – 1.760, No – Ne – 0.008. The chemical analyses of corundum is shown in table 3.



Fig.10. Corundum from the Bela Pola



Fig. 11. Corundum from the Bela Pola

The amount of trace elements in corundum can vary considerably within the same deposit. The differences in chemical compositions of corundum from one deposit type to another are sometimes smaller than the variation within the same locality. Therefore it is difficult to assign a typical trace element pattern of ruby and/or sapphire to a specific deposit. Nevertheless, some elements may be useful for deducing a possible geological setting of formation. A completely different picture is given by the oxygen isotope composition ( Dufour, M at. all. 2007). The geological setting determines the isotopic compositions: (1) corundum from ultramafic xenoliths have 2–3 ‰  $\delta^{18}O$ . Corundum xenoliths in basalts have an isotopic signature in the range of typical basaltic rocks, which is between 4 and 6 ‰. Corundum from amphibolites, where a gabbro or basalt is the precursor rock also have an

isotopic composition around 5 – 6 ‰  $\delta^{18}O$ . Rubies of metamorphic and/or metasomatic origin have ~12 – 14 ‰  $\delta^{18}O$ . Rubies and sapphires which are associated to marbles have a typical sedimentary signature with 18 – 24 ‰  $\delta^{18}O$  (Okrusch, M at al. 1976). The lower values probably indicate some interaction with a metamorphic fluid.

### Fluorite ( $CaF_2$ )

Fluorite from the Bela Pola occurs in crystal forms with different sizes (from very small to samples with sizes up to 2 – 3 cm.) on which are grown hexahedral and octahedral forms. Cleavage is perfect. Streak-white. Usually has light purple colour (Fig. 12). Crystal system – cubic, lustre-vitreous, hardness 4, specific gravity is 3,18  $g/cm^3$ . Optical is positive. The refractive index is 1.433. Chemical analyses of fluorite are shown in table 3. Yttrium and cesium may substitute for calcium (Klein and Hurlbut, 1993). The yttrium and other trace impurities in fluorite are thought to be the activator causing fluoresces in fluorite (Robbins, 1994).



Fig. 12. Fluorite from Bela Pola

Table 3

#### Trace elements of corundum and fluorite (mg/kg)

	Corundum	Fluorite
Mn	4.81	2.12
P	16.75	13.45
Sr	2.62	18.33
Ba	13.51	18.74
Ni	1	5.01
Cr	10.11	1.26
Zn	8.31	14.30
Cu	7.74	8.92
Pb	1.61	9.00
Co	<1	<1
Cd	<0.5	<0.5
V	7.312	1.946
Mo	5.78	1.19
Ag	1.37	<0.5
As	<5	<5

## CONCLUSION

Based on these investigation we came up with the following conclusions.

Marbles from Bela Pola deposit are dolomite–white marbles and calcite – gray marbles. Dolomite marbles occurs in south–western parts of the marble mass, and calcite marbles occurs in north–eastern higher part of the marble mass.

Microscopic investigations have shown that marbles from Bela Pola have granoblastic structure, but at some places it can be found with porphyroblastic structures.

Percentage on calcite and dolomite is: 94.08% dolomite, 6.25% is calcite in white marble. On the

other hand, calcite is present with 93% in gray marbles.

Except dolomite and calcite appear individual crystals of calcite fluorite, corundum and paragonite.

In general, after summarizing all the facts, which have resulted from this research we could say that, Bela Pola marbles are massive, compact and white with high quality.

In accordance to all formerly mentioned features, this marbles can be classified in the commercial group of marbles suitable for external application or internal design.

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## Резиме

## МИНЕРАЛОШКО ХЕМИСКИ КАРАКТЕРИСТИКИ НА МЕРМЕРОТ ОД НАОЃАЛИШТЕТО БЕЛА ПОЛА

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**Клучни зборови:** мермер; доломит; калцит; корунд; флуорит

Мермерот од Бела Пола во основа е доломитски и доломитско калцитски. Доломитски мермери се појавуваат во југозападниот дел на мермерната маса, а калцитските мермери ги градат североисточните повисоки делови на мермерната маса.

Со микроскопските испитувања е утврдено дека мермерот има ситнозрнеста гранобластична структура со преоди кон порфиробластична. Процентуалната застапе-

ност на доломит и калцит кај белиот мермер е 94.08% доломит и 6.25% калцит, додека кај сивиот мермер калцитот е застапен со 93%.

Врз основа на сите претходно споменати минерално-хемиски карактеристики овој мермер може да се класифицира во групата на комерцијални мермери и може да се користи за надворешни апликации или како материјал за внатрешно уредување.

## REE IN SOME TERTIARY VOLCANIC COMPLEXES IN THE REPUBLIC OF MACEDONIA

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**Abstract:** Petrological and geochemical features of the Tertiary magmatic rocks from the Republic of Macedonia were subject of study in this paper. The latest K-Ar,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and REE data for samples from Kratovo–Zletovo, Sasa–Toronica and Damjan–Buchim ore districts are presented. Whole rock XRF analyses confirmed host rock composition as dacites, quartz-latites, trachyandesites, rhyolites and rhyodacites. Absolute age determinations by the K-Ar dating method have shown ages range from 31 to 14 Ma confirming Oligocene-Miocene age as previously determined by relative methods. Determinations of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.70504 to 0.71126) suggest material is sourced from the contact zone between the lower crust and upper mantle where contamination of primary melt occurred. New REE data including negative Eu anomalies along with previously determined La/Yb ratios ranging from 13.3 to 43.0 (Serafimovski 1990) confirm inferred material source. These new data reconfirm previous results, provide insight into the Tertiary magmatic history of the district, and suggest the exact origin of the material that produced the Tertiary magmatic rocks.

**Key words:** rare earth elements (REE); Sasa; Toronica; Kratovo; Zletovo; Damjan; Buchim; volcanic rocks; age; Tertiary

### INTRODUCTION

Surface manifestations of the Tertiary magmatism within the Republic of Macedonia were determined almost at whole of its territory, but were of different intensities and scales. This magmatism/volcanism mainly occurred as extrusive and effusive, which at certain regions, as Kratovo-Zletovo volcanic area is, reached surface of 1200 km<sup>2</sup> (Serafimovski, 1990, 1993; Stojanov and Serafimovski, 1990b) and represents one of the largest complexes at the Balkans and wider. The most common and the most important occurrences of the Tertiary magmatism are located in the Eastern parts of the Republic of Macedonia, excluding Kožuf magmatism (Boev, 1988; Boev et al., 1997), which has been located in the southern parts of the Vardar zone, close to the Greece national border, continuing into the volcanic complex Aridea.

The basic characteristics of the Tertiary magmatism within the Republic of Macedonia were given by Karamata (1982), Karamata et al., (1992), Serafimovski (1993), Boev et al. (1995), and others, while certain petrological, geochemical and geochronological features of particular volcanic

complex could be found in Boev (1988), Stojanov and Serafimovski (1990 a, b), Boev et al. (1992), etc. Geochronological data of studied rocks from certain localities, characterized by occurrence of Tertiary magmatism, pointing out the existence of Oligo-Miocene magmatism, whose absolute age ranges from 33 Ma for the alkali trachyte dykes near the Mrdaja, Dojran (Stojanov and Sveshnikova, 1985) up to 1.8 Ma at Kožuf (Boev, 1988). Absolute age of Oligo-Miocene volcanics in the Eastern Macedonia (Kratovo–Zletovo, Damjan–Bučim, Osogovo) most often is within the range of 32–16 Ma (Serafimovski, 1990; Aleksandrov, 1992; Tasev, 2003). Intrusive facies of this magmatism have been studied in central parts of the Vardar zone and were defined as Cretaceous-Tertiary (Boev and Lepitkova, 2004). Certain facies of the Neogene volcanism within the Vardar zone have shown emphasized alkali character or they were grouped within the ultraalkaline rocks (Yanev et al., 2003).

The study of REE in Tertiary volcanic rocks at the territory of the Republic of Macedonia was

not of any systematic programme. Certain data, explaining geochemical features of volcanic rocks, could be found in Karamata et al. (1992), Serafimovski (1990), Boev (1988) etc., or REE data were presented in papers related to particular localities in the Republic of Macedonia (Serafimovski, 1993; Serafimovski et al., 2003; Tasev et al., 2005; Serafimovski et al., 2006).

## METHODOLOGY

Samples were prepared and analyzed in a batch system. Each batch contained a method reagent blank, certified reference material and 17% replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt was immediately poured into a solution of 5% nitric acid containing an internal standard, and mixed continuously until completely dissolved (~30 minutes). The samples were run for major oxides and selected trace elements on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP and Varian Vista 735 ICP. Calibration was performed using 7 prepared USGS and CANMET certified reference materials. One of the 7 standards is used during the analysis for every group of ten samples. For REE determination the sample solution prepared as mentioned above was spiked with internal standards to cover the entire mass range, then further diluted and introduced into a Perkin Elmer SCIEX ELAN 6100 ICP/MS using a proprietary sample introduction methodology. Accuracy (assessed using an in-house standard) was better than 10% for most elements.

### *Some geological features of the Tertiary magmatism*

The Cenozoic basins at the territory of the Republic of Macedonia are mainly filled in by volcanogene-sedimentary and sedimentary complexes (margin sediments – Eocene, and continental sediments in higher parts Oligocene-Miocene). The profile of Eocene sediments has been characterized by conglomerates, which interchange with flysch and terrigene-carbonaceous formations. In Oligocene dominate volcanics-quartzlatites and hornblende biotitic andesites. The Miocene volcano-sedimentary complexes include ignimbrites. The Pliocene tuffaceous series interchange with lake clays, sands and andesite breccias. The Tertiary

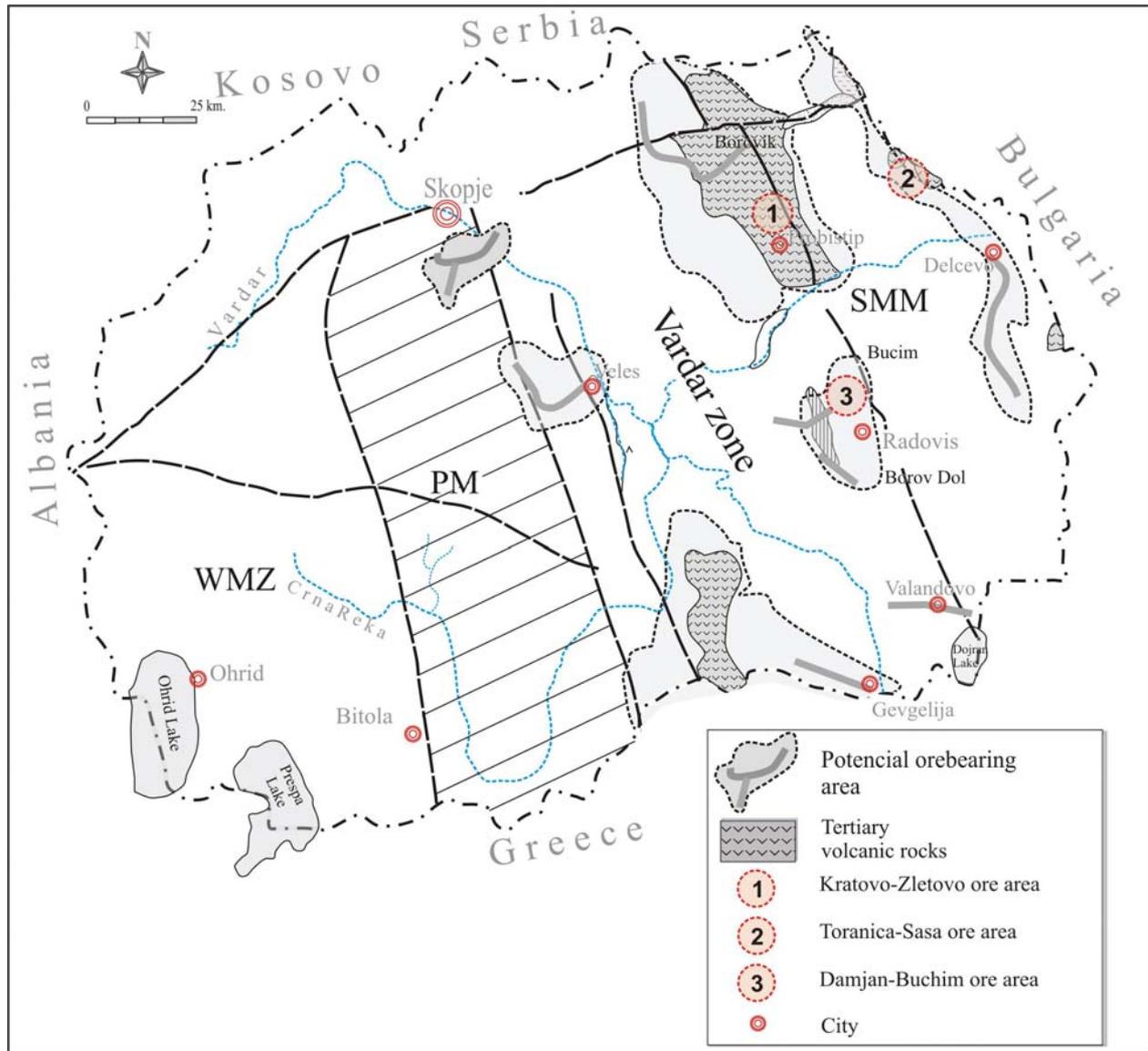
We have to point out that at the territory of the Republic of Macedonia with the Tertiary magmatism have been related numerous polymetallic deposits and occurrences of lead, zinc, copper, gold, arsenic, iron, uranium, etc., while some of them are very productive (Serafimovski et al., 2003).

magmatism in this area occurred from Oligocene up to Pliocene. The existing geochronological data are pointing to a Lower Pliocene magmatism present in a wide area within the Kratovo–Zletovo volcanic area (32–25 Ma; Fig. 1) while certain andesite dykes near the Žguri locality have shown absolute age of 16 Ma (Serafimovski, 1993) as in Bučim–Damjan–Borov Dol region (32–23 Ma; Fig. 1). Pliocene magmatism occurred within the range of 7–1.8 Ma (Boev, 1988). The most common are latites of age 5–4.5 Ma. Volcanogeno-intrusive complex composed of andesites, quartzlatites and rhyolites of Pliocene age has been localized in the southern parts of the Republic of Macedonia near to Alshar close to the Greek-Macedonian border (Boev, 1988; Janković, 1993). It can be stated that during the process of the Cenozoic activation at the territory of the Republic of Macedonia occurred three stages of magmatic pulsations in Oligocene, Miocene and Pliocene. The processes of ore mineralization formation, spatially and timely, were closely related to the occurrence of the magmatism. For example, porphyry copper mineralizations in the Bučim and Borov Dol are related to the Oligocene dykes and latite stocks. The Pliocene mineralizations in the Alshar area are closely related to the Pliocene volcanism in that area. The age of polymetallic mineralizations in the Sasa and Toranica are closely related to the latite and quartzlatite dykes intruded during the Miocene (24–17 Ma; Fig. 1). The Tertiary magmatism in the Eastern Macedonia has been located in the rim NE parts close to the border with Bulgaria in a belt wide 50–70 km. That belt has been controlled by the fissure system, which is product of the Cenozoic activation oriented under steep angle versus the Mesozoic structures in the Vardar zone. The three main fissure systems of general NW–SE have controlled the spatial distribution of volcanogeno-intrusive rocks at that territory.

## RESULTS AND DISCUSSION

The present results concerning the REE in the Tertiary volcanic rocks in the Republic of Macedonia represents the most representative volcanic

complexes, Kratovo–Zletovo volcanic area, Osogovo volcanic area and Damjan–Bučim volcanic area, localized in Eastern Macedonia (Fig. 1).



**Fig. 1.** Distribution of the Tertiary magmatism at the area of the Republic of Macedonia and position studied areas (Tasev et al., 2005; Serafimovski et al., 2006)

Within these volcanic complexes were localized even productive polymetallic mineralizations of Pb-Zn and Cu-Au. Quite often, mineralized areas were intensively hydrothermally altered, which has been confirmed by analyses of different volcanic rocks. The review of the results from studied volcanic rocks and obtained REE data has been organized by the most important regions with Ter-

tiary volcanic rocks, such as Kratovo–Zletovo, Osogovo and Damjan–Bučim.

#### *Kratovo–Zletovo*

Our first subject for this study was the Kratovo–Zletovo as the largest magmatic area in Ma-

cedonia with a surface of 1200 km<sup>2</sup>. This area is also a very important mining area with significant Pb-Zn deposits. Many authors have studied this area and their studies can be found in Stojanov (1974), Stojanov and Denkovski (1974), Serafimovski (1990), Stojanov and Serafimovski (1990b), Serafimovski (1993), etc. Volcanic deposits predominate in the area, but plutonic rocks are also be found. Effusive volcanic products are represented by latites, andesites, andesite-dacite ignimbrites, dacite. Volcanic activity, which have produced magmatic rocks described above, migrated from NW to SE direction. Some intrusive bodies also occur in Kratovo–Zletovo area. One pluton is situated near Karlukovo village and one diorite-porphyrite dyke near Borovic village (Boev and Yanev, 2001). The Karlukovo pluton is of quartz-monzonitic to monzonitic composition.

REE analyses of magmatic rocks from the Kratovo–Zletovo area were performed at the *Active Labs, Canada*. Obtained results are given in Table 1.

Table 1

*Rare earth elements content in rocks  
from the Kratovo–Zletovo ore area (ppm)*

Element	MAK-15 III	MAK-18 II	MAK-20 I	MAK-21 IV
La	58.4	32.7	50.7	28.6
Ce	106	61.1	90.4	53.9
Pr	12.1	7.35	9.98	6.25
Nd	43.6	27.5	35.2	22.8
Sm	7.7	5.4	5.9	4.3
Eu	1.79	1.40	1.34	1.13
Gd	6.1	5.0	5.0	4.1
Tb	0.8	0.8	0.7	0.7
Dy	4.2	4.5	3.7	3.8
Ho	0.8	0.9	0.7	0.7
Er	2.2	2.7	2.1	2.2
Tm	0.33	0.42	0.33	0.34
Yb	2.1	2.7	2.1	2.2
Lu	0.32	0.41	0.31	0.35

In accordance with data from Table 1, was preformed normalization of REE values versus chondrite ones, plot was constructed and illustrated on Figure 2.

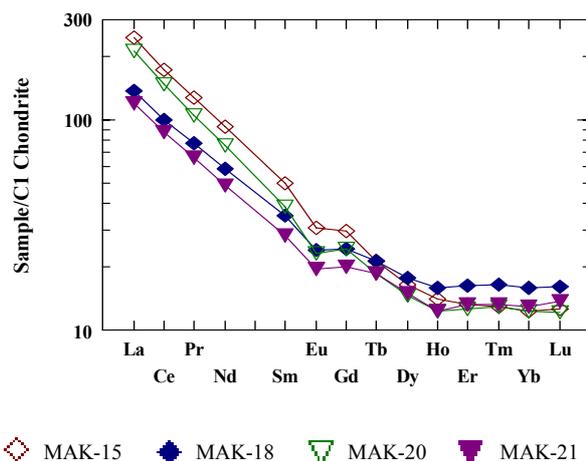


Fig. 2. Plot of normalized values of rare earth elements in comparison to those in chondrites, for rock samples from the Kratovo–Zletovo ore region

From the Figure 2 can be seen that the REE in the Kratovo–Zletovo ore area, going from left to right, exhibits a decreasing trend. Analyzing the left and right side of the plot, can be concluded that there is a decrease (right part) of heavy rare earth elements (HREE, with an atomic number higher than those of Eu or atomic number higher than 63) in comparison with light rare earth elements (LREE, with an atomic number lower than those of Eu or lower than 63). Such values are product of fractionation of light rare earth elements and their increase in comparison to the chondritic values. That fractionation occurred as a direct consequence of partial melting, which according to the angle of the line in the diagram was not of higher intensity. Analyzing the middle part of the plot can be seen that there is a slight negative Eu anomaly, which shows decreasing of Eu values compared to the “ideal” line between the Sm and Gd. Calculations of such an anomaly (using the formula given by Taylor and McLennan, 1985) are given in Table 2.

Table 2

*Values of Eu anomaly in samples  
from the Kratovo–Zletovo ore region*

Samples	Value of Eu anomaly
MAK-15 III	0.797654
MAK-18 II	0.822415
MAK-20 I	0.755663
MAK-21 IV	0.820559

From the Table 2 can be seen that Eu anomaly values are within the range from 0.755662705 to 0.822415183 or smaller than 1 confirming negative anomaly (Rollinson, 1992). Eu anomalies are mainly controlled by feldspars.  $\text{Eu}^{2+}$  is compatible in plagioclase and K-feldspar in comparison to  $\text{Eu}^{3+}$ , which is incompatible. Removal of feldspar from the melt by fractional crystallization or partial melting of rock that contained feldspar can lead to increase of negative Eu anomaly. The variations of Ba content vs. constant Rb content confirmed that fractionation of K-feldspar and amphibole is the predominant differentiation process and the Eu anomaly – the limited participation of the plagioclase in this process (Boev and Yanev, 2001).

Such character of the Eu anomalies and HREE and LREE trends in the Tertiary volcanic rocks mostly are related to the oceanic and continental arcs of Cenozoic age (Titley and Beane, 1981; Richards, 2003; Cooke et al., 2005), and occasionally to old and folded belts, while both settings are characterized by compression tectonic areas and thinned continental crust (Titley and Beane, 1981).

#### Sasa–Toranica

Volcanic and volcano-intrusive rocks in the Sasa–Toranica ore area belong to one bigger metallogenic unit, in literature known as metallogenic zone Besna Kobilica–Osogovo–Tasos, with north-west direction with total length of a 100 km, on both sides of Macedonia-Bulgaria interstate border (Serafimovski, 1990; Serafimovski, 1993; Alexandrov, 1992; Janković et al., 1995). Volcanic rocks in that zone have similar morphological, petrological and geochemical features and all of them are of Tertiary age. At the territory of the Republic of Macedonia they were determined in their marginal north-eastern parts on the state border with Republic of Bulgaria (Fig. 1). It should be mentioned that similar rocks were determined in Bulgaria also. Volcanic rocks in the area occur as elongated dykes with north-western direction, with thickness of around 50 m and azimuth of  $260^\circ$ . Composition of these rocks is mainly dacitic tuffs, dacites, quartzlatites, rhyolites, trachyandezites, andesite-latites and occasionally lamprophyre veins (Sasa and Toranica localities).

Certain samples from the Sasa–Toranica ore area were analyzed for contents of rare earth elements (REE). This type of analyses were performed

in *Active Labs, Canada*. Results obtained from this analysis are given in Table 3.

Table 3

*Rare earth elements content in rocks from the Sasa–Toranica ore region (ppm)*

Element	MAK1 I	MAK7 I	MAK9 II	MAK13 II
La	53.10	52.00	39.60	44.90
Ce	106.00	95.40	72.10	79.30
Pr	13.30	11.40	8.08	9.72
Nd	52.50	42.10	28.30	35.20
Sm	9.20	7.50	5.10	6.80
Eu	2.22	1.68	1.11	1.65
Gd	7.30	5.90	4.30	6.50
Tb	0.90	0.80	0.60	1.00
Dy	4.50	4.00	3.30	5.20
Ho	0.80	0.70	0.60	1.00
Er	2.10	2.10	1.80	2.80
Tm	0.30	0.31	0.28	0.38
Yb	2.00	2.00	1.90	2.30
Lu	0.30	0.30	0.29	0.35

In accordance with data from the table above was performed normalization of values in comparison with chondritic values and it was plotted a diagram of normalized values (Figure 3).

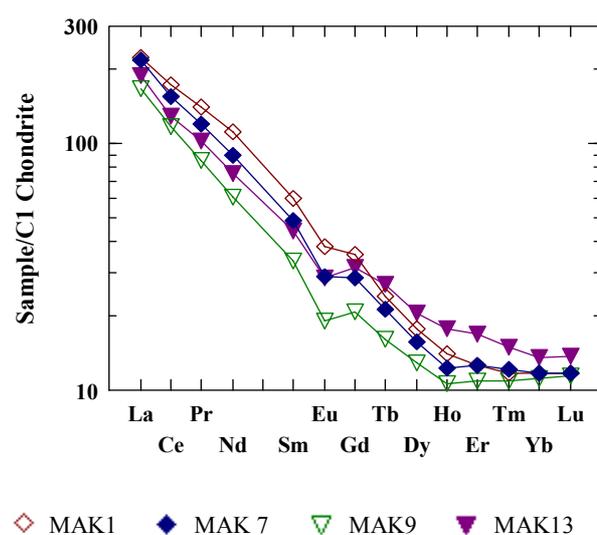


Fig. 3. Plot of normalized values of rare earth elements in comparison to those in chondrites, for rock samples from the Sasa–Toranica ore region

From the Figure 3 can be seen that the REE in the Sasa–Toranica ore region have decreasing trend. Analyzing the left and right side of the di-gramme can be concluded that there is a decrease (right part) of heavy rare earth elements (HREE, with an atomic number higher than those of Eu or atomic number higher than 63) in comparison with light rare earth elements (LREE, with an atomic number lower than those of Eu or lower than 63). Such values are product of fractionation of light rare earth elements and their increase in comparison to the chondritic values. That fractionation occurred as a direct consequence of partial melting, which according to the angle of the line in the di-gramme was not of higher intensity.

Looking closely into the middle part of the diagram it can be seen that the value of Eu, slightly and negatively, discloses from the "ideal" line between Sm and Gd or more precisely there is a negative Eu anomaly. In that direction was performed calculation of Eu anomaly, as a geometric mean value (Rollinson, 1992). Calculated values are shown in Table 4.

Table 4

*Values of Eu anomaly in samples from the Sasa–Toranica ore region*

Samples	Value of Eu anomaly
MAK-1 I	0.82891
MAK-7 I	0.77403
MAK-9 II	0.72767
MAK-13 II	0.75975

From the Table 4 it can be seen that Eu anomaly values are in range from 0.727669702 up to 0.828905716, or they are smaller than 1, which implies to the small negative Eu anomaly (Tasev, 2003; Tasev et al., 2005; Serafimovski et al., 2006). Eu anomalies, mainly, are controlled by presence of feldspars.  $\text{Eu}^{2+}$  is compatible in plagioclase and K-feldspar, in contrast to the  $\text{Eu}^{3+}$  which is incompatible. Thus the removal of feldspar from a felsic melt by crystal fractionation or the partial melting of a rock in which feldspar is retained in the source will give rise to a negative Eu anomaly in the melt.

According the data for Eu in analyzed samples and its negative anomaly it can be concluded that Eu has been removed from the melt as a com-

patible  $\text{Eu}^{2+}$ , in frame of processes of crystal fractionation or partial melting.

### *Damjan–Bučim*

The Damjan–Bučim is a small volcanic area, but it is of high metallogenic importance because it contains the large Bučim porphyry copper deposit. Many authors have studied this area (Djordjevic and Karamata, 1976; Djordjević and Knežević, 1980; Serafimovski, 1990; Čifliganec, 1993) and more of the area can be found in their investigations.  $\text{SiO}_2$  contents in volcanic rocks within the area vary from 57 to 71% and contents of all major elements gradually decrease. According to the chemical composition, the volcanic rocks vary from latites, through trachydacites-trachytes to trachyrhyolites. The latites and trachytes rocks form necks and subvolcanic bodies (e.g. the Bučim copper deposit) and lava flows associated with the central volcanoes. The trachyrhyolites form dykes. With regard to petrochemistry, unlike the Kratovo–Zletovo area, the volcanic rocks of Bučim–Borov Dol area belong to the shoshonite series only.

On certain samples from volcanic rocks sampled from the Damjan–Bučim ore area were performed analyses of rare earth elements. The results from this analysis are given in Table 5.

Table 5

*Rare earth elements content in rocks from the Damjan–Bučim ore region (ppm)*

Element	MAK-27 I	MAK-30 I	MAK-31 II	MAK-31 II rep	MAK-32 II
La	32.8	68.3	44.9	43.7	67.5
Ce	59.5	119	86.7	84.5	118
Pr	7.12	13.6	10.5	10.2	13.0
Nd	27.1	48.2	38.8	37.5	45.9
Sm	5.1	8.3	7.0	6.8	7.7
Eu	1.45	2.00	1.52	1.49	1.86
Gd	4.7	6.8	5.6	5.5	6.1
Tb	0.7	0.9	0.8	0.7	0.8
Dy	3.9	4.5	3.8	3.7	4.3
Ho	0.8	0.8	0.7	0.7	0.8
Er	2.3	2.3	1.9	1.8	2.3
Tm	0.34	0.33	0.28	0.28	0.33
Yb	2.3	2.3	1.9	1.8	2.3
Lu	0.33	0.34	0.28	0.28	0.34

Values from Table 5 were normalized versus chondritic values. In accordance with that was constructed a plot of normalized values as shown on Figure 4.

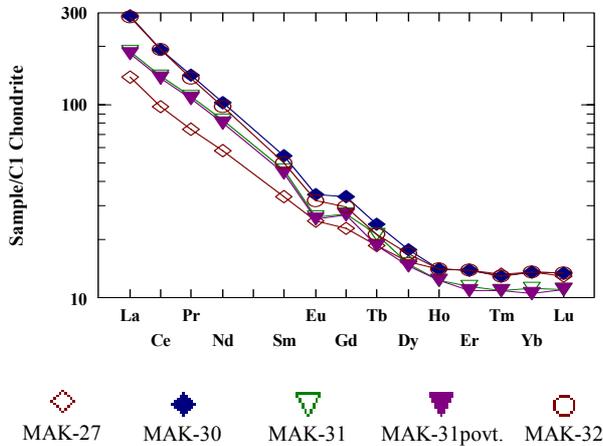


Fig. 4. Plot of normalized values of rare earth elements in comparison to those in chondrites, for rock samples from the Damjan–Buchim ore region

From the plot above it is obvious that REE's have shown decreasing trend going from left to right. Comparing left and right side of the plate we can notice that there is depletion of LREE (right side) in comparison to the HREE (left side). Analyzing the central part of the plot we have noticed that there is a slight negative Eu anomaly. In an attempt to determine an absolute value of the Eu anomaly we have calculated it, as it is shown in Table 6.

## CONCLUSION

From the results of the REE of the Tertiary volcanic rocks in the Republic of Macedonia, discussed above, can be seen that within all samples was pronounced negative Eu anomaly, which is mainly controlled by feldspars. Namely,  $\text{Eu}^{2+}$  has been compatible in plagioclase and K-feldspar in comparison to  $\text{Eu}^{3+}$ , which is incompatible. Removal of feldspar from the melt by fractional crystallization or partial melting of rock that contained feldspar led to increase of negative Eu anomaly. The variations of Ba content vs. constant Rb con-

Table 6

*Values of Eu anomaly in samples from the Damjan–Bučim ore area*

Sample	Value of Eu anomaly
MAK-27 I	0.90361
MAK-30 I	0.81331
MAK-31 II	0.74419
MAK-31 II rep	0.74089
MAK-32 II	0.82746

From the Table 6 it can be concluded that values of the Eu anomaly are in range 0.74089 to 0.90361 or they are slightly lower than 1, which point out to a negative Eu anomaly (Rollinson, 1992). As well as for previously mention ore areas, Kratovo–Zletovo and Sasa–Toranica, we may conclude that removal of feldspar from a felsic melt by crystal fractionation or eventual partial melting of a rock in which feldspar was contained could give rise to a negative Eu.

The igneous rocks of Kratovo–Zletovo and Buchim–Borov Dol areas using available trace elements data can be classified as subduction-related volcanic arc magmatic rocks (Serafimovski, 1990; Boev and Yanev, 2001). The similarity with the trace elements contents of the Buchim–Borov Dol rocks with the rocks of the active continental margins is indicated by Boev et al. (1992).

tent confirmed that fractionation of K-feldspar and amphibole is the predominant differentiation process and the Eu anomaly – the limited participation of the plagioclase in this process.

Such character of the Eu anomalies and HREE and LREE trends in the Tertiary volcanic rocks mostly are related to the oceanic and continental arcs of Cenozoic age, and occasionally to old and folded belts, while both settings are characterized by compression tectonic areas and thinned continental crust.

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## Резиме

## REE ВО НЕКОИ ТЕРЦИЕРНИ ВУЛКАНСКИ КОМПЛЕКСИ ВО РЕПУБЛИКА МАКЕДОНИЈА

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**Клучни зборови:** елементи на ретки земји (REE); Саса; Тораница; Картово; Злетово; Дамјан; Бучим; вулкански карпи; старост; терциерни

Предмет на проучување во овој труд се петролошки-те и геохемиските карактеристики на терциерните магматски карпи од Република Македонија, Презентирани се најновите податоци за K-Ar,  $^{87}\text{Sr}/^{86}\text{Sr}$ , и REE во примероци од рудните областа Кратово–Злетово, Саса–Тораница и Дамјан–Бучим. Рендгенските анализи на цели карпи ги потврдија составите на карпите како дацити, кварц-латити, трахиандезити, риолити и риодацити. Одредувањето на апсолутната старост со методот K-Ar покажа дека таа се движи од 31 до 14 Ма, потврдувајќи ја така олигоценско-миоценската старост, претходно одредена преку релативните методи. Утврдените односи  $^{87}\text{Sr}/^{86}\text{Sr}$  (0,70504 до

0,71126) сугерираат дека материјалот потекнува од контактната зона помеѓу горната мантија и долната кора, каде што се одвивала контаминација на примарниот растоп. Новите податоци за REE, вклучувајќи ги негативните аномалии на Eu, покрај претходно утврдените односи La/Yb кои се во распон од 13.3 до 43.0 (Серафимовски, 1990), ги потврдуваат заклучоците за изворот на материјалот. Овие нови податоци ги потврдуваат претходните резултати, овозможуваат увид во терциерната магматска историја на областа и го сугерира точното потекло на материјалот кој ги создал терциерните магматски карпи.

## DISTRIBUTION OF CADMIUM IN SURFACE SOILS IN K. MITROVICA REGION, KOSOVO

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**A b s t r a c t:** The results of the study of spatial distribution of cadmium in topsoil (0–5 cm) over the K. Mitrovica region, Kosovo, are reported. The investigated region (300 km<sup>2</sup>) is covered by a sampling grid of 1.4×1.4 km. In total 159 soil samples from 149 locations were collected. Inductively coupled plasma – mass spectrometry (ICP-MS) and inductively coupled plasma – atomic emission spectrometry (ICP-AES) were applied for the determination of cadmium. Data analysis and construction of the map were performed using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. It was found that the average content of Cd in the topsoil for the entire study area is 3.25 mg/kg (with a range of 0.10–46.8 mg/kg) which exceeds the estimated European Cd average of topsoil by a factor of 27. It is evident that the content of cadmium is very high in the topsoils from the areas of the lead and zinc smelter plant, as well as in the topsoils from the part of the city of K. Mitrovica. In the region of Zvečan and K. Mitrovica several topsoil samples with extremely high content of cadmium are present. The main polluted area was found that covers 5.9 km<sup>2</sup> with the average concentration of Cd is 14 mg/kg (from 12 to 47 mg/kg).

**Key words:** soil; cadmium; ICP-MS; ICP-OES; K. Mitrovica; Kosovo

### INTRODUCTION

The main sources of pollution with heavy metals are heavy industries. These heavy industries tend to increase the deposition of heavy metals in the environment. There are many different sources of heavy metal contaminants including chemical and metallurgical industries (Kabata-Pendias and Pendias, 2001). When considering these different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity (Goyer, 1996). Heavy metals are known to have adverse effects on the environment and human health. They are significantly toxic even in small amounts and can cause diseases in humans and animals as they cause irreversible changes in the body especially in the central nervous system (Goyer, 1996).

It is obvious from the articles published recently that lead and zinc mines and smelter plants activities lead to enormous soil contamination (Li et al., 2005; Li et al., 2006; Tembo et al., 2006;

Cappuyns et al., 2006; Stafilov et al., 2008, 2010). Mining and metallurgic activities in Kosovo have a long history. Trepča Mine Limited in Mitrovica was built in 1927 produced lead, arsenic and cadmium from the 1930s until 2000. The smelter close to Zvečan commenced work in 1939. Because of the smelter and three huge tailing dams of the factory, environmental pollution in Mitrovica increased dramatically. The smelter had worked sporadically since the 1999 conflict in Kosovo. However, an environmental audit ordered by UNMIK and conducted in March and April 2000, warned that it should be closed as an "unacceptable source of air pollution" (Palariet, 2003; Frese et al., 2004; OSCE, 2009).

The total production of Trepča from 1931 to 1998 is estimated at 34,350,000 t run-of-mine ore at grades of 6 % Pb, 4 % Zn, 75 g/t Ag and 102 g/t Bi. The ore was beneficiated in the Prvi Tunel (Tuneli Pare) flotation with the capacity of 760,000 t/y.

The lead concentrates were brought to the lead smelter of Zvečan (capacity 80,000 t/y), the zinc ones to the zinc smelter of Mitrovica (capacity 50,000 t/y); there was also a unit for the production of fertilizers using the sulfuric acid by-product of the hydrometallurgy, and lines of battery production and battery recycling. The metal produced was 2,066,000 t Pb, 1,371,000 t Zn, 2,569 t Ag and 4,115 t Bi. Gold production is estimated at 8.7 t from 1950 to 1985, i.e. and average of 250 kg/y; the Cd production is estimated at 1,655 t from 1968 to 1987. Traces of Ge, Ga, In, Se and Te in the run-of-mine ore have been also reported, which were valorized at the level of the smelters ((Palarriet, 2003; Frese et al., 2004; OSCE, 2009).

The effect on the environment of mines and mining industries in Kosovo is difficult to ascertain

as little data exist since 1999. The problems are wide from hazardous material to air/soil/water pollution. Several reports indicate that current levels of lead exposure were extremely high in soil and in the air as well (Di Lella et al., 2003; Jia et al., 2004; Arditsoglou and Samara 2005; Prathumratana et al., 2008; Borgna et al., 2009).

The main objectives of the present investigation were to determine the content of cadmium, very toxic element which minerals are always present in the lead and zinc minerals (Lieber, 1973, 1975; Féraud, 1974, 1979; Dušanić et al., 1982; Pruthi and Kastrati, 2002; Monthel et al., 2002), to establish its spatial distribution in soils from the broad area of K. Mitrovica (Figs. 1 and 2) and to assess the size of the area affected by the smelter plant situated nearby.

## MATERIAL AND METHODS

### Study area

The Kosovska Mitrovica (Figs. 1 and 2) is a city located in the north of Kosovo (Fig. 1) approximately 40 kilometers north of Priština (capital of Kosovo). It is bordered by Vučitrn and Serbia to the south, Zvečan and Zubin Potok to the west and Podujevo to the east. The complete investigated region (300 km<sup>2</sup>) was covered by a sampling grid of 1.4 × 1.4 km<sup>2</sup> (Fig. 2).

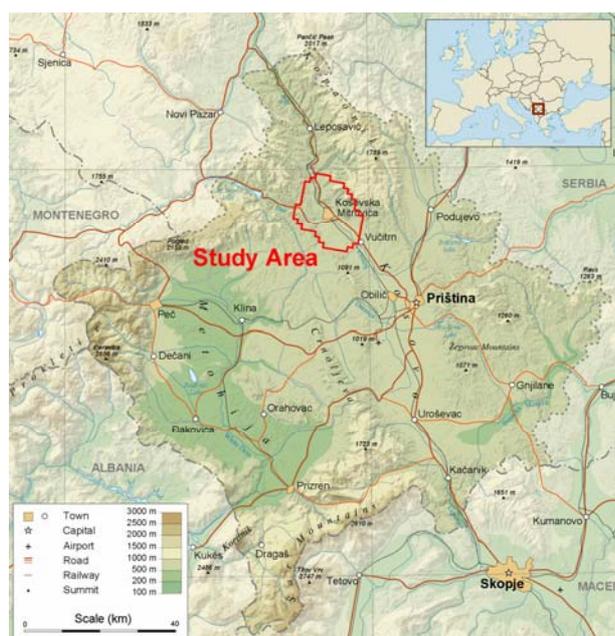


Fig. 1. Location of the study area

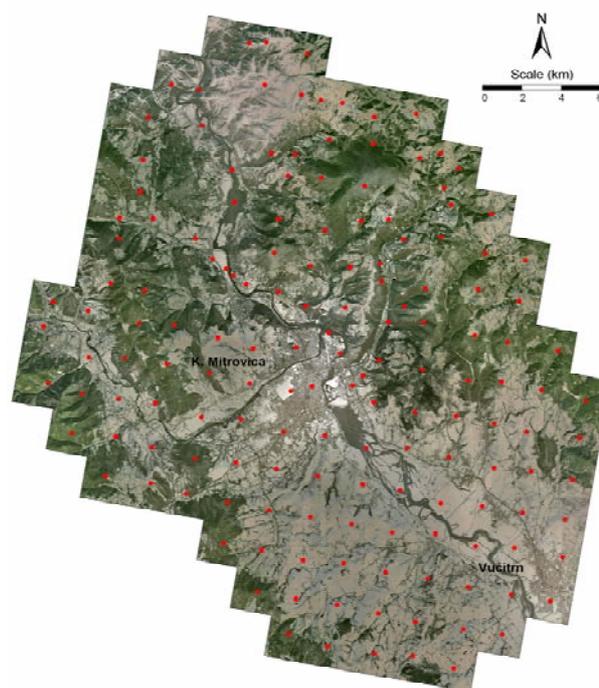


Fig. 2. Sampling locations

### Sampling

The sampling is done from January to May 2009. Surface soil samples (0 cm to 5 cm depth) were collected in the town of Mitrovica and surrounding region (Fig. 2). In total 159 samples were collected from 149 locations, including locations near mining centers of K. Mitrovica. The samples were located using Global Positioning System

(GPS) and topographic maps at scale of 1:25,000. One sample represents the composite material collected at the central sample point itself and at least four points with the radius of 10 m around it towards N, E, S and W. The composite of each sample (about 1 kg) was placed into plastic self-closing bags and bring to the laboratory for atomic spectroscopy at the Institute of Chemistry, Faculty of Science, the University of Skopje, Republic of Macedonia, where they were prepared for analysis.

#### *Sample analysis*

After being returned to the laboratory, soil samples were air dried, crushed, cleaned from extraneous material and sieved through a plastic sieve with 2 mm mesh. The sieved mass was quartered and milled in agate mill. 0.5 g of each sample was used for digestion with HNO<sub>3</sub> (Tracepur, 69% m/V, Merck), HF (Tracepur, 48% m/V, Fluka), HClO<sub>4</sub> (*p.a.*, 70% m/V, Alkaloid) and HCl (Tracepur, 36% m/V, Merck) according to ISO 14869-1:2001(E) method.

Procedure: Weigh precisely 0.500 g of the milled soil sample and placed in a teflon digestion vessel and add 10 ml of nitric acid. Place the dish on the asbestos net plate at ring at 100 °C and evaporate until approximately 1 ml of nitric acid remains. Note that several successive additions of nitric acid may be necessary until the emission of nitrous vapors ceases to remove all organic matter. After the last addition of nitric acid, remove the dish from the hot plate and cool to room temperature before undertaking the digestion. After cooling add 10 ml hydrofluoric acid and 3 ml of perchloric acid to the pretreated portion. Heat this mixture on the hot plate until the dense fumes of

perchloric acid and silicon tetrafluoride cease. Do not allow the mixture to evaporate to complete dryness. Remove the vessel from the hot plate allow cooling, adding 2 ml of hydrochloric acid or 2 ml of nitric acid and approximately 5 ml of water to dissolve the residue. Transfer this solution quantitatively to the 50 ml volumetric flask, fill to the mark and mix well.

#### *Preparations of solutions*

Stock standard Cd solution (1000 mg/l) supplied by Merck was used for calibration. Working standards were prepared by appropriate diluting of stock solution. During the preparation and measurements great care was taken to prevent contaminating any of the solutions. Deionized water was always used for the dilutions and for final rinsing of glassware. The concentrations of standard solutions for calibration are 1 µg/ml, 10 µg/ml and 200 µg/ml. All the chemicals used were of analytical reagent grade.

#### *Instrumentation*

An optical emission spectrometer with inductively coupled plasma, ICP-OES (Varian 715-ES), was employed to determine Cd concentration using argon plasma. The instrumentation and operating conditions for this ICP-AES system are given in Table 1. Also all collected soil samples were shipped to ACM Analytical Laboratory in Vancouver, Canada. Analyses were conducted using mass spectrometry with inductively coupled plasma (ICP-MS) after Aqua Regia Digestion (1DX1 and DISP2 method).

## RESULTS AND DISCUSSION

Data from the descriptive statistics of measurements of cadmium by both techniques (ICP-MS and ICP-AES) in topsoil from whole investigated region are given in Table 2 and its spatial distributions with the results obtained by ICP-MS and ICP-AES are presented on Figs. 3 and 4, respectively. As it can be seen, in general the obtained average and median values obtained by ICP-MS are low than those obtained by ICP-AES. Namely, the correlation factor between the results from both methods are 0.94 (for normal distribution), 0.73 (for logarithmic) and 0.72 (for rank). The reason for these differences is the limit of detection of

ICP-AES (1.0 mg/kg) which lead in statistical calculation to higher average and median values (missing values below 1.0 mg/kg). On Fig. 5 the logarithmic correlation between both data sets is given.

The average amount of Cd in soils in the world is 0.35 mg/kg (Bowen, 1979), in the European topsoil is 0.12 mg/kg (Salminen et al., 2005). The average amount of Cd in the topsoil for the entire study area is 3.25 mg/kg, with a range of 0.10–46.8 mg/kg (Table 1). This means that the Cd average for the whole area exceeds the estimated European Cd average of topsoil by a factor of 27.

It is evident from the obtained results (Table 2, Figs. 3 and 4) that the content of cadmium is very high in the topsoils from the areas of the lead and

zinc smelter plant, as well as in the topsoils from the part of the city of K. Mitrovica (Fig. 6).

Table 1

*Instrumentation and operating conditions for ICP-AES system*

RF generator			
Operating frequency	40.68 MHz free-running, air-cooled RF generator.		
Power output of RF generator	700–1700 W in 50 W increments		
Power output stability	Better than 0.1%		
Introduction area			
Sample nebulizer	V- groove		
Spray chamber	Double-pass cyclone		
Peristaltic pump	0–50 rpm		
Plasma configuration	Radially viewed		
Spectrometer			
Optical arrangement	Echelle optical design		
Polychromator	400 mm focal length		
Echelle grating	94.74 lines/mm		
Polychromator purge	0.5 l min <sup>-1</sup>		
Megapixel CCD detector	1.12 million pixels		
Wavelength coverage	177 nm to 785 nm		
Wavelength for Cd measurement	214.439 nm		
Conditions for program			
<i>RFG power</i>	1.0 kW	Pump speed	25 rpm
Plasma Ar flow rate	15 L min <sup>-1</sup>	Stabilization time	30 s
<i>Auxiliary Ar flow rate</i>	1.5 L min <sup>-1</sup>	Rinse time	30 s
Nebulizer Ar flow rate	0.75 L min <sup>-1</sup>	Sample delay	30 s
Background correction	Fitted	Number of replicates	3

Table 2

*Descriptive statistics of measurements for cadmium in soil (values given in mg/kg)*

Technique	<i>N</i>	<i>Dis.</i>	<i>X</i>	<i>s</i>	<i>Xg</i>	<i>sg</i>	<i>Md</i>	<i>P</i> <sub>10</sub>	<i>P</i> <sub>90</sub>	Min	Max
AES-MS	156	Log	3.25	5.25	1.64	3.05	1.40	0.40	10.0	0.10	46.8
AES-ICP	157	Log	5.5	4.4	4.5	1.8	4.3	2.1	10	1.0	43.0

*N* – number of observation; *Dis.* – distribution (Log – lognormal); *Md* – median; *X* – arithmetical mean, *Xg* – geometrical mean; *s* – arithmetical standard deviation; *sg* – geometric standard deviation; Min – minimum; Max – maximum; *P*<sub>10</sub> – 10 percentile; *P*<sub>90</sub> – 90 percentile.

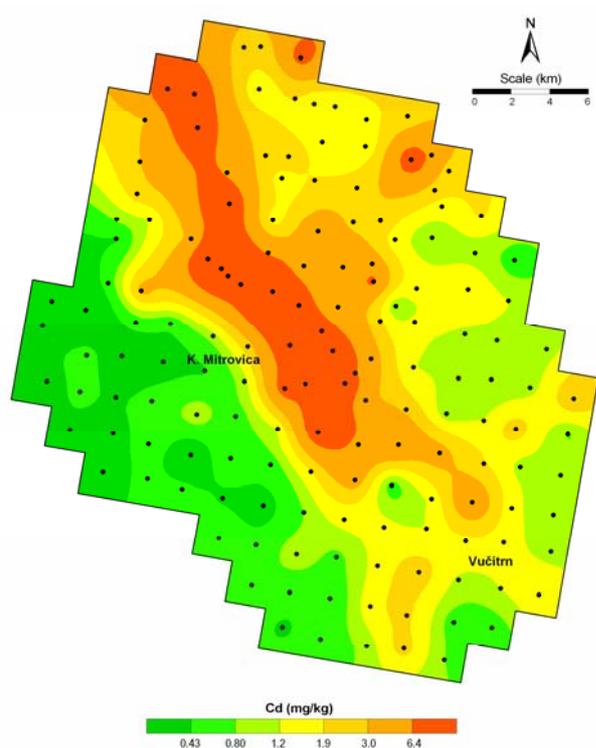


Fig. 3. Spatial distribution of cadmium in K. Mitrovica area from the results obtained by ICP-MS

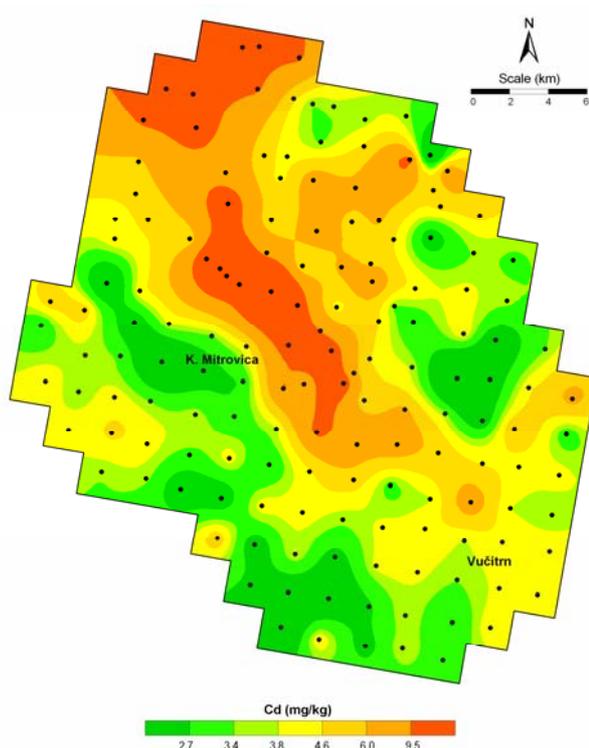


Fig. 4. Spatial distribution of cadmium in K. Mitrovica area from the results obtained by ICP-AES

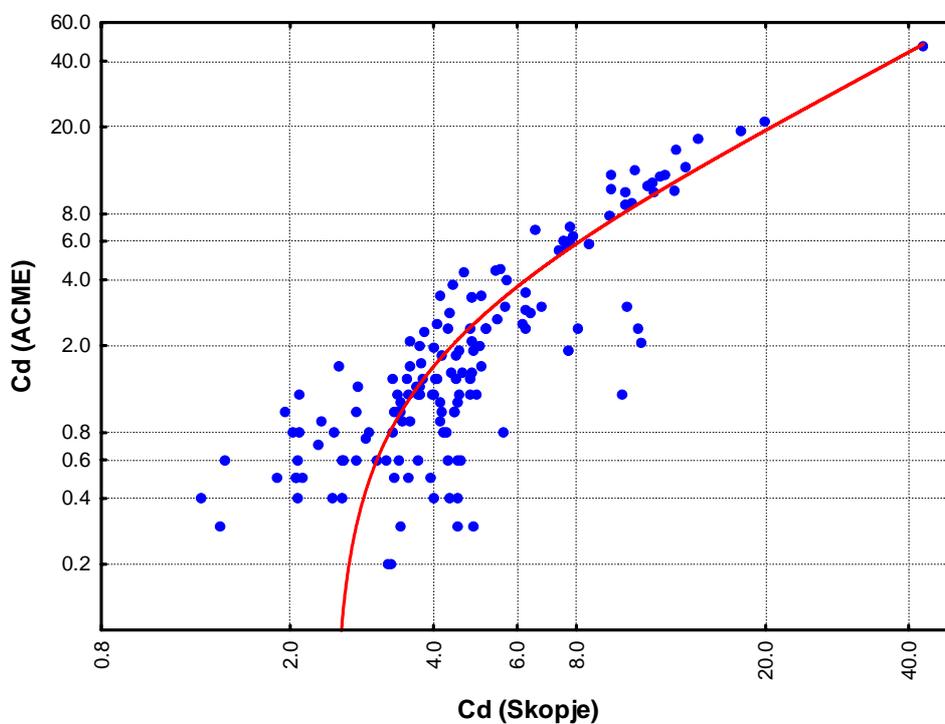
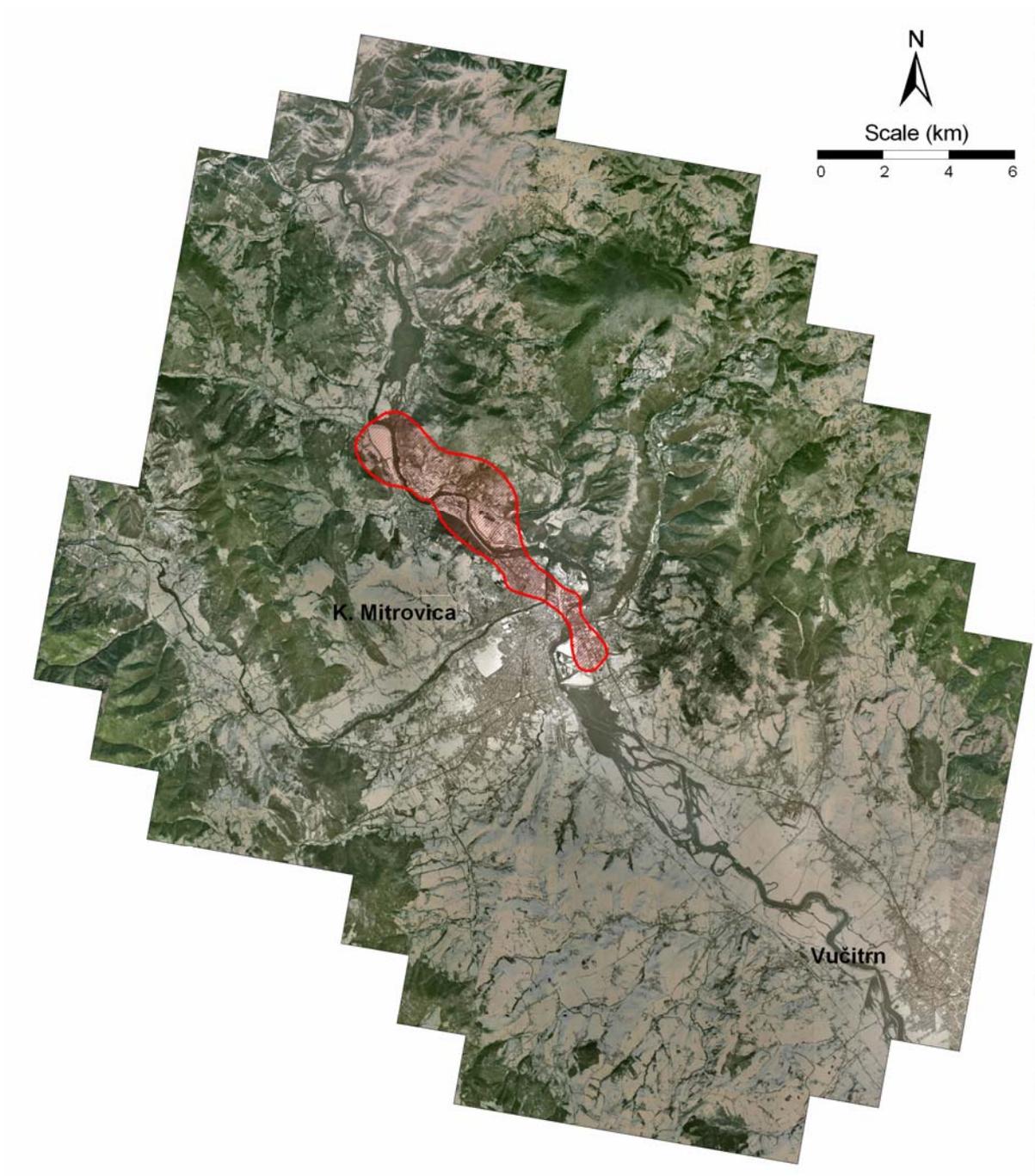


Fig. 5. Scatter-plot diagram between data obtained for Cd by ICP-MS (ACME) and ICP-AES (Skopje)



**Fig. 6.** Critically polluted topsoil with cadmium in K. Mitrovica area according to New Dutchlist

In the region of Zvečan and K. Mitrovica several topsoil samples with extremely high content of cadmium are present. It should be noted that sample No. 93 with the content of 46.8 mg/kg is 390 times higher than the European topsoil average of 0.12 mg/kg (Salminen et al., 2005). The main polluted area was established by marking the sites with the content over the intervention value of 12 mg/kg according to New Dutchlist (<http://www.contaminatedland.co.uk/std-guid/dutch-l.htm>). It was found that this main polluted area covers 5.9 km<sup>2</sup> (Fig. 6)

with the average Cd of concentration 14 mg/kg (from 12 to 47 mg/kg) which is more than 110 times higher than the European Cd average (Table 3).

**Table 3**

*Statistical data for the main polluted are*

	Area	Average	Min	Max
Cd	5.9 km <sup>2</sup>	14 mg/kg	12 mg/kg	47 mg/kg

## CONCLUSION

The results of the study of spatial distribution of cadmium in topsoil (0–5 cm) over the K. Mitrovica region, Kosovo, show that the average content of Cd in the topsoil for the entire study area is 3.25 mg/kg (with a range of 0.10–46.8 mg/kg) which exceeds the estimated European cadmium average by a factor of 27. It is evident that the content of cadmium is very high in topsoils from the

areas of the lead and zinc smelter plant, as well as in the topsoils from the part of the city of K. Mitrovica. In the region of Zvečan and K. Mitrovica several topsoil samples with extremely high content of cadmium are present. The main polluted area was found that covers 5.9 km<sup>2</sup> with the average Cd of concentration 14 mg/kg (from 12 to 47 mg/kg).

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The New Dutch List (<http://www.contaminatedland.co.uk/std-guid/dutch-l.htm>)

## Резиме

### ДИСТРИБУЦИЈА НА КАДМИУМ ВО ПОЧВИТЕ ВО РЕГИОНОТ НА К. МИТРОВИЦА, КОСОВО

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**Клучни зборови:** почва; кадмиум; ICP-MS; ICP-OES; К. Митровица; Косово

Во трудот се презентирани резултатите од испитувањата на дистрибуцијата на кадмиумот во површинските почви (0–5 cm) од областа на К. Митровица, Косово. На целото испитувано подрачје (300 km<sup>2</sup>) поставена е мрежа за земање примероци од 1,4×1,4 km. Земени се вкупно 159 примероци почва од 149 локации. Определувањето на кадмиумот е извршено со примена на масената спектрометрија со индуктивно спрегната плазма (ICP-MS) и атомска емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES). Обработката на податоците и изработката на картите на дистрибуција е извршена со примена на софтверите Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map

(ver. 2008) и Surfer (ver. 8.09). Утврдено е дека средната вредност на содржината на кадмиумот во почвите од испитуваното подрачје изнесува 3,25 mg/kg (од 0,10 до 46,8 mg/kg), што ја надминува средната вредност за содржината на кадмиумот во почвите од Европа за 27 пати. Најдено е дека содржината на кадмиумот е многу висока во површинските почви во околината на топилницата за олово и цинк, како и во почвите во дел од градот. Во областа на Звечан и К. Митровица неколку примероци од почвите имаат екстремно високи содржини на кадмиум. Областа со најголемо загадување опфаќа површина од 5,9 km<sup>2</sup> со средна вредност за Cd од 14 mg/kg (од 12 до 47 mg/kg).

## ATMOSPHERIC POLLUTION WITH COPPER AROUND THE COPPER MINE AND FLOTATION, "BUČIM", REPUBLIC OF MACEDONIA, USING BIOMONITORING MOSS AND LICHEN TECHNIQUE

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**A b s t r a c t:** This paper has studied the atmospheric pollution with copper due to copper mining and flotation "Bučim" near Radoviš, Republic of Macedonia. The copper ore and ore tailings continually are exposed to open air, which occur winds carry out the fine particles in to atmosphere. Moss (*Hyloconium splendens* and *Pleurozium schreberii*) and lichen (*Hypogymnia physodes* and *Parmelia sulcata*) samples were used for biomonitoring the possible atmospheric pollution with copper in the mine vicinity. Moss and lichen samples were digested by using of microwave digestion system and copper was analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES). The obtained values for the content of copper in moss and lichen samples were statistically processed using the nonparametric and parametric analysis. Maps of areal deposition of copper show an increase content of copper in the vicinity of mine, but long distance distribution of this element is not established yet.

**Key words:** air pollution; copper; copper mine; biomonitoring; Bučim; Macedonia

### INTRODUCTION

Mine and flotation activities lead to large amounts of waste material (Salomons, 1995; Dudka et al., 1997). Most serious consequence in atmospheric terms is acid deposition, which removes other pollutants in contact within chemical reactions (Repley et al., 1996; Sengupta, 1993). Copper founds in environment as an essential element, but increase content lead to its toxicity (Flemming and Trevors, 1989).

Very useful technique for determining atmospheric pollution with copper and other heavy metals, in different geographical areas, has proved biomonitoring with different bioindicators (Buse et al., 2003; Stamenov, 2002; Frontasyeva, 2004; Coşkun, 2005; Culikov, 2005; Ermakova, 2004; Harmens et al., 2008; Markert et al., 2003). Mosses and lichen despite of all disadvantages represent suitable bioindicators, due to their occurrence in almost all terrestrial ecosystems and ability to tol-

erate long periods of extreme environmental condition (Gjengedal and Steinnes, 1990; Aceto et al., 2003; Bargagli, et al., 2002; Loppi and Bonini, 2000). In addition, moss and lichen elemental content can be converted into atmospheric deposition values, provided metal uptake efficiency had been previously estimated in the species used as a bioindicators (Čeburnis et al., 1999; Wolterbeek, 2002).

In the Republic of Macedonia the first systematic study for atmospheric pollution with heavy metals using moss technique was undertaken in order to assess the general situation regarding heavy metal pollution and to jointly report these results to the European Atlas of Heavy Metal Atmospheric Deposition issued by UNECE ICP Vegetation (Barandovski et al., 2006, 2008). In the eastern part of the country the appearance of increase content of copper in air is related to a presence of copper mine and flotation "Bučim" near

the city of Radoviš. In this area there has been determined also an influence from the former iron mine, Damjan (Serafimovski et al., 2005).

The Bučim mine is in operation from 1980 and process about 4 million tons of ore annually. The deposit is a porphyry copper type deposit and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites (Serafimovski et al., 1995). The open ore body is approximately 500 m in diameter and 250 m in vertical extent, which actually allows direct exposure of ore particles to the atmosphere. The content of copper in ore is at on the average of 0.3 % Cu. Characteristic

metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite (Serafimovski et al., 1996; Alderton et al., 2005). Ore is concentrating by flotation on site and tailings are disposed to a dam in an adjacent valley near village Topolnica. Therefore, it was found that it is important to investigate the atmospheric pollution with copper due to copper mining and flotation “Bučim”. For that purpose, moss and lichen biomonitoring was applied. Moss and lichen samples were digested by using of microwave digestion system and copper was analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES).

## STUDY AREA

The study area is located in eastern part of the Republic of Macedonia (Fig. 1), with largeness of 20 km (W-E) × 20 km (S-N), total 400 km<sup>2</sup>, which is limited with coordinates N: 41°32' – 41°44' and E: 22°15' – 22°30'. The copper mine Bučim is located in the centre of the study area, concerning 10 km air line north-west from town Radoviš and 16

km air line south-east from town Štip. The region is characterized by moderate continental climate. Most frequent winds in the region are wind from west with frequency 199 ‰ and 2.7 m s<sup>-1</sup> speed wind from the east to the 124 ‰ frequency and 2.0 m s<sup>-1</sup> speed, which is important for the distribution of atmospheric dust with copper contained.

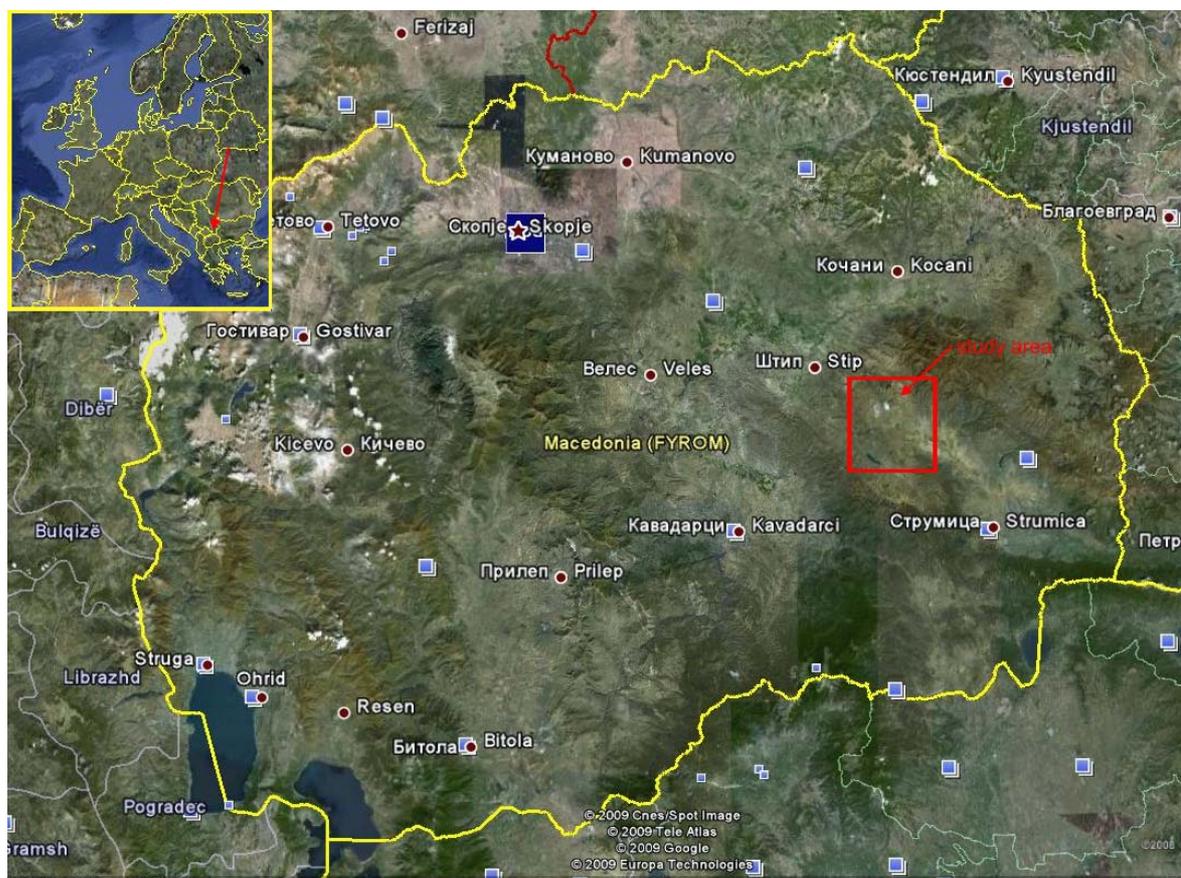


Fig. 1. Study area

## EXPERIMENTAL

*Sampling*

The collection of moss samples was performed according to the protocol adopted within the European Heavy Metal Survey. The networks for moss and lichen species collection are given in Figs. 2 and 3. In the study area the dominant moss species were *Hyloconium splendens* (Hedw.) and *Pleurozium schrebery* (Brid.). As dominant lichen species were *Hypogymnia physodes* (Nyl.) and *Parmelia sulcata* (Tayl.). Moss samples were collected at 52 localities, alongside with lichen spe-

cies, collected at 50 localities in period of November 2008 to March 2009. The sampling protocol was in this order: one sampling spot is formed by collecting five sub-spots in area of  $50 \times 50 \text{ m}^2$ . Every spot of sampling network was in a distance of minimum 300 m from main roads, 100 m from local roads, and 200 m from villages. Collected material was stored in paper bags and air dried. After drying the moss species were cleaned from other plant species and soil. In thus way prepared, moss species were ready for digestion.

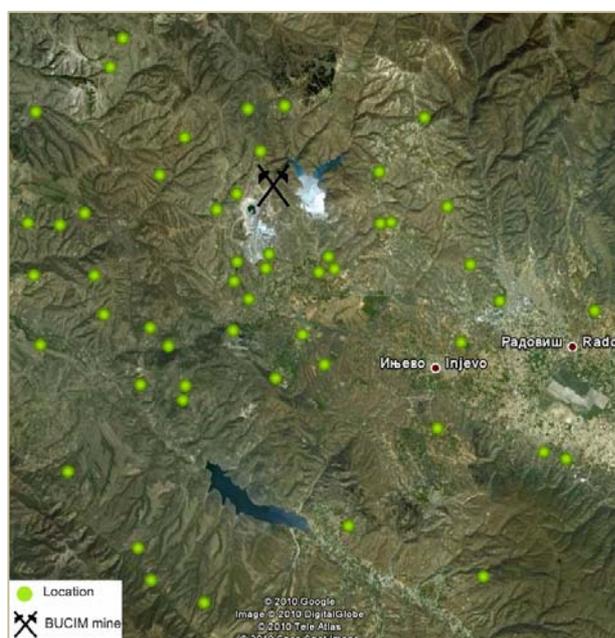


Fig. 2. Moss sampling network

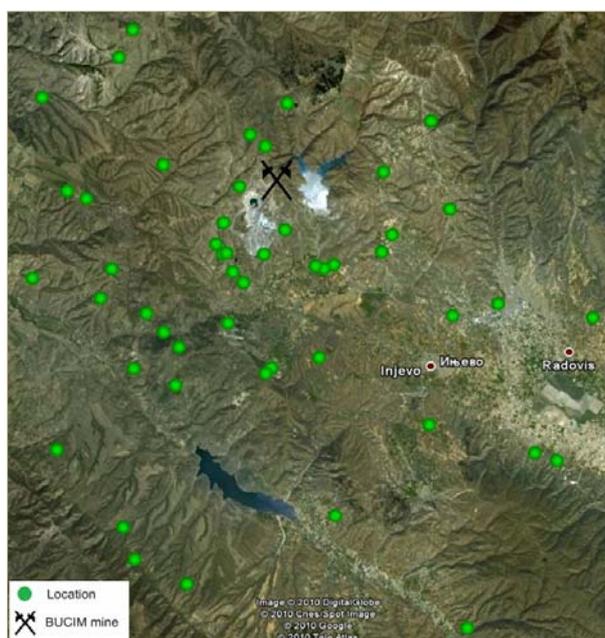


Fig. 3. Lichen sampling network

*Sample preparation*

For digestion of moss and lichen samples microwave digestion system was applied. Precisely measured mass of samples (0.5 g) were placed in teflon digestion vessels, 5 ml concentrated nitric acid,  $\text{HNO}_3$  and 2 ml hydrogen peroxide,  $\text{H}_2\text{O}_2$  (30%,  $\text{m V}^{-1}$ ) were added and the vessels were closed, tightened and placed in the rotor of a microwave digestion system (Mars, CEM, USA). The digestion was carried out with two steps program: 1 step (ramp) and 2 step (hold): temperature  $180^\circ\text{C}$ , 5 min ramp time, with power of 500 W and 20 bar pressure. Finally the vessels were cooled, carefully opened, and digests quantitatively transferred to 25 ml calibrated flasks.

*Reagents and standards*

For this study reagents with analytical grade or better were used for preparation of all solutions: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and redistilled water. Standard solutions of metals were prepared by dilution of  $1000 \text{ mg l}^{-1}$  solutions (11355-ICP multi Element Standard).

*Instrumentation*

The content of copper in moss and lichen samples was analyzed by atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian, 715ES). The operating instrumental conditions are given in Table 1.

Table 1

*Instrumentation and operating conditions for ICP-AES system*

RF generator			
Operating frequency	40.68 MHz free-running, air-cooled RF generator.		
Power output of RF generator	700–1700 W in 50 W increments		
Power output stability	Better than 0.1 %		
Introduction area			
Sample nebulizer	V- groove		
Spray chamber	Double-pass cyclone		
Peristaltic pump	0–50 rpm		
Plasma configuration	Radially viewed		
Spectrometer			
Optical arrangement	Echelle optical design		
Polychromator	400 mm focal length		
Echelle grating	94.74 lines/mm		
Polychromator purge	0.5 l min <sup>-1</sup>		
Megapixel CCD detector	1.12 million pixels		
Wavelength coverage	177 nm to 785 nm		
Wavelength for Cu measurement	324.754 nm		
Conditions for program			
<i>RF power</i>	1.0 kW	Pump speed	25 rpm
Plasma Ar flow rate	15 l min <sup>-1</sup>	Stabilization time	30 s
<i>Auxiliary Ar flow rate</i>	1.5 l min <sup>-1</sup>	Rinse time	30 s
Nebulizer Ar flow rate	0.75 l min <sup>-1</sup>	Sample delay	30 s
Background correction	Fitted	Number of replicates	3

## RESULTS AND DISCUSSION

The descriptive statistic of analyzed element is shown in Table 2. Normality tests were compared with histograms of distribution for the content of copper in moss and lichen samples, the normality was assumed on the bases of the loga-

rithms of contents in moss and lichen samples. Median values for copper contents were compared with the median values for the same element for the entire territory of Republic of Macedonia.

Table 2

*Descriptive statistic of measurements for Cu content in moss and lichen samples*

Biomonitor	<i>n</i>	Dis	$X_a$	$X_g$	Md	min	max	P <sub>10</sub>	P <sub>90</sub>	Var	s	CV	A	E
Moss	52	log	20.7	11.5	9.95	2.14	198	3.75	54.0	1141	33.8	163	3.69	15.6
Lichen	50	log	12.1	7.8	6.85	1.50	134	3.55	23.5	369	19.2	159	5.47	34.3

Dis – distribution (log – lognormal);  $X_a$  – arithmetical mean;  $X_g$  – geometrical mean; Md – median; min – minimum; max – maximum; P<sub>10</sub> – 10 percentile; P<sub>90</sub> – 90 percentile; Var – variance; s – standard deviation; CV – coefficient of variance; A – skewness; E – kurtosis

From descriptive statistic, median values for copper show deviation, compared with medians for this element for whole territory of Macedonia 22 mg kg<sup>-1</sup> for Cu (Barandovski et al., 2008), Table 3.

Smaller median for Cu was not expected in this area, because of the influence of copper mine. However, the range of values shows much higher copper content in the moss and lichen samples.

Table 3

Comparison of median values of element content in moss and lichen between data of present work and data for whole territory of Macedonia (given in  $\text{mg kg}^{-1}$ )

Biomontior	Study area (present work)				Republic of Macedonia (Barandovski et al., 2008)	
	Whole area		Mine and flotation area		Median	Range
	Median	Range	Median	Range		
Moss	10	2.1–198	91.0	29.2–198	22	3–83
Lichen	7.0	1.5–134	24.5	20.4–134	–	–

The logarithmic values were used for normalization, because of the curved distribution, and the big difference of the median and arithmetical mean.

The obtained values for copper content in lichen, compared with appropriate values from moss samples, show lichen less uptake retention of copper (Table 3). This is probably because the particle absorption in lichen is influenced by acid precipitation which is characteristic for this study area, due to present acid mine drainage (Conti and Cecchetti, 2001; Pandey et al., 2007). Comparative analysis of median values for copper content in moss samples obtained from the present work with median values of copper content for whole territory of Republic of Macedonia ( $22 \text{ mg kg}^{-1}$ ), confirms that the atmospheric dust distribution is of short range (Table 3). Concerning the median value for copper content from moss samples collected near mine

and flotation plant, it can be seen (Table 3) that the atmospheric pollution with copper is 4 times higher ( $91 \text{ mg kg}^{-1}$ ), in terms of median value for the country and for the whole study area ( $10 \text{ mg kg}^{-1}$ ). Distribution of copper in the study area was present using Google Earth program software. From the obtained maps (Figs. 4 and 5) it can be seen that the copper content in moss and lichen samples collected in the close vicinity of the mine are much higher than in the samples from the surrounding (more than 9 times). From the obtained results it can be concluded that the pollution of the atmosphere with copper is only present in the very close vicinity of the copper mine and flotation plant and flotation tailings deposit. Higher content of copper in moss and lichen samples was found near the villages Bučim and Topolnica, which could be assumed as most polluted settlements, from aspect of risk for human health.

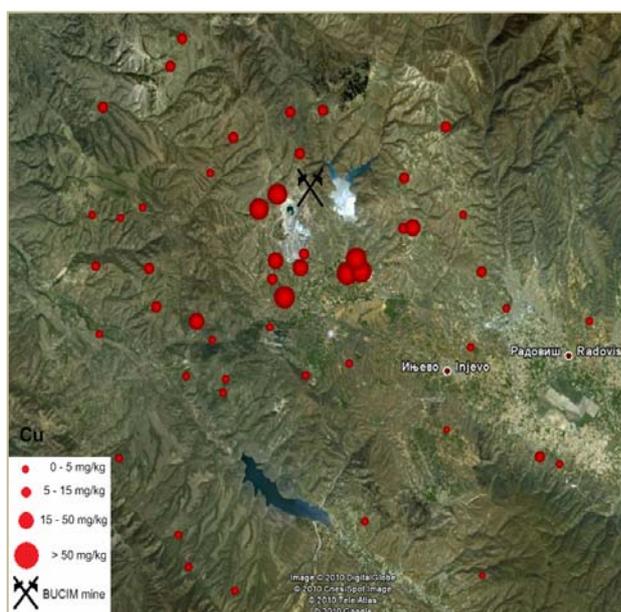


Fig. 4. Map of areal deposition of copper from moss samples

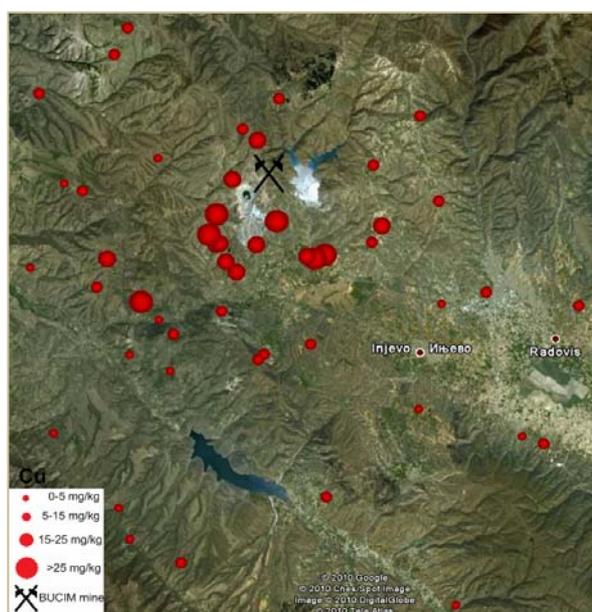


Fig. 5. Map of areal deposition of copper from lichen samples

## CONCLUSION

The mining and flotation plant activities, as well as the flotation tailings from Bučim mine, near Radoviš, Republic of Macedonia, was investigated by using moss and lichen biomonitoring. It was found that the copper content in moss and lichen samples collected in the close vicinity of the

mine are much higher than in the samples from the surrounding (more than 9 times). The highest values for copper content in moss and lichen samples were found near the villages Bučim and Topolnica, because of appearance of adverse effects on human health and environment.

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## Резиме

## ЗАГАДУВАЊЕ НА ВОЗДУХОТ СО БАКАР ВО ОКОЛИНАТА НА РУДНИКОТ И ФЛОТАЦИЈАТА ЗА БАКАР „БУЧИМ“, РЕПУБЛИКА МАКЕДОНИЈА, СО ПРИМЕНА НА БИОМОНИТОРИНГ СО МОВОВИ И ЛИШАИ

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**Клучни зборови:** загадување на воздухот; бакар; рудник за бакар; биомониторинг; Бучим; Македонија

Во трудот се презентирани резултатите од извршените испитувања на атмосферското загадување во околината на рудникот и флотацијата за бакар „Бучим“ близу Радовиш, Република Македонија. Изложеноста на рудничката и флотационата јаловина на воздух и влага доведува до појава на повисоки содржини на бакар во околината. Во студијата е применет биомониторинг со мовови и лишайи, а определувањето на бакарот е вршено со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма. Целта на испитувањето е да се утврди областа на загадувањето на воздухот со бакар, кое може да се очекува како резултат на активностите на рудникот и флотацијата. За таа цел се земени примероци мов од 52 локации, како и примероци лишайи од 50 локации во испитуваниот регион. Добиените резултати покажуваат значи-

телно високи вредности на содржината на бакар во примероците од мов и лишай земени од поблиската околина на рудникот „Бучим“. Вредностите на медијаната за содржината на Си во примероците мов од целата испитувана област ( $10 \text{ mg kg}^{-1}$ ) се пониски од онаа за целата територија на Република Македонија ( $22 \text{ mg kg}^{-1}$ ), што укажува на тоа дека поширокиот регион не е засегнат од работата на рудникот. Ако се споредат, пак, вредностите на медијаната за содржината на бакар во мововите земени во непосредната околина на рудникот и флотацијата со медијаната за бакар за Македонија, се добива фактор на зголемување од околу 5 пати ( $91 \text{ mg kg}^{-1}$ ). Изработените карти на депозиција го потврдуваат фактот за влијанието на активностите во рудникот врз загадувањето на воздухот во блиската околина на рудникот.

## DISTRIBUTION OF COBALT IN SOIL FROM KAVADARCI AND THE ENVIRONS

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**A b s t r a c t:** The results of the study of spatial distribution of cobalt in surface soil and subsoil over of the Kavadarci region, Republic of Macedonia, are reported. From the investigated region (360 km<sup>2</sup>) in total 344 soil samples from 172 locations were collected. At each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and subsoil soil (20–30 cm). Inductively coupled plasma – mass spectrometry (ICP-MS) was applied for the determination of cobalt. Data analysis and construction of the map were performed using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. It was found that for both topsoil and subsoil the median and average values are 15 mg/kg, ranges between 6.7 and 58 mg/kg. The highest content of cobalt is present in the soil from the area of Paleozoic and Mesozoic rocks (Pz-Mz) on the western part of the investigated area and Flysch (E) – Eocene upper flysch zone (on the northern part) and the lowest in the soils from the Holocene alluvium of the rivers Crna Reka and Vardar. There are no significant differences between the surface and subsoil in terms of its average quantities. It was found that the critically high contents are related primarily to high contents of cobalt in the sampling points from the western part of the investigated region. The contents of cobalt are higher in subsoil than in topsoil from which it can be concluded that the occurrence is natural.

**Key words:** soil; cobalt; pollution; Kavadarci; Republic of Macedonia

### INTRODUCTION

Soils differ widely in their properties because of geologic and climatic variation over distance and time. Even a simple property, such as the soil thickness, can range from a few centimeters to many meters, depending on the intensity and duration of weathering, episodes of soil deposition and erosion, and the patterns of landscape evolution. Beside this, soils have a unique structural characteristic that distinguishes them from mere earth materials and serves as a basis for their classification: a vertical sequence of layers produced by the combined actions of percolating waters and living organisms (Kabata-Pendias and Pendias, 2001). The presence of substances in soil that are not originated from naturally processes is of great public concern. Many of these chemicals have been

found to be carcinogens or may accumulate in the environment with toxic effects on the ecosystems. Although human exposure to these substances is primarily through inhalation or drinking water, soils play an important role because they affect the mobility and biological impact of these toxins.

The abundance of heavy metals in soil has been increased dramatically by the accelerated rate of extraction of minerals and fossil fuels and by highly technological industrial processes. Most of the metals were typically found at very low total concentrations in pristine waters – for this reason they often are referred to as trace metals. Rapid increases of trace metal concentrations in the environment are commonly coupled to the development of exploitative technologies. Soils contain

trace elements of various origin (Kabata-Pendias and Pendias, 2001): lithogenic elements which are directly inherited from the lithosphere, pedogenic elements which are of lithogenic origin, but their concentration and distribution in soil layers and soil particles are changed due to pedogenic processes or anthropogenic elements which are all those deposited into soil as direct or indirect results of man's activities. The behaviour of trace elements in soil and in consequence their bioavailability differs as to their origin. However, regardless of the forms of the anthropogenic heavy metals in soil, their phytoavailability is significantly higher than those of pedogenic origin.

Urban pollution with heavy metals has recently become a subject of many studies (Šajn et al., 1998; Šajn, 2004; Chen et al., 2005; Bretzel and Calderisi, 2006; Diawara et al., 2006; Kaur and Rani, 2006; Davidson, 2006; Stafilov et al., 2008). The regional contamination of soil occurs mainly in industrial regions and within centres of large settlements where factories, motor vehicles and municipal wastes are the most important sources of trace metals (Kabata-Pendias and Pendias, 2001). Because of heterogeneity and ceaseless changing of urban areas, it is necessary first to understand the natural distribution and the methods for distinguishing man-made anomalies in nature. However, there are cases when the industrial enterprises, especially mining and metallurgical plants, situated near cities can increase the pollution. It is obvious from the papers published recently that mining and metallurgical activities lead to enormous soil con-

tamination (Razo et al., 2004; Li et al., 2005, 2006; Tembo et al., 2006; Cappuyns et al., 2006), including soil contamination due to nickel smelter plants or another industrial activities (Krishna et al., 2005; Simeonov et al., 2005; Everhart et al., 2006; Mico et al., 2006).

The subject of this study is to present the results of a spatial distribution of cobalt in surface and subsurface soil over of the Kavadarci region, Republic of Macedonia, known for its ferronickel industrial activity in the nearest past. This smelter plant uses the nickel ore from the Ržanovo mine, about 30 km south of the plant. The Ržanovo ore body has the following lithological rock types: hematite, magnetite-ribecite schists, dolomite-talc schists, talc schists and serpentine (Maksimović, 1982; Boev and Janković, 1996). In the last 4 years beside ore from Ržanovo mine, ore mainly from Gebe nickel mine, Indonezia (saprolite-limonite type), reach in nickel (2–2.5 %), is used. It is well known that the nickel ores contain cobalt as well (in average of 0.05 % for Ržanovo ore) (Maksimović, 1982; Boev and Janković, 1996). Therefore, the dust from this plant has the same content like ore used as a raw material including some of the heavy metals like nickel, cobalt and chromium (Maksimović 1982, Boev and Jankovic 1996). For that reason, the goal of this work was to determine the content of cobalt in the soil from the town of Kavadarci and its surroundings and to assess the size of the area eventually affected by the ferro-nickel smelter plant situated near the town.

## STUDY AREA

Town Kavadarci is located in Tikveš valley, Republic of Macedonia (Fig. 1). The city is known by its vineyards and it is main vine production region in Macedonia. The urban area is located on 200–300 m altitude, surrounded with hills from east and south sides of the valley (with height difference between 300 and 770 m). The climate in Kavadarci is of a continental type of climate with a reduced Mediterranean climate and with hot summer and cold winter (Lazarevski, 1993). The major wind direction is from the north and northwest.

The study area is large 18 (W-E) × 20 (S-N) km (Fig. 2) and is located in the south-central part of Macedonia, which is limited with coordinates (Gauss Krueger zone 7) 7574000 (W) – 7592000 (E) and 4582000 (S) – 4602000 (N). Of the total 360 km<sup>2</sup> of the study area (Fig. 2), the water sur-

face (rivers and lakes) covers 6 km<sup>2</sup> (2 %), cultivable land 221 km<sup>2</sup> (61 %), non-cultivable area (mainly forests) 120 km<sup>2</sup> (33 %) and urbanized area (settlements, industry zones, archaeological sites, quarries and tailings) 13 km<sup>2</sup> (4 %).

The complete investigated region (360 km<sup>2</sup>) is covered by a sampling grid of 2×2 km<sup>2</sup>; in the urban zone and around the ferronickel smelter plant (117 km<sup>2</sup>) the sampling grid is denser, 1×1 km<sup>2</sup>. All together, in 172 locations 344 soil samples were collected. At each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and subsoil (20–30 cm).

Two divisions of soils were determined in the investigated region: automorphic and hydromorphic soils.

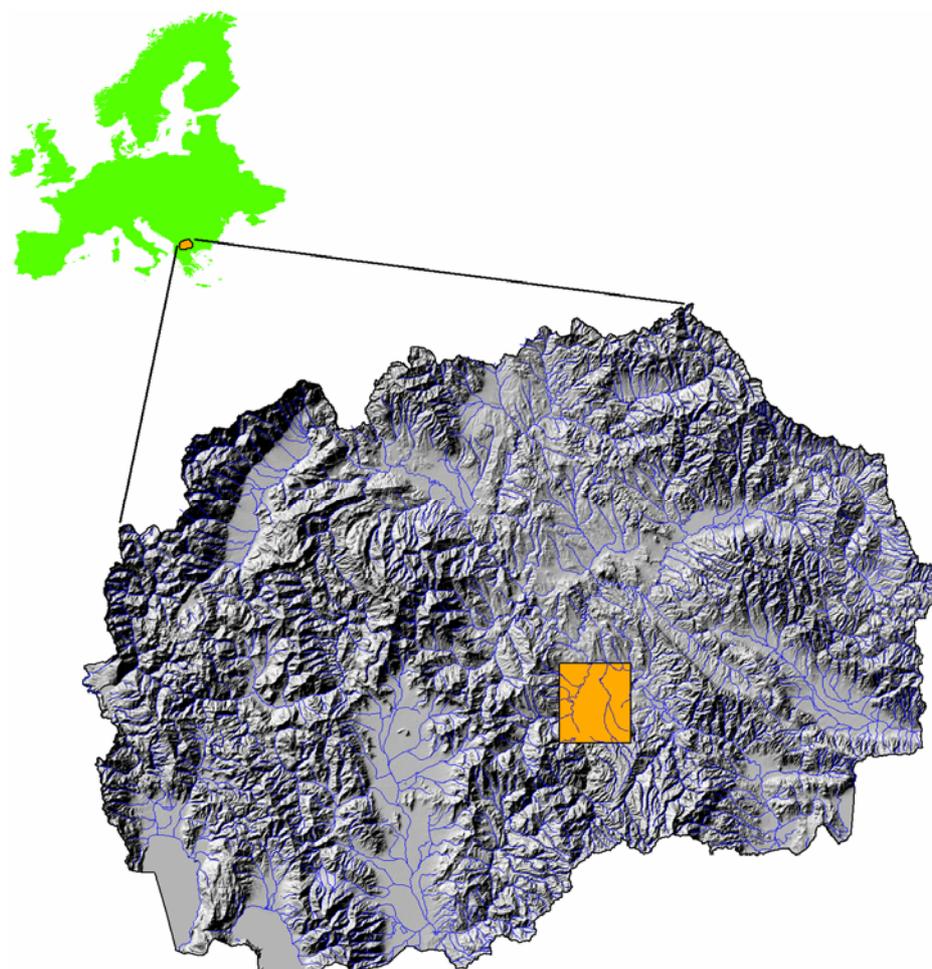


Fig. 1. Location of the study area

## SOIL CONDITIONS

### *Automorphic soils*

Several types of automorphic soils were established: lithosols, regosols, different soil complexes (regosols-lithosols, lithosols-regosol-rendzinas, lithosols-regosols-rankers), deluvial (coluvial) soils, rendzinic soils, vertisols, chernozems, and cinnamonic forest soils.

Lithosols with (A)-R<sub>1</sub>-R<sub>2</sub> type of soil profile are undeveloped or weakly developed soils with maximum soil depth of 20 cm, formed on a solid or slightly defragmented rock. These soils have a low productive capability, due to the shallow solum and small amount of clay and have no importance for agricultural production.

Regosols with (A)-C type of soil profile are formed on a loose substrates. They are formed with

severe erosion of the soil profile of the formerly developed soils and with an initial process of pedogenesis which leads to formation of an undeveloped top layer (A). These soils are prone to surface or dice erosion, so antierosive measures should be implemented. Regosols are characterized with low soil fertility in comparison with the adjacent soil types, which were transformed into regosols with severe erosion.

Soil complex: regosols-lithosol. In the Tikveš region these two soil types alter on a very small distances and it's very difficult to delineate them as separate cartographic units. This complex is spread on slopy terrains west of the Tikveš Lake in the districts of Debrište, Kamen Dol and Kruševica villages and north-west of Dolno Čičevo village.

Soil complex: lithosol, regosols and rendzinas. Series of lithosol-regosols-rendzinas can be

often noticed in the region of Tikveš valley. Lithosols occupy the highest parts of the terrain. Very often the solid rock can be noticed on the surface. Regosols are developed on inclined terrains where due to the erosion processes the solum is constantly in its initial phase of development, while the rendzinic soils are developed on amore flat terrains at foothills and are altering with regosols on very small distances. This soil complex is extended over the districts of Drenovo, Sirkovo, Kamen Dol, Mrzen Oreovec, Debrešte and east of Gradsko settlement on the left side of Vardar river.

Soil complex: Lithosols, regosols and rankers. This series is delineated on the highland Vitačevo, nearby Kavadarci. Lithosols and rankers are formed on compact volcanic rocks, while regosols are developed with erosion processes and degradation of the top soil of rankers.

Deluvial (coluvial) soils with (A)-C type of soil profile are undeveloped or weakly developed soils with (A) or Ap top layer, formed with erosion of the material from the upper part of the terrain with surface and torrent erosion and its deposition in the foothill. The hor. (A) contains a bit higher amounts of organic matter than hor. C, but still there are no obvious signs of formations of soil structure. Deluvial soils posses big spatial and vertical (in depth soil profile) heterogeneity of all its properties. In comparison with the bordering alluvial soils, deluvial soils have lower productivity.

Rendzinic soils with an A-AC-C type of profile are formed on a loose silicate-carbonate substrate, with mollic A horizon. The depth of the top soil is up to 40 cm, with dark gray, dark brown or black color with well developed soil structure. Carbonates are present from the surface or deeper in the soil profile. The major part of these soils is used for intensive agricultural production, while a small part is under pastures. On the soil map these soils are indicated as a complex of lithosols-regosols-rendzinas. The complex of rendzinas and regosols covers the biggest part of the investigated area. In the area of village Dolno Čičevo on a small area a complex of cinnamonic forest soils and regosol is presented.

Vertisols are formed on a clay sediment (mostly carbonate) with more than 30 % of clay content with ability for swelling (smectites) or on basic or ultrabasic rocks which with decaying derives such type of clay. Vertisols at the examined area are formed on clay terciar sediment on moderately wavy landscape with small inclination. The profille type is A-AC-C. The soil contains more

than 30 % clay and hor. A hase vertical character: cracks, and specific prismatic structure. The aggregate surface is shiny („slickensides”). Hor. A is deaper than 30 cm, while the AC hor. is on 20–30 cm depth. In the examined area vertisols are detached as a separate soil type. These soils are spread in the adjacent surroundings of the Ribarci, Trstenik and Vozarci, northern of the city of Kavadarci.

Chernozems are commonly developed in semi-arid steppe regions with typical mollic hor. Amo thicker than 40 cm and an intermediate hor. AC (25–30 cm). This soil contains carbonates which appears from the soil surface, in some cases from the lower part of hor. A or from hor. AC. Hor. A has a well developed, stabile granular soil structure. In the examined area chernozems contains carbonates at its surface, while in some cases carbonates are washed out at certain depth of the soil profile. Chernozems are delineated as a separate cartographic unit (Fig. 3). On the soil map a big areas are detached north from Rosoman village, and some small units east from Palikura village and between villages Timjanik and Dolni Disan.

Cinnamonic forest soils with Ap-(B)<sub>v</sub>-C or Ap-(B)<sub>v</sub>-(B)<sub>v</sub>C-C type of profile are characterized with the presence of clay cambic hor. (B). The cambic hor. (B) always contains more clay than the hor. A. It is denser with reduced capillary porosity and stability of the structural aggregates and lower water conductivity. Production capability is medium due to the bad soil structure, low humus content, insufficient quantities of nutrients and appearance of erosion on sloppy terrains.

#### *Hydromorphic soils*

Alluvial soils are recent layers of river or lake sediments, and usually have hor. (A) or Ap, hor. C and in some cases hor. G. Unlike deluvial soils, they have good fractionation of the parent material. The alluvial sediments which serve as a parent material for formation of this soil have hetero-organic mineralogical composition. In terms of its mechanical composition these are light soils, with weakly emphasized soil structure and high dependence of the physical characteristic to the mechanical composition. They are characterized with good air, water and temperature regime. These are very fertile soils with intensive agricultural production. They are represented as a separate soil type along the river beads of the rivers Vardar, Crna Reka and Luda Mara.

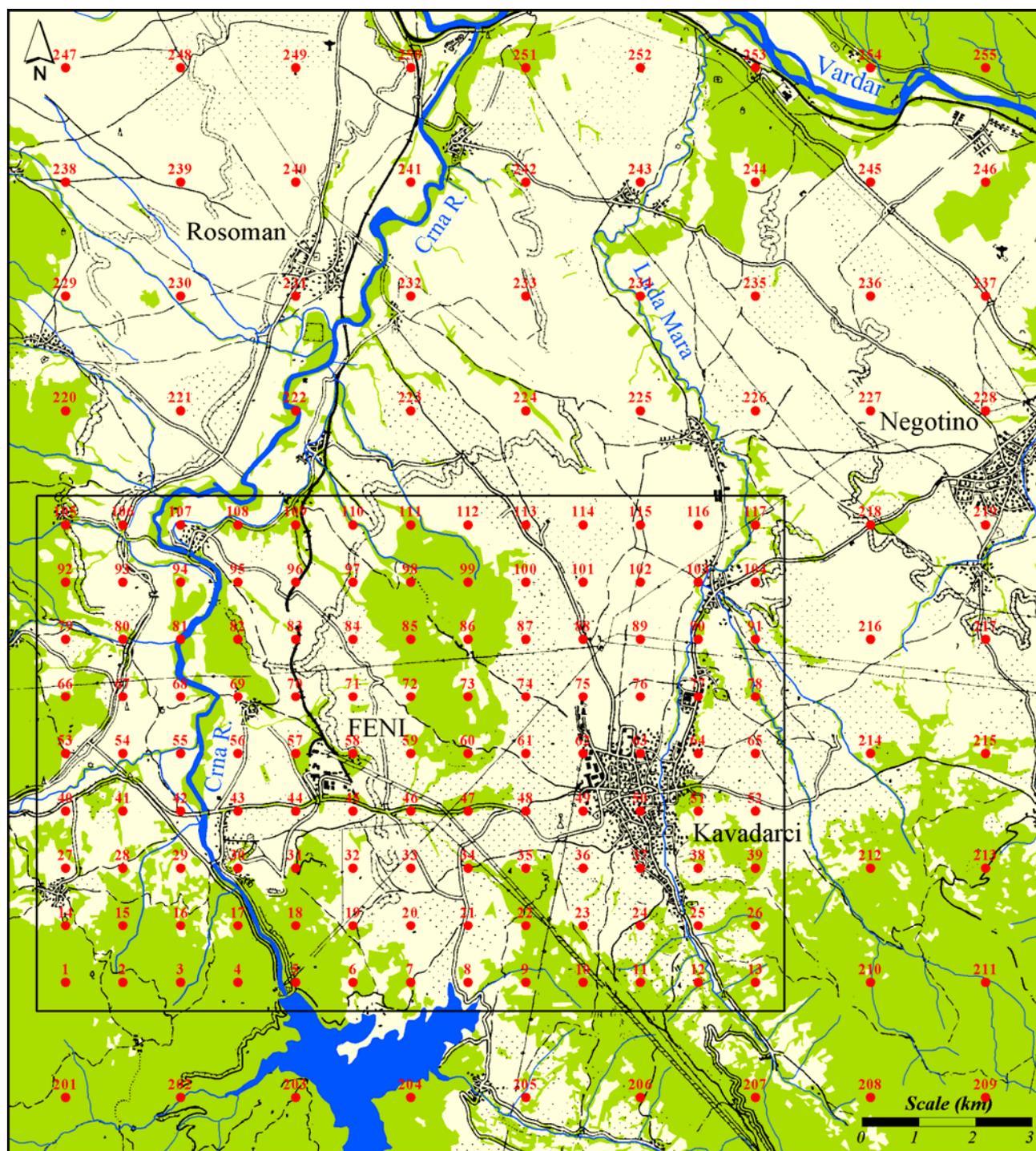
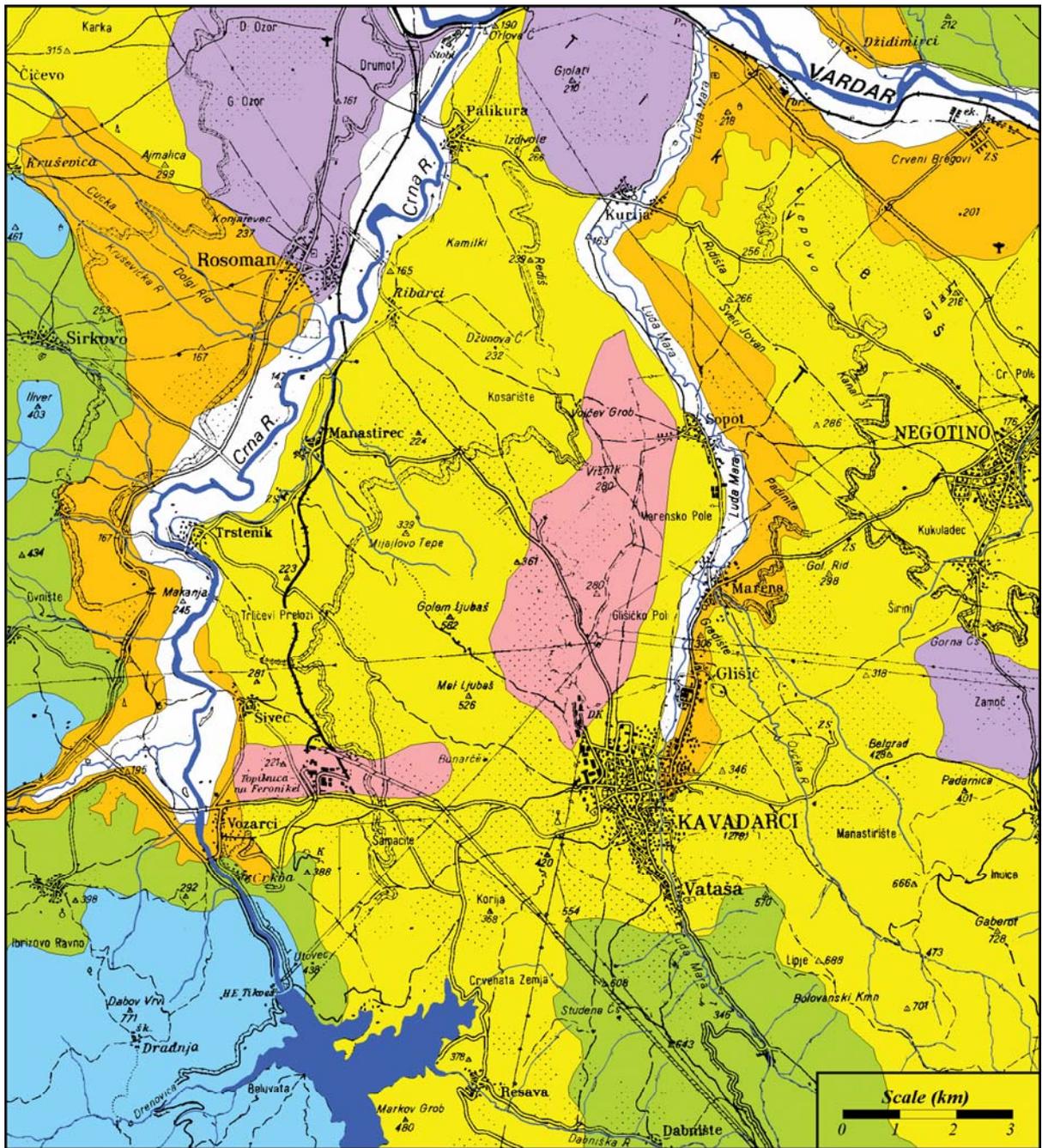


Fig. 2. Land use map and soil samples locations in the Kavadarci area



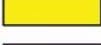
	Fluvisol
	Delluvial soil
	Complex lithosol - regosol
	Complex regosol - lithosol
	Complex rendzina - regosol
	Chernozem
	Vertisol

Fig. 3. Soil map of Kavadarci area

## MATERIAL AND METHODS

### *Sampling*

Soil samples in the town of Kavadarci and the surrounding region were collected according to the European guidelines for soil pollution studies (Theocharopoulos et al. 2001; Darnley et al. 1995; Šajn 2004, Reimann et al. 2008). The complete investigated region (360 km<sup>2</sup>) was covered by a sampling grid 2×2 km<sup>2</sup>, but in urban zone of Kavadarci and around the ferronickel smelter plant (117 km<sup>2</sup>), the sampling grid was denser, 1×1 km (Fig. 2). Altogether 344 soil samples were collected from 172 locations. In each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and subsoil (20–30 cm). The possible organic horizon was excluded. One sample represents the composite material collected at the central sample point itself and at least four points within the radius of 10 m around it towards N, E, S and W. The mass of such composite sample was about 1 kg (Darnley et al. 1995).

With regard to the basic lithological units, 24 location of sampling are located on the area of Paleozoic and Mesozoic rocks (39 km<sup>2</sup>), 10 on the Eocene upper flysch zone (34 km<sup>2</sup>), 90 on the Pliocene sandy series (182 km<sup>2</sup>), 29 on the Pleistocene tuff, Holocene deluvium and Holocene alluvium of the river Luda Mara (46 km<sup>2</sup>), 10 on the Holocene river terraces (23 km<sup>2</sup>) and 9 on the Holocene alluvium of the rivers Crna and Vardar (21 km<sup>2</sup>).

### *Preparation*

The soil samples were air dried indoors at room temperature for about two weeks. Then they were gently crushed, cleaned from extraneous ma-

terial and sifted through a plastic sieve with 2 mm mesh (Salminen et al., 2005). The shifted mass was quartered and milled in agate mill to an analytical grain size below 0.125 mm.

### *Chemical analyses*

Mass spectrometry with inductively coupled plasma (ICP-MS) determination of cobalt was performed in the laboratory of ACME Ltd. in Vancouver, Canada, after aqua regia digestion (mixture of HCl, HNO<sub>3</sub> and water at 95°C – 1DX method).

### *Data processing and construction of maps*

Data analysis and production of maps were performed on a PC using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. The methods of parametric and nonparametric statistics were used for the data analysis (Snedecor and Cochran, 1967; Davis, 1986). On the basis of the results of the normality tests and visual inspection of the distribution histograms the logarithms from the content for the normal distribution was used.

The universal method kriging with linear variogram interpolation (Davis, 1986) was applied for construction of the areal distribution map of cobalt in topsoil (0–5 cm) and subsoil (20–30 cm). The basic grid cell size for interpolation was 20×20 m. For class limits the percentile values of distribution of the interpolated values were chosen. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

## RESULTS AND DISCUSSION

The basic data obtained from the descriptive statistics for cobalt content in the soil in the investigated area are given in Table 1 and the averages of the cobalt content in the soil according to basic lithological units for both topsoil and subsoil are given in Table 2. It can be seen (Table 1) that the median and average values are the same (15 mg/kg) and that the content of cobalt in the whole investigated area ranges between 6.7 and 58 mg/kg. From data given in Table 2 it can be concluded that the highest content of cobalt is present

in the soil from the area of Paleozoic and Mesozoic rocks (Pz-Mz) on the western part of the investigated area and flysch (E) – Eocene upper flysch zone (on the northern part), and the lowest in the soils from the Holocene alluvium of the rivers Crna and Vardar.

On the Fig. 4 the spatial distribution of cobalt in topsoil (left) and subsoil (right) is presented. It can be seen that the spatial distribution of cobalt in both soil layers is closely dependent on the lithogenesis. The highest contents were found in areas

of Paleozoic and Mesozoic rocks and Eocene upper flysch zone and the lowest values in area of the Pleistocene tuff, Holocene deluvium (W from the town of Kavadarci) and Holocene alluvium of the rivers Luda Mara, Crna Reka and Vardar.

The ferronickel smelter plant, in spite of the obvious environmental pollution has not contributed significantly to the measured amount of this element, which occurs in high concentrations in the background. It was found (Fig. 4) that the critically high concentrations are related primarily to high concentrations of cobalt in the sampling points from the western part of the investigated region. In some cases the content of this element is higher in subsoil than in topsoil from which it can be concluded that the occurrence is natural.

Table 1

*Descriptive statistics of measurements for cobalt content in top and subsoil layers the investigated area (data given in mg/kg)*

Number of samples	344
Distribution (Log – lognormal)	Log
Md – Median	15
$X_g$ – geometrical mean	15
$s_g$ – geometrical standard deviation	1.4
A – skewness	0.98
E – kurtosis	1.96
Minimum	6.7
Maximum	58
P <sub>10</sub> – 10 percentile	11
P <sub>90</sub> – 90 percentile	24

Table 2

*Average of the cobalt content in the soil according to basic lithological units (in mg/kg)*

Soil layer/ number of samples (n)	Mean All	Rocks (Pz-Mz)	Flysch (E)	Sand (Pl)	Tuff (Q)	Terraces (Q)	Alluvium (Q)
n	172	24	10	90	29	10	9
Topsoil (depth 0–5 cm)	16.2	26	10	14	13	15	12
Subsoil (depth 20–30 cm)	17.2	29	22	14	14	16	13

Mean (EU) – European topsoil average (Salminen et al., 2005); Rocks (Pz-Mz) – area of Paleozoic and Mesozoic rocks (39 km<sup>2</sup>); Flysch (E) – Eocene upper flysch zone (34 km<sup>2</sup>); Sand (Pl) – Pliocene sandy series (182 km<sup>2</sup>); Tuff (Q) – Pleistocene tuff, Holocene deluvium and Holocene alluvium of the river Luda Mara (46 km<sup>2</sup>); Terraces (Q) – Holocene river terraces (23 km<sup>2</sup>); Alluvium (Q) – Holocene alluvium of the rivers Crna and Vardar (21 km<sup>2</sup>)

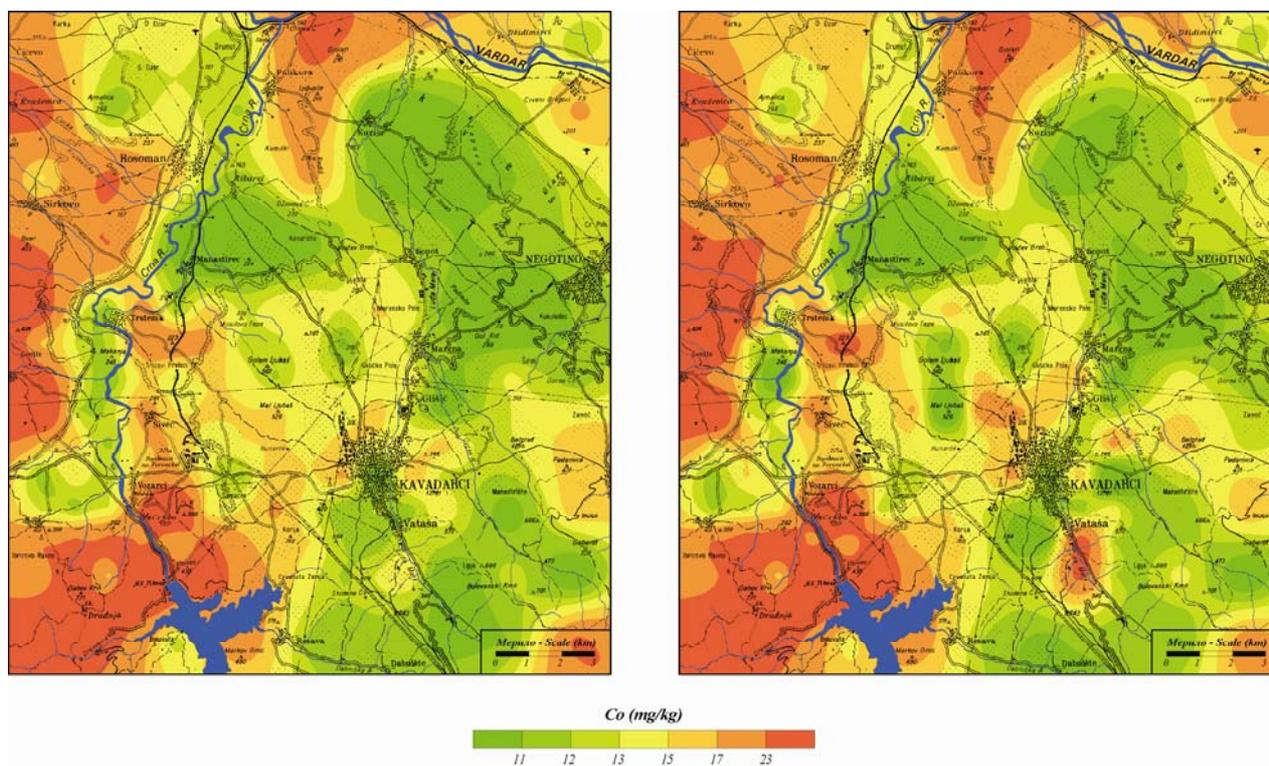


Fig. 4. Spatial distribution of cobalt in topsoil (left) and subsoil (right)

Average and border contents (max. and min.) of Co in different soil types of the investigated region are presented in Table 3. Average contents of Co in topsoil of the complex regosols-lithosols is significantly higher (24.2 mg/kg) comparing with the Co content in the topsoil of all other soil types which vary in the ranges of 12.0–17.8 mg/kg. There are no significant differences between the surface and subsoil in terms of its average quantities. The differences of quantities between the soil types are following the same logic as in the surface

layer. The highest quantities are noticed in the complex regosols-lithosols (25.3 mg/kg) while the lowest values are detected in the subsoil of fluvisols. Maximum and minimum contents of Co differ in broad ranges in all soil types, either in the surface or in a subsurface layer.

Generally speaking, the average contents in almost all soil types are slightly higher in subsoil (20–30 cm), which again leads to a conclusion that there is no human induced surface accumulation of Co in soils in Kavadarci region.

Table 3

*Average of the cobalt content in the soil according to basic pedological units (in mg/kg)*

Soil layer	Co content	All samples	Complex regosol-lithosol	Complex lithosol/regosol	Delluvial soil	Fluvisol	Complex rendzina-regosol	Chernozem	Vertisol
No of samples ( <i>n</i> )		172	13	23	19	13	80	8	16
Topsoil (depth 0–5 cm)	Average	16.2	24.2	17.8	16.0	12.0	15.0	13.9	14.5
	Max.	54.3	54.3	47.9	26.9	16.7	28.6	20.3	17.3
	Min	7.6	11.8	10.4	10.9	9.3	7.6	7.9	10.1
Subsoil (depth 20–30 cm)	Average	17.2	25.3	19.2	17.9	12.4	15.0	15.2	15.2
	Max.	57.8	57.8	55.7	30.9	17.6	29.3	21.1	21.0
	Min	6.7	12.9	9.9	10.7	8.2	6.7	11.3	9.3

## CONCLUSION

It was found that the averages of the cobalt content in the soil according to basic lithological units for both topsoil and subsoil with the median and average values of 15 mg/kg, ranges between 6.7 and 58 mg/kg. The highest content of cobalt is present in the soil from the area of Paleozoic and Mesozoic rocks (Pz-Mz) on the western part of the investigated area and Flysch (E) – Eocene upper flysch zone (on the northern part) and the lowest in the soils from the Holocene alluvium of the rivers Crna and Vardar. It was also found that the average contents of Co in topsoil of the complex regosols-lithosols is significantly higher (24.2 mg/kg) comparing with the Co content in the topsoil of all

other soil types which vary in the ranges of 12.0–17.8 mg/kg. There are no significant differences between the surface and subsoil in terms of its average quantities. The ferronickel smelter plant, in spite of the obvious environmental pollution, has not contributed significantly to the measured amount of this element, which occurs in high concentrations in the background. It was found that the critically high concentrations are related primarily to high concentrations of cobalt in the sampling points from the western part of the investigated region. The contents of this element are higher in subsoil than in topsoil from which it can be concluded that the occurrence is natural.

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## Резиме

## ДИСТРИБУЦИЈА НА КОБАЛТ ВО ПОЧВИТЕ ВО КАВАДАРЦИ И НЕГОВАТА ОКОЛИНА

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**Клучни зборови:** почви; кобалт; загадување; Кавадарци; Република Македонија

Во трудот се презентирани резултатите од просторната распределба на кобалт во почвите во Кавадарци (Република Македонија) и неговата околина. Од испитуваната област (360 km<sup>2</sup>) се земени вкупно 344 примероци од 172 локации. На секоја локација се земени почви од две длабочини, површински слој почва (0–5 cm) и потповршински слој (20–30 cm). Определувањето на кобалтот е вршено со индуктивно спрегната плазма со масена спектрометрија (ICP-MS). Обработката на податоците и конструирањето на картата на дистрибуција се вршени со примена на софтверите Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) и Surfer (ver. 8.09). Утврдено е дека вредноста за медијаната и средната вредност на содржината на кобалт во површинските и потповршинските

почви изнесува 15 mg/kg (од 6,7 до 58 mg/kg). Највисоки содржини се најдени во областите на палеозојските и мезозојските стени и во зоната на горноеоценскиот флиш, а најниските вредности во областа на плеистоценскиот туф, холоценскиот делувиум (западно од градот Кавадарци) и холоценскиот алувиум на реките Црна Река и Вардар. Не е забележана значителна разлика помеѓу содржините на кобалт во површинските и потповршинските почви. Утврдено е дека високи вредности за кобалт се најдени во примероците почва од западниот дел на испитуваното подрачје. Исто така, утврдено е дека во овие примероци повисоки вредности на кобалт се најдени во потповршинските почви во однос на површинските, што укажува на природната застапеност на кобалтот во овие почви.

## DISTRIBUTION OF Pb AND Zn AND THEIR CHEMICAL SPECIFICATIONS IN THE PADDY SOILS FROM THE KOČANI FIELD (MACEDONIA)

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**A b s t r a c t:** The distribution and chemical specifications of Pb and Zn in the paddy soils of Kočani Field, Macedonia, were investigated using a sequential extraction procedure. This study was carried out in order to develop an understanding of the metal contamination found in the area which is due to historical and recent mining operations around Kočani Field. The paddy soil sample from location VII–2 in the vicinity of Zletovo mine in the western part of Kočani Field was found to contain highly elevated concentrations of Pb and Zn which are under reduction conditions very unstable and mobile. According to the total Pb and Zn concentrations, their mobility characteristics and the index of geoaccumulation for all studied soil samples, it is observable that the paddy soil sample from location VII–2 represents a potential environmental risk.

**Key words:** Pb and Zn contamination; paddy fields; sequential extraction procedure; Kočani Field; Macedonia

### INTRODUCTION

An numerous areas of the world soil contamination has become a serious problem. Soil contamination by anthropogenic heavy metals resulting from the application of sewage sludge, fertilizers, industrial historical and recent mining activities is widespread, and extensive investigations have been carried out recently in some countries and regions (Chlopecka et al., 1996; Culbard et al., 1998; Lu et al., 2003; Alloway, 1990; Colbourn & Thornton, 1978; Davies, 1983; Li & Thornton, 1993, 2001; Verner & Ramsey, 1996). The contamination of soils by heavy metals has long term environmental and health implications, because heavy metals are usually persistent in soil and can remain at significant levels for millennia (Mcgrath, 1987). The distribution of heavy metals in soils is influenced by the nature of parent materials, climate and their relative mobility characteristics depending on soil parameters, such as mineralogy, texture and classification of soil (Krishna & Govil, 2007). The bioavailability of heavy metals in soils affects soil quality and its use in food production. Therefore,

the assessment of heavy metal contamination in soils is of vital important to the affected areas.

Figures describing the total content of heavy metals in soils present limited information on the mobility and bioavailability of the heavy metals found (Leschber et al., 1985; Kramer & Allen, 1988). They give information concerning possible enrichment of the soil with heavy metals, but the severity of pollution also depends on the proportion of their mobile and bioavailable forms which determines their mobilisation capacity and how they will behave in the environment. Consequently, sequential extraction procedures have been developed to define the amounts and proportions of metals present in different forms of soil: water soluble, exchangeable and carbonate fractions are considered readily mobile and bioavailable, whereas a residual fraction, is considered immobile and may not be expected to be released under natural conditions. The sequential extraction procedure provides information about the differentiation between the relative bonding strengths of metals in

various phases, and about their potential reactivity under different physicochemical environmental conditions. It is considered useful for evaluating mobility and bioavailability of heavy metals in soils (Tessier et al., 1979; Shuman, 1985).

Limited information exists concerning the spatial distribution and availability of heavy metals in soils of the Kočani Field in Macedonia (Dolenc et al., 2007). Soil contamination with heavy metals is due to historical and recent mining operations, the irrigation of paddy fields using acid mine

drainage water, the release of untreated mine effluent into riverine water as well as the application of sewage sludge and fertilizers which are growing practices in this area.

In this study, the index of geoaccumulation was used to assess the pollution of the investigated soils and a systematic investigation of the Pb and Zn contamination of surficial soils was carried out using the sequential extraction procedure in order to explore the mobility and potential bioavailability of heavy metals.

## MATERIALS AND METHODS

### *Study area*

Kočani Field lies in the valley of the Bregalnica River, which is situated in eastern Macedonia, about 115 km from the capital city Skopje (Fig. 1). The broader region is well known as an agricultural area (paddy fields), for its thermal waters and for its long mining history dating to the pre-Middle Ages.

The most recent phase of mining began after the Second World War. Several Pb–Zn ore deposits are related to the Tertiary acidic to intermediate volcanogeno-intrusive complexes of the Besna Kobila–Osogovo–Tassos metallogenic zone in the east of the region and the Tertiary volcanogenic complexes of the Lece–Chalkidiki metallogenic zone in the north of Kočani Field (Serafimovski & Aleksandrov, 1995).



Fig. 1: Study area, Kočani Field, Macedonia

The Zletovo Pb–Zn deposit lies in the eastern part of the Kratovo–Zletovo volcanogenic complex and occupies the central part of the Kratovo–Zletovo ore district. It is located in the area of the village of Dobrev, about five kilometres northwest of the Zletovo settlement. The mineral association is comprised of galena (principal ore mineral) and sphalerite, with subordinate pyrite, lesser amounts of siderite, chalcopyrite, pyrrhotine, marcasite and magnetite. The Zletovo Mine is active up to the present day with an annual capacity of about 350, 000 tonnes of approximately 8% Pb and Zn concentrate.

The mining activities, the abandoned sites of old mines, the large amounts of untreated waste material and the effluents from the Pb–Zn ore deposit Zletovo have all caused expansion of high heavy metal loads across the entire region. The acid mine waters and the effluents from the ore processing facilities are discharged untreated into the Zletovska and Bregalnica rivers and this represents a further pollution source that could seriously affect the soil as well as the food and feed crops of

Kočani Field. Untreated municipal waste and domestic sewage from the cities of Kočani and Orizari are discharged into the Kočanska and Orizarska rivers, which are also used for irrigation purposes, and therefore this represents a potential pollution source for the surrounding paddy fields.

#### Soil sampling and analysis

The paddy soil of Kočani Field originates from the composite material of the sediment derived from igneous, metamorphic and sedimentary rocks transported by the Bregalnica River and its tributaries and deposited in the Kočani depression (Dolenec et al., 2007).

The sampling of the soil was carried out in autumn 2005 in order to determine the concentration and distribution of the potentially toxic heavy metals, Pb and Zn. The soil was collected from 5 locations (I–3, II–6, III–5, VI–4, and VII–2) across the Kočani paddy fields (Fig. 2).

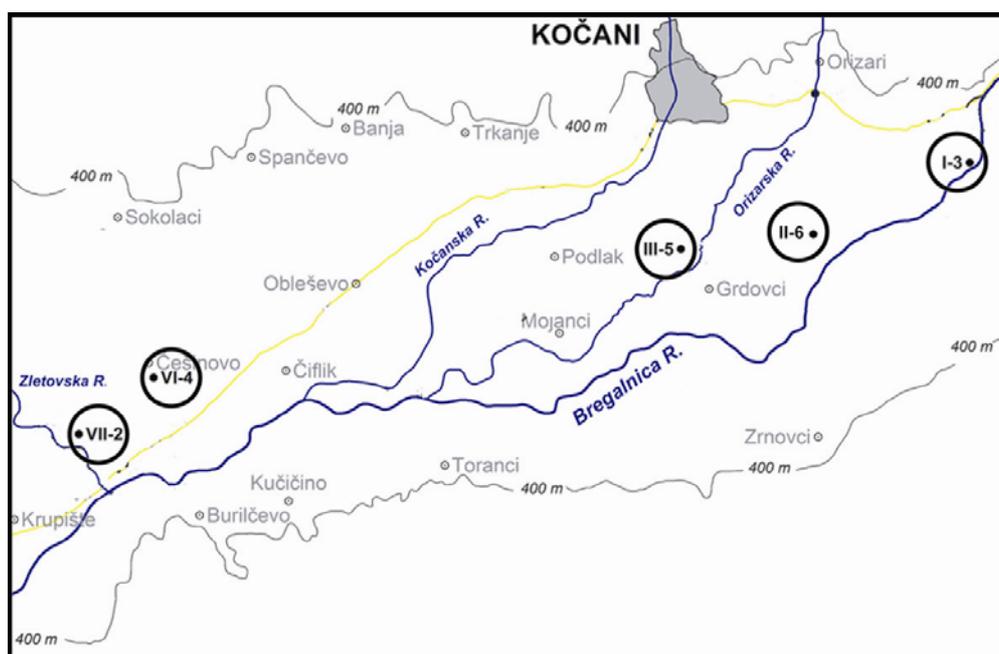


Fig. 2. Sampling points located in the study area

Near-surface paddy soils (0–20 cm in depth) were sampled because in agricultural soil it is not possible to distinguish the A, B and C horizons. Each soil sample was made up of a composite of five sub-samples taken from within a 1×1 m square. The soil samples were then air dried at room temperature (about 25 °C) for one week and

sieved through a 2-mm polyethylene sieve to remove plant debris, pebbles and stones. Afterwards the samples were ground in a mechanical agate grinder to a fine powder (< 63 μm) for subsequent geochemical analysis.

The paddy soil samples were analyzed for Pb and Zn concentrations in a certified commercial

Canadian laboratory (Acme Analytical Laboratories, Ltd.) after extraction for 1 h with 2-2-2-HCl-HNO<sub>3</sub>-H<sub>2</sub>O at 95 °C by inductively coupled plasma mass spectrometry (ICP-MS). The accuracy and precision of the soil analyses were assessed by using international reference material such as CCRMR SO-1 (soil) and USGS G-1 (granite). The analytical precision and the accuracy were better than  $\pm 5\%$  for the analyzed elements.

#### *Sequential extraction procedure*

A sequential extraction procedure, modified method by TESSIER et al. (1979) was applied to study the soil samples. The main purpose of performing a sequential extraction was to investigate the association of chemical elements with a different fractionation in soil through several diverse dissolution steps.

The soil samples weighing 1g were placed in screw-top test tubes. For the sequential leaching procedure, the sample was leached, centrifuged, decanted, washed and then the residue was leached again in a process of five steps moving from the weakest to strongest solution: water  $\rightarrow$  ammonium acetate  $\rightarrow$  sodium pyrophosphate  $\rightarrow$  cold hydroxylamine hydrochloride  $\rightarrow$  hot hydroxylamine hydrochloride. The concentration of Pb and Zn in the

solution was then measured by using a Perkin Elan 6000 ICP-MS for the determination of sixty or more elements. QA/QC protocol meant that a sample duplicate was incorporated to monitor analytical precision, and a reagent blank measured background and aliquot of an in-house Reference Material to monitor accuracy. Raw and final data went through a final verification by a British Columbia Certified Assayer.

The sequential extraction method operationally determines Pb and Zn in five different chemical fractions:

- water soluble fraction (distilled water),
- exchangeable and carbonate bound fraction (1 M ammonium acetate),
- organic (oxidizable) fraction (0.1 M sodium pyrophosphate),
- Mn hydroxide (reducible) fraction (cold 0.1 M hydroxylamine hydrochloride) and
- Fe hydroxide (reducible) plus crystalline Mn hydroxide (residual) fraction (hot 0.25 M hydroxylamine hydrochloride).

The highly stable metal forms incorporated into residual fractions are unlikely to be released under weathering conditions. On the other hand, soluble, exchangeable, oxidizable and reducible fractions are quite labile, and hence more accessible to plants and thus the food chain (Kabata-Pendias, 1993).

## RESULTS AND DISCUSSION

#### *Total heavy metal concentration*

The critical total soil heavy metal concentration is defined as the range of values above which toxicity is considered to be possible. Total heavy metal concentrations of Pb and Zn in the paddy soil samples from Kočani Field together with the assumed permissible level of heavy metals adopted by the National Environmental Protection Agency of Slovenia (Uradni List RS, 1996), the maximum allowable concentrations (MAC) of trace elements in agricultural soil proposed by the German Federal Ministry of Environment (1992) and the critical soil total heavy metal concentration ranges defined by Kabata-Pendias & Pendias (1984) are displayed in Table 1.

Table 1

#### *Total elemental concentrations in the paddy soil samples of Kočani Field*

Element	Pb (mg/kg)	Zn (mg/kg)
Location		
I-3	81	162
II-6	32	100
III-5	24	102
VI-4	41	105
VII-2	892	1134
1	100-400	70-400
2	85	200
3	100	200

1) Critical soil total concentration ranges given by Kabata-Pendias and Pendias; 2) limits for elemental concentrations in soil (Environmental Protection Agency of Slovenia (Uradni list RS 1996); 3) Maximum allowable concentrations (MAC) of trace elements in agricultural soils proposed by the German Federal Ministry of the Environment (1992).

### Lead (Pb)

Agricultural soils usually include a wide range of Pb content, which depends on a number of factors such as the parent rock material, pedogenic processes and the anthropogenic input from surrounding ecosystems (Adriano, 1986).

The Pb concentrations determined in all paddy soil samples were in a range from 24 to 892  $\mu\text{g g}^{-1}$ . The highest Pb concentration (892  $\mu\text{g g}^{-1}$ ) was measured in a paddy soil sample from location VII-2 and this value is above the limits provided by the environmental protection agencies of Slovenia and Germany (85  $\mu\text{g g}^{-1}$  and 100  $\mu\text{g g}^{-1}$ ) and the limit values given by Kabata-Pendias & Pendias (1984) (100–400  $\mu\text{g g}^{-1}$ ) (Table 1). It is also above the median values of Pb content in contaminated agricultural soil reported by Lee et al. (2005) and Liu et al. (2005).

### Zinc (Zn)

As an average Zn content present in world soils figures showing concentrations of 90  $\mu\text{g g}^{-1}$  have been given by Bowen (1979).

In the present study Zn concentrations in paddy soil samples were in the range of 100–1134  $\mu\text{g g}^{-1}$ . Increased concentration of Zn (1134  $\mu\text{g g}^{-1}$ , Table 1) was again noticed in the paddy soil sample from VII-2. The Zn concentration in sample VII-2 exceeded all given heavy metal limit values (Table 1).

The data clearly shows that the paddy soil samples from locations I-3, II-6, III-5 and VI-4 contain slightly enhanced Pb and Zn concentrations but that the paddy soil sample from VII-2, located in the vicinity of the Zletovska River is highly impacted by Pb and Zn. The investigated heavy metals are important ore-forming elements in the Pb-Zn polymetallic mineralisation of the Zletovo–Kratovo ore district (Zletovo mine) drained by the Zletovska River (Dolenec et al., 2007). Acid mine water in untreated effluents from Zletovo mine is discharged into the Zletovska River, which is used for the irrigation of the nearby paddy fields. It is therefore the soil sample VII-2 contains such excessively high values of Pb and Zn.

### Index of geoaccumulation

The index of geoaccumulation ( $I_{\text{geo}}$ ) can be used to estimate whether or not soils have been

contaminated by heavy metals (Müller, 1969, 1979) :  $I_{\text{geo}} = \log_2 C_N / 1.5 B_N$ .  $C_N$  is measured concentration of element  $N$  in soils and  $B_N$  is the content of the element  $N$  in “average shale” (Turekian & Wedepohl, 1961), either directly measured in texturally equivalent uncontaminated soils or taken from the literature. The factor 1.5 is initiated to include possible differences in the background values due to lithological variations.

The Müller Index of Geoaccumulation,  $I_{\text{geo}}$ , consists of seven grades ranging from unpolluted to very seriously polluted (Table 2). Grade 6 indicates a 64-fold enrichment over the background values (Singh et al., 1997).

Table 2

### Index of geoaccumulation ( $I_{\text{geo}}$ ) and contamination level

$I_{\text{geo}}$	$I_{\text{geo}}$ class	Contamination level
< 0	1	Uncontaminated
0–1	2	Uncontaminated to moderately contaminated
1–2	3	Moderately polluted
2–3	4	Moderately to highly polluted
3–4	5	Highly polluted
4–5	6	Highly to very highly polluted
> 5	7	Very seriously polluted

In our calculation of  $I_{\text{geo}}$ ,  $B_N$  is the concentration of studied elements (Pb and Zn) in the earth's crust (Taylor & McLennan, 1995). The  $I_{\text{geo}}$  values of Pb and Zn in the studied soils are displayed in Table 3.

Table 3

### The results of the $I_{\text{geo}}$ values for the studied soils

Soil sample	$I_{\text{geo}}$ (Pb)	$I_{\text{geo}}$ (Zn)
I-3	2.75	0.43
II-6	1.42	-0.26
III-5	1	-0.23
VI-4	1.77	-0.19
VII-2	6.21	3.24

According to the  $I_{\text{geo}}$  classes the soils from location VII-2 were very seriously polluted with Pb and highly polluted with Zn. The soil samples from other locations were moderately to highly polluted

with Pb and uncontaminated to moderately contaminated with Zn.

### *Pb and Zn chemical partitioning*

The water soluble fraction comprises highly mobile and thus potentially bio available metal species. An exchangeable fraction contains weakly bound metal species, that can be released by ion-exchange reaction with cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{NH}_4^+$ . The metals present in exchangeable fractions are also accessible for plant uptake and therefore very labile. The oxidisable fraction includes metals bound to organic matter, which can, under oxidising conditions, be released into the surrounding ecosystem. In the reducible fraction the unstable metal forms are connected with amorphous Mn hydroxides and this connection can, under reducing conditions, be easily discharged and approachable for the biota. For the reducible plus residual fraction the metals found were linked to amorphous Fe hydroxides (reducible fraction) and to crystalline Mn hydroxide minerals (residual fraction). Under reducing conditions the metals in a reducible fraction can be expected to be released into nature. The residue was made up of heavy metals defined as being within their crystalline matrix and thus, these metals are not likely to be discharged under normal environmental conditions

(Dean, 2007; Filgueiras et al., 2002; Kazi et al., 2002). Figure 3 represents the results of the sequential extraction procedure (heavy metal binding forms).

### *Lead (Pb)*

The presence of Pb in extraction fractions of all investigated soil samples was arranged in this way: reducible plus residual > reducible > oxidisable > exchangeable > water soluble fraction. The highest share of Pb in reducible plus residual fraction was detected in the paddy soil sample from location VII-2 (54.46%) and the highest part of Pb in reducible fraction was found in soil sample VI-4 (38.96%) (Fig. 3).

### *Zinc (Zn)*

The amount of Zn present in extraction fractions in all samples was arranged in the following order: reducible > reducible plus residual > oxidisable > exchangeable > water soluble fraction. The highest amount of Zn in reducible plus residual and residual fraction phase was determined in the paddy soil sample from sampling site III-5 (49.19% and 36.9%) (Fig. 3).

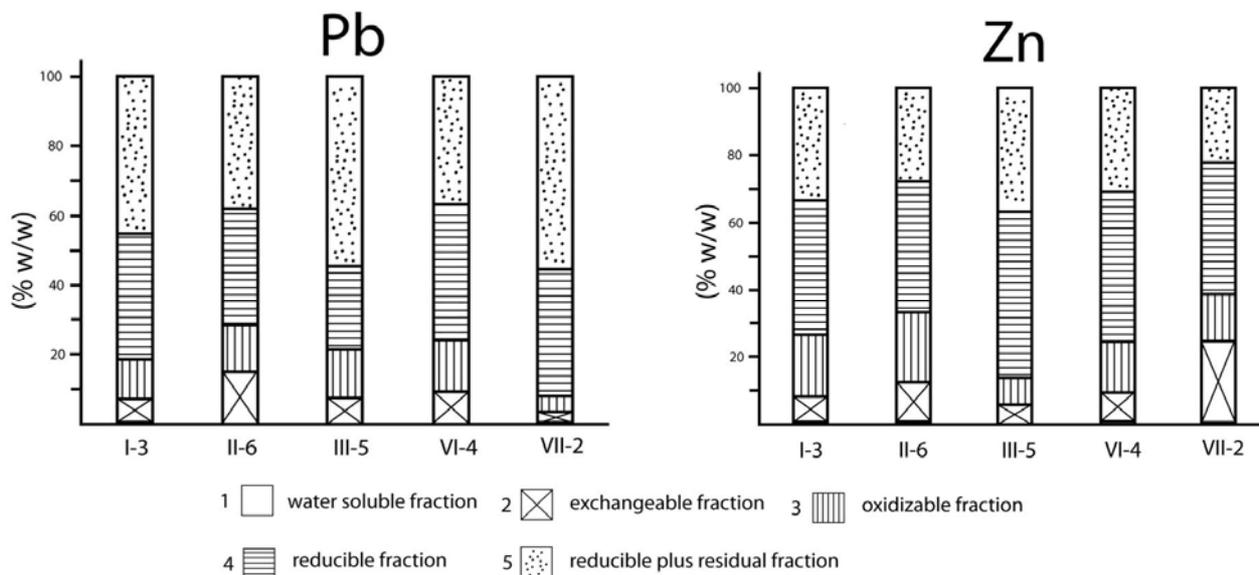


Fig. 3. Heavy metal binding forms for Pb and Zn.

A large part of the Pb is defined as non-mobile because of its containment within a crystalline matrix in residual fraction. To some extent Pb was

connected with amorphous Mn hydroxides and amorphous Fe hydroxides in reducible fraction. Zn was dominantly associated with amorphous Mn

hydroxides and amorphous Fe hydroxides in reducible fraction as well. For that reason the Pb and Zn are under reduction conditions and therefore very unstable and mobile.

From the environmental and utilisation points of view it is notable that the paddy soil sample

from location VII-2 near Zletovska River and Zletovo mine with its highly elevated Pb and Zn concentrations, its rating under the introduced index of geoaccumulation and its mobility characteristics represents a potential risk for surrounding ecosystems.

## CONCLUSIONS

Total Pb and Zn distribution characteristics in paddy soil samples from Kočani Field, Macedonia, were reported. The total amount of Pb and Zn concentration was measured with ICP-EAS, and Pb and Zn binding forms were determined using a sequential extraction procedure.

The results showed that the paddy soil sample (section VII-2) from the western part of Kočani Field in the vicinity of the Zletovska River exhibited very high concentrations of Pb and Zn which significantly exceeds the limits proposed by the Slovenian and German environmental agencies and critical soil total concentration ranges given by Kabata-Pendias and Pendias. Thus, the Pb and Zn surface enrichment in soil sample VII-2 clearly revealed an anthropogenic origin of the pollution.

According to the  $I_{geo}$  classes the soils from location VII-2 were very seriously polluted with Pb and highly polluted with Zn.

Pb was dominantly present in reduction and residual fraction, which indicates that some part of the Pb is non-mobile and thus potentially the least harmful. Zn and also part of the Pb were bounded to amorphous Fe and Mn hydroxides in reducible fraction. Therefore, under varied reduction conditions, the mobilisation and release of Zn and Pb from the soils can be expected.

The paddy soil sample from location VII-2 with its highly elevated Pb and Zn concentrations, calculated index of geoaccumulation and their described mobility characteristics represents a potential environmental risk. To assess the possible health risk, more detailed studies on various heavy metal contaminations in surrounding areas are needed.

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## Резиме

## ДИСТРИБУЦИЈА НА Pb И Zn И НИВНАТА ФОРМА ВО ОРИЗОВИТЕ ПОЧВИ ВО КОЧАНСКО ПОЛЕ (МАКЕДОНИЈА)

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**Клучни зборови:** Pb и Zn контаминација; оризови полиња; процедура на секвенцијална екстракција; Кочанско Поле; Македонија

Со употреба на процедурата на секвенцијална екстракција беа проучувани дистрибуцијата и хемиските карактеристики на Pb и Zn во оризовите почви во Кочанското Поле, Македонија. Ова проучување беше спроведено со цел да се објасни контаминацијата со метали откриена во оваа област која се должи на историските и современи рударски активности. Во примерокот на оризната почва од локацијата VII–2 во близина на рудникот Злетово, во западниот дел на

Кочанско Поле, се откриени силно покачени концентрации на Pb и Zn кои при редукциони услови се многу нестабилни и мобилни. Според вкупните концентрации на Pb и Zn, а со оглед на нивната мобилност и индексот на геоаккумуляција може да се заклучи дека од сите проучувани примероци почва примерокот од локацијата VII–2 претставува потенцијален ризик за животната средина.

## STABILITY ANALYSIS OF ROCK WEDGES WITH MULTIPLE SLIDING SURFACES

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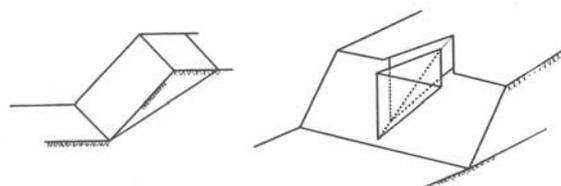
**Abstract:** Although wedge and plane sliding stability analyses are well established in the geotechnical literature, certain geologic environments produce blocks which cannot be adequately modelled as either wedges or plane slides. An example is blocks forming in cylindrically folded sedimentary rocks, where the surface of sliding is neither a single plane nor a double plane but is curved. This type of block may be idealized as a prismatic block with multiple sliding planes, all with parallel lines of intersection. If the sliding planes number three or more, the distribution of normal forces and hence the factor of safety is indeterminate. A new analytical model for sliding stability analysis is described in which the distribution of normal forces on the contact planes is chosen to minimize the potential energy of the system. The classic wedge and plane solutions are shown to be special cases of this more general model, which allows determination of the safety factor for any shape of prismatic contact surface. An example from block part of Bregalnica river with a curved sliding surface is described and the factor of safety compared with the standard wedge analysis. It is shown that with three or more contact planes, the safety factor may be significantly lower than that calculated from the wedge model, which provides an upper limit on stability.

**Key words:** rock slope stability; wedge slides

### INTRODUCTION

Stability analyses for wedge and plane failures are now well established in the geotechnical literature. Some of the early work on the subject is due to Londe et al. (1969,1970), John (1968), Wittke (1965, 1990) and Goodman (1976, 1989). Other developments and useful summaries are given by Hoek and Bray (1981), Goodman and Shi (1985), Giani (1992), Warburton (1993), Einstein (1993) and Watts (1994), among others. The requirements for sliding may be summarized as follows. Plane failures can occur when the strike of a discontinuity plane such as bedding is approximately parallel to the strike of the slope face and the weak plane daylights in the free face at a dip angle greater than the friction angle. Wedge failures can occur for a block defined by two planes whose line of intersection daylights in the free face and plunges sufficiently steeply that the destabilizing forces exceed the shear resistance. Typical geometries for wedge and plane failures are depicted in Fig. 1.

The important factors in the solution of stability problems are the shear strength, dip and dip direction of the discontinuity planes, the geometry of the slope and the loading conditions.



**Fig. 1.** Typical geometries for rock slope translational failures: (a) plane failure; (b) wedge failure

The system of forces governing plane slides is statically determined and the frictional shear resistance can be determined by resolution of forces. Wedge slides are rendered statically determinate by making an assumption about shear stresses in the contact planes, namely that shear stresses vanish in the plane perpendicular to the potential sliding direction. Although this assumption is rarely discussed in the literature (Chan and Einstein, 1981), it is implicit in the classic wedge analysis (e.g., Hoek and Bray, 1981). With the above-mentioned assumption, and if strengths and water pressures, etc., are known, the factor of safety for plane and wedge slides can be obtained directly by limiting equilibrium methods, either by direct cal-

ulation or by graphical methods based on stereographic projection. With three or more sliding planes, however (e.g., Fig. 2), the distribution of normal forces is statically indeterminate and the net frictional resistance to sliding, and hence the factor of safety, cannot be uniquely determined. In this paper (see also Ureta, 1994; Mauldon and Ureta, 1994, 1995) we describe an energy method for determination of the factor of safety against sliding failure for blocks with multiple sliding planes that form a cylindrical surface. Such a block is referred to as a prismatic block.

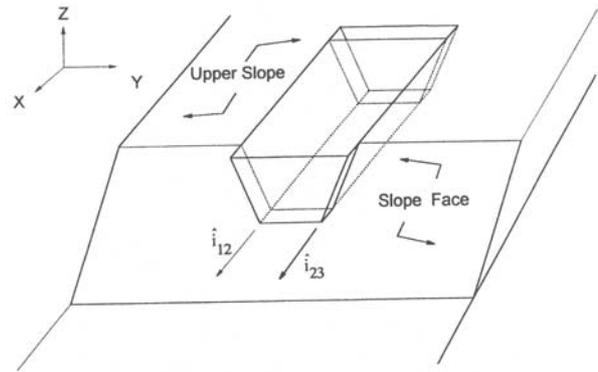


Fig. 2. Prismatic rock block with three contact planes; coordinate system defined

## PRISMATIC BLOCKS

A prismatic block is a rock block bounded by  $n$  contact planes, where the lines of intersection of the contact planes are all parallel. Fig. 2 shows a special case of a prismatic block with three planes of contact with the rock mass. Also, in Fig. 2, a Cartesian coordinate system is defined with the  $X$  axis parallel to the line of intersection (the potential sliding direction) and  $Y$  horizontal. The contact planes of a prismatic block are cozonal (to use crystallographic terminology, e.g., Bloss, 1961), with zone axis parallel to the line of intersection, so that the normals of the contact planes fall on a great circle when plotted in stereographic projection (Fig. 3). As the number of planes ( $n$ ) approaches infinity ( $n \rightarrow \infty$ ), the contact surface approaches a curved cylindrical shape. Thus a block defined by cylindrically folded bedding or foliation is a limiting case of a prismatic block. Plane and wedge failures, with one and two contact planes, and zero and one lines of intersection respectively, are special cases of prismatic blocks.

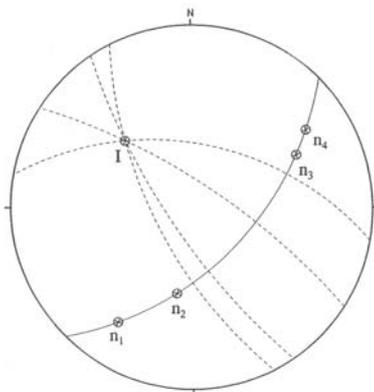


Fig. 3. Stereographic projection showing geometry of a prismatic block. Contact plane normals fall on a great circle. The lines of intersection of contact planes are parallel to the zone axis I

### Statement of problem

As discussed above, if  $n \leq 2$  the distribution of normal forces on the contact plane(s) is statically determinate. If  $n \geq 3$ , however, the normal forces on the planes of contact between a prismatic block and the rock mass are statically indeterminate and the stability conditions cannot be determined directly by limiting equilibrium methods. In this paper we describe an energy method to determine the contact forces and to evaluate the factor of safety against sliding of prismatic rock blocks as a function of shear strength, block geometry, and loading conditions. The block is assumed to be supported at each face by a series of normal springs, each with stiffness  $k_i$  and each spring subject to a “no tension” condition. The magnitude of the stiffness  $k_i$  at each contact face is assumed to be proportional to the planar contact area per unit length. We assume an elastic, conservative system to obtain the distribution of normal forces that minimizes the potential energy of the system

### Assumptions

The stability analysis is based on a simplified model of rock mass geometry and strength, with the following assumptions:

- Contact faces of the prismatic block are planar.
- The displacement of the block is purely translational.
- Frictional shear stresses act parallel to the sliding direction only. Note that this assumption is standard in limiting equilibrium analysis of plane and wedge slides.

- The block is undeformable, except for elastic contacts at the bounding faces.
- The block is acted on by an active resultant  $\vec{R}$  which includes self-weight, and may in addition include hydraulic forces, seismic forces, or supporting forces due to anchors or bolts. The effect of moments is not considered in the analysis.
- The normal stiffness of each contact plane is proportional to its surface area.

*Analytical model*

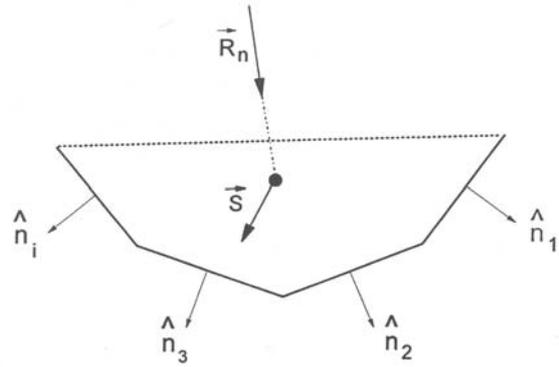
The total potential energy of a system consisting of a prismatic rock block supported by  $n$  contact planes is given by:

$$V = \sum_{i=1}^n V_i - W_r \tag{1}$$

where  $V_i$ , is the elastic potential energy associated with each discontinuity surface  $i = 1, 2, \dots, n$ , and  $W_r$  is the work done by the active forces acting on the block. If self-weight is the only active force, the work done by the active forces is the negative of the change in gravitational potential energy. We assume that the block itself is undeformable, but that elastic deformation occurs at the contacts between the block and the rock mass. We assume that the block-rock mass contacts behave like linear springs, with stiffness proportional to surface area and we establish a datum for the gravitational potential energy such that the contact springs initially have zero extension.

The first task will be to find the equilibrium distribution of forces in the  $YZ$  plane (the plane perpendicular to the potential sliding direction), such that the total potential energy is a minimum. We assume that the equilibrium position in the  $YZ$  plane of the block results from a small translational displacement of the block in the  $YZ$  plane (i.e., perpendicular to the sliding direction) under the action of the active forces. Elastic strain energy in the spring contacts is stored as a result of this displacement. We denote this small displacement by a vector  $\vec{s}$  at an angle  $\theta_s$  and with magnitude  $s$  (see Fig. 4). Then, for unit normal  $\hat{n}_i$  and stiffness  $k_i$  corresponding to each contact plane, the elastic potential energy  $V_i$  at each contact face is given by

$$V_i = \begin{cases} 1/2k_i(\hat{n}_i \cdot \vec{s})^2 & \text{if } (\hat{n}_i \cdot \vec{s}) > 0 \\ 0 & \text{if } (\hat{n}_i \cdot \vec{s}) \leq 0 \end{cases} \tag{2}$$



**Fig. 4.** Prismatic block in the  $YZ$  plane showing unit normal vectors  $n_i$ , normal component  $R_n$  of active resultant and displacement vector  $S$

The latter condition means that we do not admit tensile contact forces. In order to ensure no tension, it is convenient to introduce an index set  $A$ , denned for any displacement  $s$  by

$$A = (\theta_s) = \{i : \hat{n}_i \cdot \vec{s} > 0, \quad i = 1, 2, \dots, n\} \tag{3}$$

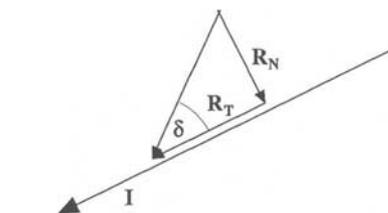
This index set  $A$  is a function of the angle of displacement  $\theta_s$  and is essentially a list of contact planes for which the block face maintains a positive normal contact force with the rock mass. Now the potential energy of the system can be written as

$$V = \sum_{i \in A} 1/2k_i(\hat{n}_i \cdot \vec{s})^2 - \vec{R}_N \cdot \vec{s} \tag{4}$$

where  $\vec{R}_N$  is the component of the active resultant force acting in the plane perpendicular to the potential sliding direction (Fig. 5). Expanding the above, and noting that the  $n_i$  are unit vectors, we obtain,

$$V = \sum_{i \in A} 1/2k_i s^2 \cos^2(\theta_s - \theta_i) - R_N \cdot s \cdot \cos(\theta_s - \theta_r) \tag{5}$$

where  $R_N$  and  $s$  are magnitudes. In the above expression,  $\theta_i$  and  $\theta_r$  give the direction of each unit normal  $\hat{n}_i$  and the resultant force vector, respectively, measured clockwise from the positive  $Y$  axis.



**Fig. 5.** Normal and tangential components of active resultant

### Equilibrium condition

With the assumption of no rotation, the block displacement in the  $YZ$  plane has two degrees of freedom,  $\theta_s$  and  $s$ . The equilibrium displacement is one for what the total potential energy  $V$  of the system is stationary. Thus, for equilibrium we have the requirements:

$$\frac{\partial V}{\partial \theta_s} = 0 \quad \text{and} \quad \frac{\partial V}{\partial s} = 0 \quad (6)$$

where we note that, although the set  $A$  changes with  $\theta_s$ , the function  $V$  is piecewise continuous. Differentiating, we obtain,

$$\frac{\partial V}{\partial \theta_s} = \sum_{i \in A} (-k_i) s^2 \cos(\theta_s - \theta_i) \sin(\theta_s - \theta_i) + R_N s \cdot \sin(\theta_s - \theta_r) = 0 \quad (7)$$

and

$$\frac{\partial V}{\partial s} = \sum_{i \in A} k_i \cdot s \cdot \cos^2(\theta_s - \theta_i) - R_N \cos(\theta_s - \theta_r) = 0 \quad (8)$$

Assuming for the present that the stiffness  $k_i$  is known for each contact plane, we now have two Equations (7 and 8), and two unknowns,  $\theta_s$  and  $s$ . We let  $\theta_s^*$  and  $s^*$  denote, respectively, the values of  $\theta_s$ , and  $s$  which satisfy Equations 7 and 8. Then, solving for  $s^*$ , we obtain,

$$s^* = \frac{R_N \sin(\theta_s^* - \theta_r)}{\sum_{i \in A} k_i \sin(\theta_s^* - \theta_i) \cos(\theta_s^* - \theta_i)} \quad (9)$$

and

$$s^* = \frac{R_N \cos(\theta_s^* - \theta_r)}{\sum_{i \in A} k_i \cos^2(\theta_s^* - \theta_i)} \quad (10)$$

Equating Equations 9 and 10, we obtain,

$$\frac{R_N \sin(\theta_s^* - \theta_r)}{\sum_{i \in A} k_i \sin(\theta_s^* - \theta_i) \cos(\theta_s^* - \theta_i)} = \frac{R_N \cos(\theta_s^* - \theta_r)}{\sum_{i \in A} k_i \cos^2(\theta_s^* - \theta_i)} \quad (11)$$

which simplifies to

$$\tan(\theta_s^* - \theta_r) = \frac{\sum_{i \in A} k_i \sin(\theta_s^* - \theta_i) \cos(\theta_s^* - \theta_i)}{\sum_{i \in A} k_i \cos^2(\theta_s^* - \theta_i)} \quad (12)$$

The value of  $\theta_s^*$  which satisfies Equation 12 is the direction of the small displacement of the block, perpendicular to the potential sliding direction, such that the potential energy of the system is minimized. However, the equation includes the unknown spring constants  $k_i$ .

### Spring constant $k_i$

In the elastic model we assume that the spring constant  $k_i$  for each contact plane is proportional to the contact area and therefore, due to the prismatic shape, to the length  $L$  of a planar contact in the  $YZ$  plane. This assumption is reasonable given the behaviour of springs in parallel: two parallel springs each with a stiffness  $k$  yield an effective stiffness of  $2k$ . If the spring constants are replaced in Equation 12 by the product  $c, L_i$ , where the constant  $c$  is the unknown constant of proportionality, and  $L_i$  is the length of plane  $i$  perpendicular to  $R_T$  we obtain from which we obtain the value of  $\theta_s^*$ .

$$\tan(\theta_s^* - \theta_r) = \frac{\sum_{i \in A} c L_i \sin(\theta_s^* - \theta_i) \cos(\theta_s^* - \theta_i)}{\sum_{i \in A} c L_i \cos^2(\theta_s^* - \theta_i)} \quad (13)$$

Since the  $c$  is constant, it can be cancelled, yielding

$$\tan(\theta_s^* - \theta_r) = \frac{\sum_{i \in A} L_i \sin(\theta_s^* - \theta_i) \cos(\theta_s^* - \theta_i)}{\sum_{i \in A} L_i \cos^2(\theta_s^* - \theta_i)} \quad (14)$$

We then use a numerical routine to solve the equation

$$\frac{\sum_{i \in A} L_i \sin(\theta_s^* - \theta_i) \cos(\theta_s^* - \theta_i)}{\sum_{i \in A} L_i \cos^2(\theta_s^* - \theta_i)} - \tan(\theta_s^* - \theta_r) = 0 \quad (15)$$

The data required for determination of  $\theta_s^*$  are the angles  $\theta_i$ , and lengths  $L_i$ , of the  $n$  planes of discontinuity and the direction of the resultant force,  $\theta_r$ .

With  $\theta_s^*$  known, the magnitude of the displacement,  $s^*$ , for minimum potential energy can

be obtained by substituting the value of  $\theta_s^*$  into Equation 9 or 10. For example, replacing  $k_i$  by  $(c)$  ( $L_i$ ) in Equation 10, we have,

$$s^* = \frac{R_N}{c} \frac{\cos(\theta_s^* - \theta_r)}{\sum_{i \in A} L_i \cos^2(\theta_s^* - \theta_i)} \quad (16)$$

#### Distribution of normal forces

The magnitude of the normal force for each discontinuous surface due to the small displacement,  $s$  is computed as:

$$N_i = k_i (\hat{n}_i \cdot \vec{s}^*) = c L_i (\hat{n}_i \cdot \vec{s}^*) \quad (17)$$

or

$$N_i = c s^* L_i \cos(\theta_s^* - \theta_i) \quad (18)$$

The friction force can be determined for each contact plane by

$$F_i = \tan \phi_i [c s^* L_i \cos(\theta_s^* - \theta_i)] \quad (19)$$

where  $\phi_i$  is the angle of friction on plane  $i$ . If we assume the friction angle is the same for each

plane, noting that this assumption, although convenient, is by no means necessary, we arrive at

$$\sum_{i=1}^n F_i = \tan \phi c s^* \sum_{i \in A} L_i \cos(\theta_s^* - \theta_i) \quad (20)$$

for the total frictional resistance. Substituting  $s^*$  from Equation 16:

$$\sum_{i=1}^n F_i = \tan \phi \left[ \frac{R_N}{c} \frac{\cos(\theta_s^* - \theta_r)}{\sum_{i \in A} L_i \cos^2(\theta_s^* - \theta_i)} \right] \cdot \sum_{i \in A} L_i \cos(\theta_s^* - \theta_i) \quad (21)$$

which simplifies to

$$\sum_{i=1}^n F_i = R_N \tan \phi \cos(\theta_s^* - \theta_r) \frac{\sum_{i \in A} L_i \cos(\theta_s^* - \theta_i)}{\sum_{i \in A} L_i \cos^2(\theta_s^* - \theta_i)} \quad (22)$$

where  $A$  is the index set defined previously. Equation 22 represents the total resisting force against sliding for the contact faces of a prismatic rock block.

## FACTOR OF SAFETY AGAINST SLIDING

The safety factor is defined in the usual way as:

$$FS = \frac{\text{Resisting force}}{\text{Driving force}} \quad (23)$$

where the numerator is the summation of all friction forces, and the denominator is  $R_T$ , the component of the active resultant force acting parallel to the potential sliding direction. The safety factor is therefore given by:

$$FS = \frac{R_N}{R_T} \tan \phi \cos(\theta_s^* - \theta_r) \frac{\sum_{i \in A} L_i \cos(\theta_s^* - \theta_i)}{\sum_{i \in A} L_i \cos^2(\theta_s^* - \theta_i)} \quad (24)$$

Replacing  $R_N$  and  $R_T$  by  $(R \sin \delta)$  and  $(R \cos \delta)$ , respectively, the magnitude of  $R$  cancels out, so that we obtain,

$$FS = \tan \theta \tan \delta \cos \frac{\sum_{i \in A} L_i \cos(\theta_s^* - \theta_i)}{\sum_{i \in A} L_i \cos^2(\theta_s^* - \theta_i)} \quad (25)$$

### Applications

Having developed an analytical model for the factor of safety against sliding of an arbitrary prismatic block, we now apply the model to some particular cases: a two-plane wedge, a three-plane wedge and an example from Bregalnica river involving a block with a curved sliding surface.

The two plane prismatic block is the classic wedge; we use this to verify the energy-based stability model. Figure 6 shows three wedges with dip/dip direction of the bounding planes as given.

In each case the view is up the line of intersection of the two planes, i.e., opposite to the potential sliding direction. Loading is gravitational and the friction angle in each case is assumed to be  $20^\circ$ . On successive rows in the table (Fig. 6) are given the equilibrium angle of the displacement in the YZ plane (which is noticeably different for the three cases even though the loading is the same), the factor of safety as determined from the new energy-based model and the factor of safety determined from the well-known analytical solution for wedge slides. The good agreement between the

solutions lends credence to the model described in this paper. In fact, the agreement may be made ar-

bitrarily close by increasing the number of iterations in the numerical solution to Equation 15.

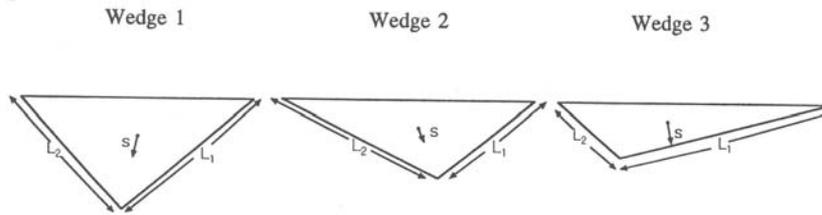


Fig. 6. Stability analysis of three wedges; comparison of results between energy-based model and analytical solution

Plane 1: 40/235	Plane 1: 40/250	Plane 1: 20/255	
Plane 2: 50/85	Plane 2: 30/100	Plane 2: 50/125	
Wedge 1      Wedge 2      Wedge 3			
$\theta_{\text{crit}}$	101.6°	67.7°	84.9°
F.S. (model)	1.9495834	2.46302	1.18806
F.S. (analytical)	1.9495835	2.46303	1.18807

We now consider prismatic block with three contact planes. The distribution of contact forces for such a block is statically indeterminate and therefore the stability cannot be determined by standard limiting equilibrium methods. The model described in this paper determines the configuration of contact forces corresponding to minimum potential energy of the system, from which the factor of safety may be calculated. The initial data are in Table 1, where  $f$  is the dip and  $a$  the dip direction of each discontinuity plane.

Table 1

Data for analysis of three-plane prismatic block

Plane	1	2	3
	45°	23°	45°
$a''$	120°	185°	250°

The friction angle on each plane is 20°. Fig. 7 graphs the factor of safety of the block against the length of the middle plane relative to the left and right planes. The main result is that there is a reduction in the factor of safety when the length ratio  $L_2/L_1$  increases. Upper and lower bounds for the factor of safety for the wedge ( $L_2 = 0$ ) and plane ( $L_2 = \infty$ ), calculated from the equations in Hoek and Bray (1981), are shown as horizontal lines. The factor of safety for the three-plane prismatic block is shown to range between these limiting values depending on the length of the middle plane. Figure 8 shows the change in the factor of safety versus the length ratio for a range of friction angles

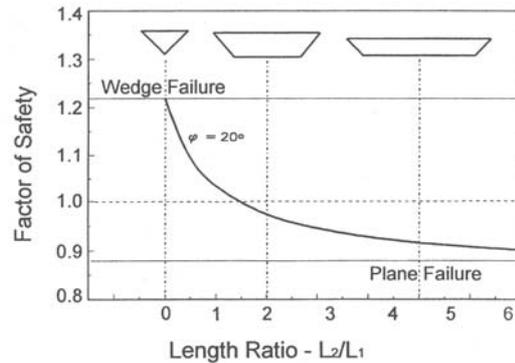


Fig. 7. Factor of safety versus length ratio  $L_2/L_1$  where  $L_1$  and  $L_2$  are the lengths of the end and middle planes, respectively. Upper and lower bounds correspond to the wedge and plane cases

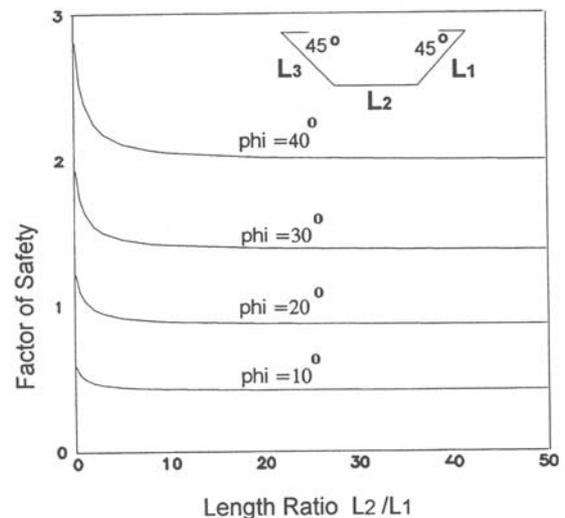
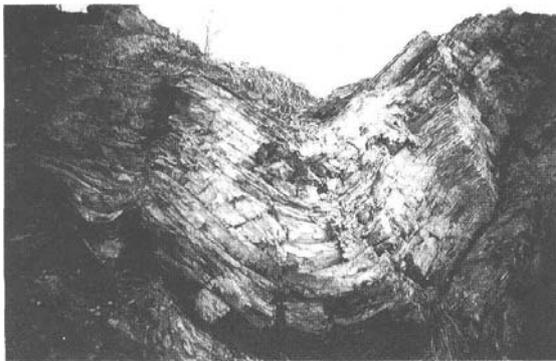


Fig. 8. Reduction of the factor of safety with change in the length ratio  $L_2/L_1$ , for a range of friction angles

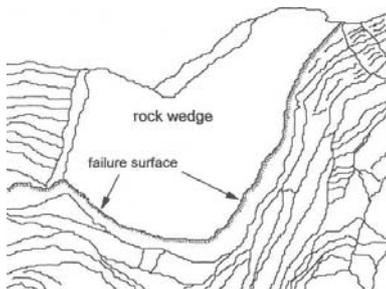
## EXAMPLE FROM FLOW TO BREGALNICA RIVER

The analytical model described above was used in a sliding stability investigation of a flow to the Bregalnica river (Bregalnica), in the east part of Macedonia. We analyzed the rock block shown in Fig. 9, in which the horizontal dimension is approximately 4 m. A line drawing of the block and the potential sliding surface is shown in Fig. 10.

The first step in the stability analysis is to discretize the sliding surface into a series of planar segments, as shown in Fig. 9. For each segment, the length  $L$ , and the angle  $\theta$ , (measured clockwise from the  $Y$  direction) corresponding to each planar segment is measured. The discretized failure surface must be a true profile, i.e. a profile in the plane perpendicular to the sliding direction (in this case, the fold axis). The plunge of the line of intersection was determined by standard structural geologic methods (e.g., Ramsay, 1967), to be  $32^\circ$ .



**Fig. 9.** Block bounded by curved sliding surface. Sevier Shale formation, Blount County, Bregalnica river. Horizontal dimension: 3 m



**Fig.10.** Line drawing of block showing potential sliding surface

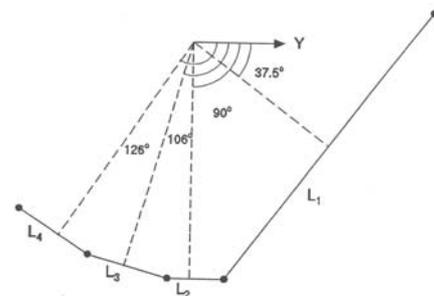
A friction angle of  $27^\circ$  was used in the analysis in accordance with friction angles for shale and siltstone reported by Hoek and Bray (1981). The applied load was assumed to include self-weight only and hydrostatic pressures on the sliding surface were assumed to be zero.

Two separate analyses were carried out, with the results presented in Table 2. For the Case 1 analysis we treated the block as a standard wedge bounded by the limiting planes in Fig. 11 and determined the factor of safety from the equation given by Hoek and Bray (1981). For Case 2 we analyzed the prismatic block with four contact planes and the geometry in Fig. 11 by the methods of this paper. As shown in Table 2, the factor of safety according to Case 1 was 1.14, whereas that determined from Case 2 was 1.0. Although there is evidence of previous translational failures in this particular road cut, we do not consider this an accurate back analysis. The friction angle used in the analysis is an estimated value and several of the other parameters, in particular the water conditions, are poorly known. What is clear, however, is that the factor of safety for the prismatic block with four sliding surfaces is significantly lower than that obtained from the wedge analysis. Thus treating this type of block as a wedge is, in general, unconservative.

**Table 2**

*Comparison of safety factor obtained from the wedge analysis ( $FS = 1.14$ ) with safety factor obtained from the prismatic block analysis ( $FS = 1.00$ ) for the block shown in Fig. 9*

Fold axis: $32^\circ$ , Trend $30^\circ$				
Plane No.	$L$ [cm]	$\theta$ ( $^\circ$ )	$\phi$ ( $^\circ$ )	$FS$
Case 1: Wedge analysis				
1	240	37.5	27	
2	117	126	27	1.14
Case 2: Prismatic block analysis				
1	193	37.5	27	
2	36	90	27	
3	36	106	27	
4	55	126	27	1.0



**Fig. 11.** Discretization of curved failure surface into planar segments

## CONCLUSIONS

In this paper we have described an energy-based approach to the determination of sliding stability of rock wedges with  $n$  cozonal sliding surfaces. Traditional methods of stability analysis of plane ( $n = 1$ ) and wedge ( $n = 2$ ) systems are based on limiting equilibrium of statically determinate systems. If the number  $n$  of contact planes is three or more, the distribution of normal forces among these planes is statically indeterminate.

We determine the distribution of normal forces corresponding to minimum potential energy of the system. Since we assume that effective normal stiffness is proportional to contact surface area, elastic moduli are not required. Thus we construct a general model for sliding stability analysis of blocks with any number of cozonal sliding surfaces. Since this is a general model, it includes plane and wedge failures as special cases, and indeed our results agree with the standard formulae for plane and wedge slides.

Field situations which give rise to  $n$  cozonal sliding surfaces with  $n > 3$  include wedges bounded by joint planes and internally subdivided by a third plane such as bedding, yielding blocks with three potential sliding surfaces such as that of Fig. 10, and blocks bounded by cylindrical folds such as that of Fig. 11. One of the practical implications of this work is that there may be a significant reduction of the factor of safety when three or more discontinuity planes form the sliding surface, as compared with the wedge case. This is important because many practitioners would analyze such blocks as wedges, and in doing so would arrive at an overly high factor of safety.

Future research plans on this topic will be directed towards development of a computer model for sliding stability analysis for digitized potential failure surfaces. This will open the way to rock slope stability analysis based on photogrammetric data and to a single coherent model which incorporates plane and wedge slides.

## APPENDIX

### *Definition of terms*

(1)  $s$  is the magnitude of a small translation of the prismatic block, directed into the rock mass, in the direction perpendicular to the potential sliding direction.

(2)  $\theta$  is the angle defining the direction of the small translation.

(3)  $k_i$  is the normal stiffness of plane  $i$ .

(4)  $n_i$  is the unit normal vector for each contact plane, directed out of the block.

(5)  $\alpha_i$  is the angle of each plane measured from the positive  $X$  axis.

(6)  $L$  is the length of each contact plane in the  $YZ$  plane.

(7)  $\theta_r$  is the angle defining the direction of the resultant force.

(8)  $R$  is the resultant of the active forces acting on the rock block.  $R$  has components  $R_N$  and  $R_T$ , perpendicular to and parallel to the sliding direction respectively.

(9)  $I$  is the line of intersection between the contact planes.

(10)  $i$  is a unit vector in the direction of the line of intersection  $I$ .

The terms defined in (3)...(10) are initially known from the loading conditions or the block geometry.

The variables (1) and (2), which determine the displacement vectors  $s$ , are initially unknown; their values are determined such that the potential energy of the system is minimized.

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## Резиме

## СТАБИЛНОСТ НА КАРПЕСТИТЕ МАСИ ПРОБИЕНИ СО ПОВЕЌЕКРАТНО ЛИЗГАЊЕ НА ПОВРШНИИ

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**Клучни зборови:** стабилност на падини; лизгави површини

И покрај тоа што стабилноста на некои падини и лизгави површини е дефинирана во геотехниката и во стручна литература, сепак во природата и во нашата окоина во која живееме секогаш не е можно лесно да се дефинира и моделира. Тие површини можат да создаваат цилиндрични геоморфолошки седиментни структури во кои јасно можат да се издвојат базични делови од цилиндарот кои се дуплираат. Новите анализи и модели на ваквите структури се дадени во овој труд. Моделите се направени најпрвин

како тие да се нормални со помош на пресметување на силите кои дејствуваат на системот и иницираната потенцијална енергија, за потоа преку овие параметри постепено да се дефинира повеќекратното лизгање на структурите спомнати погоре, со што се дефинира и коефициентот на стабилност на истражуваниот терен. На пример, земен е профил по течението на река Брегалница и направени се анализи кои се прикажани во овој труд.

## KARST AQUIFER IN MT GALIČICA AND POSSIBILITIES FOR WATER SUPPLY TO OHRID WITH GROUND-WATER

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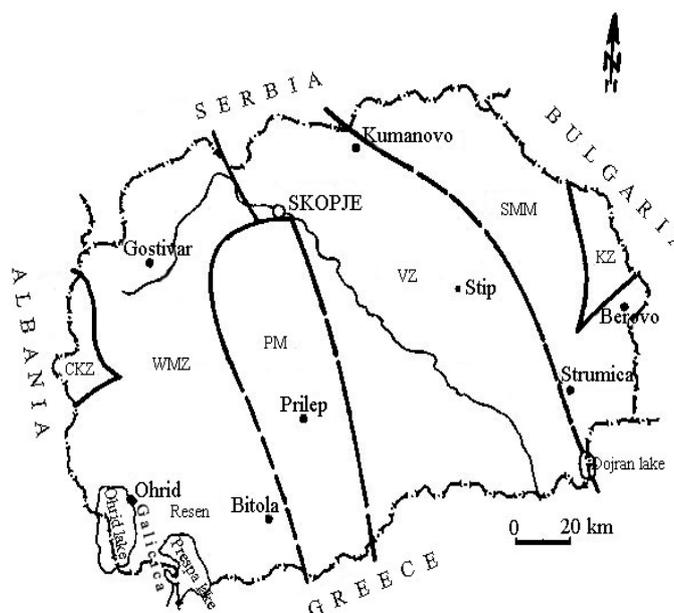
**Abstract:** In this paper are presented some hydrogeological features of the karst aquifer in Mt Galičica, which contains important quantities of ground-water that can be used for the water supply of the town Ohrid. Based on the hydrogeological data are given three solutions that can be used for water supply of Ohrid, the first one is to drill of deep wells, combination of deep and shallow wells, as well as construction of horizontal galleries.

**Key words:** karst aquifer; Mt Galičica; Triassic limestones; water supply; Ohrid

### INTRODUCTION

The karst aquifer in Mt Galičica is situated in the southwest of the country between Lake Ohrid and Lake Prespa (Fig 1). Part of it extends further to the territory of Albania and one to the territory

of neighbouring Greece. It is one of the largest karst aquifers in west Macedonia and plays an important role for the water supply of the town of Ohrid and maintains the water table of Lake Ohrid.



**Fig. 1.** Geotectonic map of the Republic of Macedonia and the position of the Mt Galičica (M. Arsovski, 1997).  
WMZ – Western Macedonian zone, PM – Pelagonian massive, VZ – Vardar zone, SMM – Serbo-Macedonian massive,  
CKZ – Cukali-Krasta zone, KZ – Kraistide zone.

## GEOLOGICAL FEATURES

Investigated area is part of the Western Macedonian zone (Fig 1), (Арсовски, 1997). The geology of the wider area of Mt Galičica is shown in the Geological map (Fig.2) (Думурџанов, Ивановски, 1972, 1973).

The geology of the surrounding of the aquifer consists of Paleozoic, Mesozoic, Tertiary and Quaternary rocks (Думурџанов, Ивановски, 1972, 1973, 1978; Ивановски, 1958.).

Paleozoic is present of sienites ( $\xi$ ), granodiorites ( $\delta\gamma$ ), metasandstones (sq), quartz-sericitic schists (Sqse).

The mesozoic rocks are present of Triassic massive limestones ( $T_2^{1,2}$ ), sandstones, slates, conglomerates ( $T_2^1$ ) and jurassic dijabases ( $\beta\beta$ ) and peridotite and serpentinite (oSe).

Tercier is made up of gravels, sands and clay ( $pl_3$ ), gravels, sands and clay and marls ( $pl_2$ ).

Quarter is present of alluvium (al), proluvium (pr), delluvium (d), terra rosa (ts); glaciofluvial sediments (fgl) and limnic sediment (j).

Mt Galičica is a horst built of Triassic massive karstified limestones overlying Paleozoic metamorphic rocks present as quartz-sericite-phyllite schists, sporadically as metasandstones.

## HYDROGEOLOGICAL FEATURES

The area of the Triassic limestones in Galičica is some 200 km<sup>2</sup>. Limestones are highly fissured and karstified with Paleozoic water impermeable schists at the foot. This makes possible the formation of karst fracture aquifers in them. Recharge of the aquifer is done by surface waters (rain water) that infiltrate through fractures, caverns, whirlpools and other vugs as well as by the water from Lake Prespa that flows underground to Lake Ohrid since Lake Prespa is situated at 160 m higher sea level than Lake Ohrid (Amataj et al., 2005)

Hydrogeological investigations carried out so far indicate that this karst-fracture type of aquifer formed in the Galičica limestones is characterized by deep karstification.

Outlet of water has been seen as many springs at the eastern and western banks of Lake Ohrid or underground.

The largest discharge the capacity of 5 – 9.5 m<sup>3</sup>/s is at the spring at St. Naum, 0.2 – 1 m<sup>3</sup>/s at Biljanini Izvori, 40 – 100 l/s at Bei Bunar. It is assumed that less 1 m<sup>3</sup>/s of water flow into the lake.

For the determination of water permeability, the degree of karstification, depth and the relationship between limestones and schists in the Galičica karst, several exploration drill holes were drilled close to the shore not far from Biljanini Izvori. (Кекиќ, 1978).

Exploration drill holes showed that the Triassic limestones at the foot of the mountain on the way to the lake are from 48 to 100 m thick. Exploration drill holes in limestones indicated that higher karstification degree could be found as far as the water impermeable base. Average porosity estimated based on investigation is from 15 to 20%.

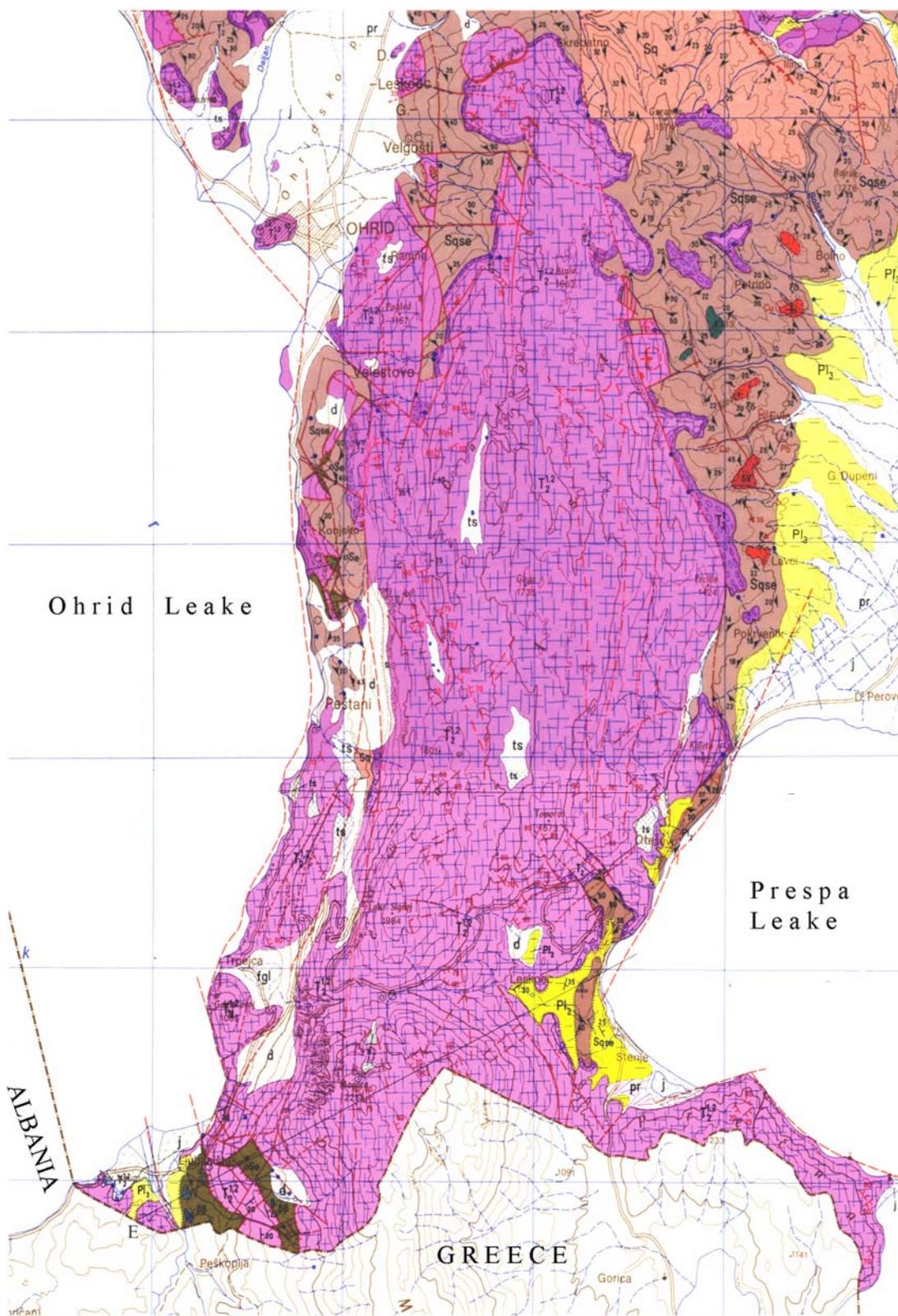
## WATER QUALITY

Water quality was studied with several chemical analyses for several karst springs. According to hardness which is from 7.4–10.8 degrees the water is classified as medium hard, whereas according to the chemical composition it is calcic bicarbonate.

According to Alekin's classification it is hydrocarbonate and belongs to the calcic group.

Total mineralization amounts from 244.6 to 325.6 mg/l and belongs to the poorly mineralized water.

pH value is from 6.6 to 7.5 and the water belongs to the neutral group of waters.



Quaternary: al – alluvium; pr – proluvium; d – deluvium; ts – tera rosa; fgl – glaciofluvial sediments; j – limnic sediment. Tercier: pl<sub>3</sub> – gravels, sands and clay; pl<sub>2</sub> – gravels, sands and clay and marls. Jurassic: ββ – dijabases; oSe – peridotite and serpentinite; Triassic: T<sub>2</sub><sup>1,2</sup> – massive limestones; T<sub>2</sub><sup>1</sup> – sandstones, slates, conglomerates. Paleozoic (Devon): ξ – sienites; δγ – granodiorites; sq – metasandstones; Sqse – quartz-sericitic schists (phyllite schists)

Fig. 2. Geological map of the area of Mt Galičica

POSSIBILITIES FOR A LONG-TERM WATER SUPPLY OF OHRID  
FROM THE KARST AQUIFER IN MT GALIČICA

The results obtained during hydrogeological investigations indicate that the karst in Mt Galičica contains significant amount of ground-water that recharge Lake Ohrid either underground or on the surface by waters that come out of numerous springs of variable yield such as Sveti Naum, Biljanini Izvori, Bej Bunar. In addition, large quantities of water are “captured” in the off shore karst towards Ohrid valley as deep ground accumulations. Explorations have also shown that the Galičica karst contains water at various depths.

According to the results obtained, including earlier results, for the understanding of the hydrogeological features of karstified limestones in Galičica, three possible solutions can be suggested in connection with the issue of water supply of Ohrid (Fig 3):

1. Deep wells,
2. Combination between deep and shallow wells,
3. Free gravitation and developing horizontal galleries

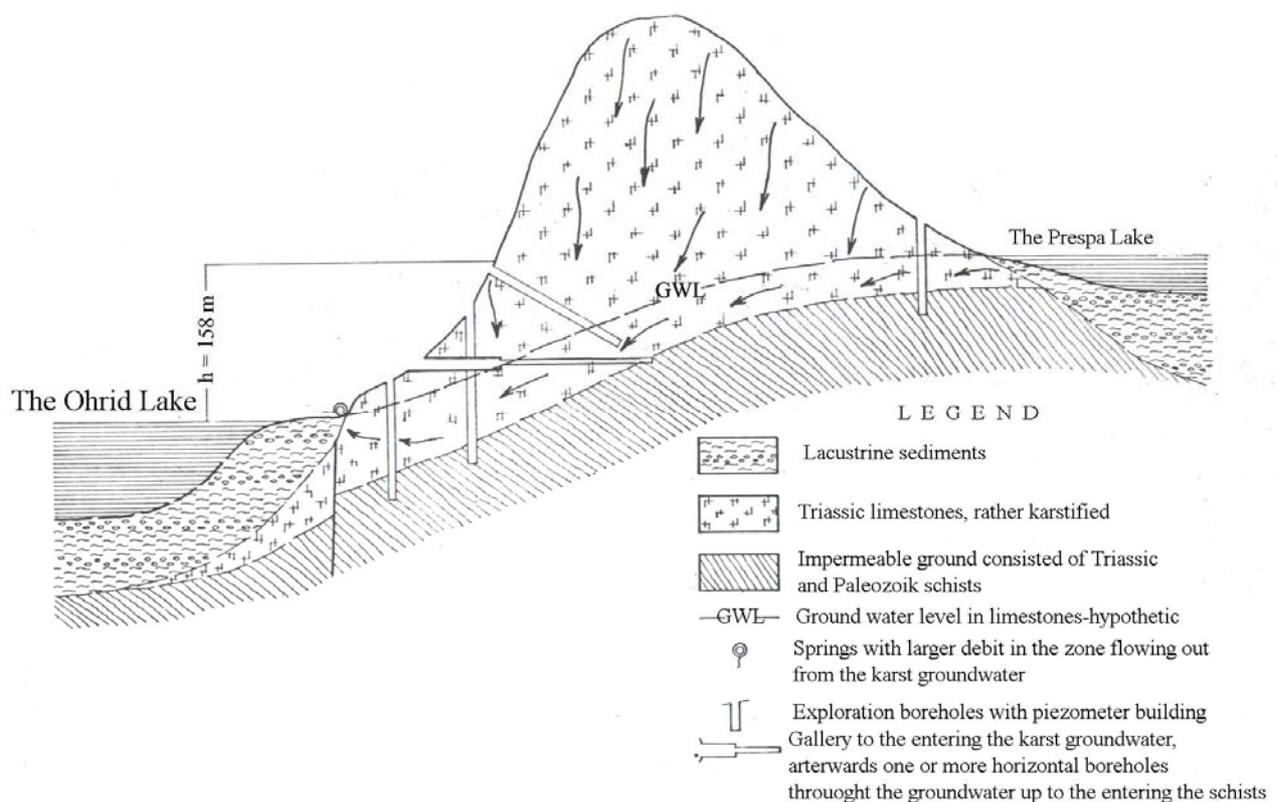


Fig. 3. Schematic hydrogeological profile from the Ohrid to the Prespa Lake across the Galičica mountain. The variant for a long-term water supply of the town Ohrid from the Galičica karst aquifer.

#### Deep wells

Water obtained from exploitation well 60 m at depth and the small lowering the level of the aquifer during test drawdown (particularly during summer and autumn) indicate that drilling several deep well is a possible solution in obtaining large amounts of water for water supply system of Ohrid.

#### Combination of deep and shallow wells

Data obtained for small lowering the dynamic level in shallow wells during test drawdown and during exploitation and the high level of groundwaters at the Biljanini Izvori – Bej Bunar strike indicate that it is possible to dig shallow wells combined with deep wells. The number will depend on the amount of water needed.

### Free gravitation and developing horizontal galleries

Favorable field conditions and the high ground-water potential make it possible to use ground-waters as free gravitation by making one or more galleries. The first possibility is the galleries

to be made 80 m above the Ohrid Lake level before they enter the karst aquifer waters and water capture by horizontal drill holes in water bearing surrounding. The second possibility is the entire length of the galleries to involve the water bearing surrounding as far as water impermeable base.

### CONCLUSION

Investigations carried out so far indicate that karstification of the Triassic limestones in Galičica is deep as far as water impermeable Paleozoic schists.

The aquifer contains important amounts of ground water, part of which is used for the water supply of Ohrid and is very promising for future water supply.

Analyses indicate that the best solution for the permanent water supply of Ohrid is the use of karst aquifer ground waters of drilling of deep wells, combination of deep and shallow wells as well as with free gravitation by the construction of horizontal galleries.

It is necessary to pay greater attention to water management and to the issue of protection of the waters against contamination.

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### Резиме

#### КАРСНИОТ ВОДОНОСНИК НА ПЛАНИНАТА ГАЛИЧИЦА И МОЖНОСТИ ЗА ВОДОСНАБДУВАЊЕ НА ОХРИД СО ПОДЗЕМНА ВОДА

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**Клучни зборови:** карстен водоносник; планина Галичица; тријаски варовници; водоснабдување; Охрид

Во овој труд се прикажани некои хидрогеолошки карактеристики на карсниот водоносник на планината Галичица, во кој се акумулирани значителни количества подземна вода, која може да се искористи за водоснабдување на градот Охрид.

Врз основа на хидрогеолошките податоци, предложени се три варијантни решенија кои можат да се искористат за водоснабдување на Охрид првата варијанта е со изработка на длабоки бунари потоа комбинација на длабоки и плитки бунари, или пак со изработка на хоризонтални галерии.

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**Original scientific papers** report unpublished results of completed original scientific research. Experimental data should be presented in a way that enables reproduction and verification of analyses and deductions on which the conclusions are based. Manuscripts should normally not exceed 6000 words.

**Short communications** should also contain completed but briefly presented results of original scientific research. Manuscripts should normally not exceed 2000 words.

**Reviews** are submitted at the invitation of the Editorial Board. They should be critical surveys of an area in which preferably the author himself is active. The reviews can be longer than typical research articles but should generally be limited to 10 000 words including references, tables and figures.

**Professional papers** report on useful practical results that are not original but help the results of the original scientific research to be adopted into scientific and production use. Manuscripts should normally not exceed 4 000 words.

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**Acknowledgement.** Financial support, advice or other kinds of assistance can be included in this section.

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### Journals:

(Boev et al., 1992): Boev Blažo, Čifliganec Vančo, Stojanov Risto, Lepitkova Sonja, 1992: Oligocene-Neocene magmatism in the region Bučim block. *Geologica Macedonica*, **6**, 23–32.

(Makreski et al., 2004): Makreski Petre, Jovanovski Gligor, Stafilov Trajče, Boev Blažo, 2004: Minerals from Macedonia, XII. The dependence of quartz and opal color on trace element composition – AAS, FT IR and micro-Raman spectroscopy study. *Bull. Chem. Technol. Macedonia*, **23**, 2, 65–212.

### Scientific meetings:

(Stojanov, 1990): Stojanov Risto, Serafimovski Todor, 1990: The volcanism in the Zletovo–Kratovo volcanic area. In:

"XII Congress of Geologists in Yugoslavia", Ohrid, 405–124.

### Books:

(Boev, 1996): Boev Blažo, Janković S., 1996: *Nickel and nickel-ferrous iron deposits of the Vardar zone (SE Europe) with particular reference to the Ržanovo–Studena Voda ore bearing series*. Faculty of Mining and Geology, Spec. Iss. No. **3**, pp. 273.

(Manahan, 2000): Manahan S. E., *Environmental Chemistry*, Seventh editions. CRC Press LLC, Boca Raton.

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