GEOLOGICA MACEDONICA

СОДРЖИНА

TABLE OF CONTENTS

CORRELATION OF STRATIGRAPHIC DISTRIBUTION OF THE FORAMINIFERS IN THE OVČE POLE AND TIKVEŠ PALEOGENE BASIN, THE REPUBLIC OF MACEDONIA

Violeta Stojanova, Goše Petrov

The "Goce Delčev" University, Faculty of Natural and Technical Sciences,
Department of Geology and Geophysics,
Goce Delčev 89, MK-2000 Štip, Republic of Macedonia
violeta.stojanova@ugd.edu.mk // gose.petrov@ugd.edu.mk

A b s t r a c t: The Ovče Pole and Tikveš Paleogene basins are big sedimentary complexes, which belong to the eastern and central part of the Vardar zone within the territory of the Republic of Macedonia.

In accordance to previos studies, the age of the Paleogene sediments (based on numerous fossilis from the microfossil groups) in the Ovče Pole and Tikveš basins has been determined as Upper Eocene.

The results of the micropaleontological investigations on the plankton of foraminifer fauna, found in the upper flysch lithozones of the OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin) drill holes. The biostratigraphical value of the plankton of foraminiferal fauna in drillings OP-1 and KR-1 gave us the cache to divide one local biostratigraphical zone in the Ovče Pole and Tikveš basin.

In relation to this, correlation of the biostratigraphical zones was made between the Ovče Pole and Tikveš Paleogene basin.

Key words: Paleogene; benthic and planktonic foraminifers; biostratigraphic zone; Ovče Pole basin; Tikveš basin

INTRODUCTION

The paleogene sediments in Macedonia are widely spread on the area of the Vardar zone, where they are divided in two main basins: Tikveš and Ovče Pole, in which the sediment accumulations are from 3000 – 3500 m thick.

Tikveš basin is situated in the south-west part of the territory of Macedonia and belongs to the central part of the Vardar zone.

Ovče Pole basin is mainly distributed in the east and central vardar subzone. To the south and south-west connects with the Tikveš basin (Fig. 1).

According to the previous explorations, the age of the paleogene sediments (based on plenty fossil remains from macrofossil groups) in the Ovče Pole and Tikveš basin is determined upper eocene.

According to the lithological characteristics, the sediment mass in the paleogene basins with 3000–3500 m thicknes, is consisted from four lithostratigraphic units (litozones): basal lithozne, lower flysch lithozones, lithozones of yellow sandstones and upper flysch lithozone. Lithostatigraphic composition of this basin is very similar or same, which is explored in the plenty discovered profiles and it is proven with the deep drill in the Tikveš and Ovče Pole basin.

In the period since year 1965 – 1968 on the area of the Vardar zone in the territory of Macedonia, several drill were done, previously selected with geological and geophysical studies, in order to determine the capabilities of the area, in relation with perspective of the possibilities to discover liquid and gas carbohydrogens.

The subject of this paper is the micropaleontological analyses on the plankton of foraminifer fauna in the Paleogene sediments on the OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin) drill holes. The subject of this paper is to present the results of the stratigraphic distribution of the plankton of foraminifer fauna in the Ovče Pole and Tikveš basin, which we consider as very significant for the biostratigraphic zones of the paleogene basins.
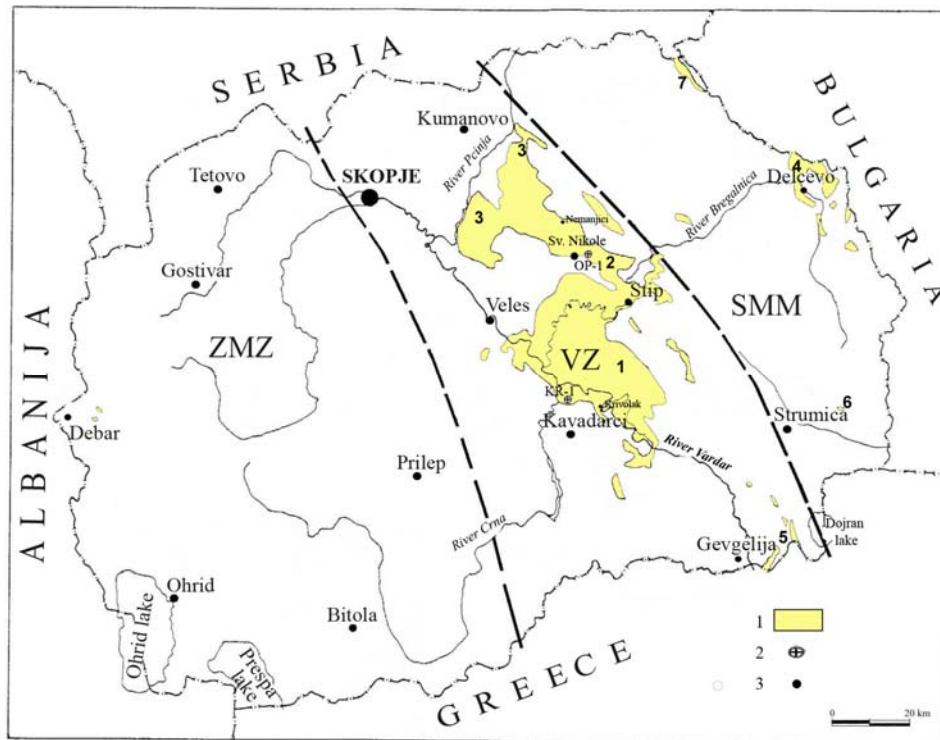
Fig. 1. Distribution of Paleogene sediments in the Republic of Macedonia
SMM – Serbian-Macedonian massif, VZ – Vardar zone, ZMZ – Western Macedonian zone,
1 – Tikveš Paleogene basin, 2 – Ovče Pole Paleogene basin, 3 – drill hole

MATERIAL AND METHODS

The study of the biostratigraphic importance of the plankton of foraminifer fauna in the studied basins is followed with stratigraphical distribution of 12 species, from 58 samples from the drill OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin), Fig. 1.

Sampling and the technical processing of foraminifer fauna from the core material of the OP-1 and KR-1 drill holes is performed using classical methods of the micropaleontological analyses (decomposition, washing, drying, selecting and determination).

RESULTS

Micropaleontological studies on foraminifer fauna of the Paleogene sediments in drill-holes OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin) have discovered rich microfossil association, which has been represents by foraminifers, ostrakodes, briozoes, algae, radiolarii, echinodermata and micro-mollusks remainings (gastropods, lamellibranhiats). The microfauna found in the profiles OP-1 and KR-1 is tiny and degenerated, where the forms are mostly badly preserved, recrystallized and agglutinated, by which their determination is difficult.

In the sections OP-1 and KR-1 rich foraminifer fauna, represented in planktonic and benthic forms, which have the characteristic of monotony of species and bigger number of samples in the analyzed tests. The benthic foraminifers which

were found are more different, dominantly included in quantity and are represented from huge number of species and genuses, and have wide vertical distribution in the Tercier and because of that they do not have particular stratigraphic importance.

The planktonic foraminifer association found in the sections OP-1 and KR-1, has allowed us to apostrophe the important stratigraphic indicators, and based on it the chronostratigraphic interpretation of the series. Biostratigraphic importance of the planktonic foraminifers represents one important criteria for separating of biozones by planktonic foraminifers is the occurence and disappearing of particular species or group of species. Based on this standard stratigraphic zone scheme was made (Cavelier, Pomerol, 1986) for the Paleogene.

According to the standard stratigraphic scheme the Paleogene sediments in the Tikveš and Ovče Pole basin from our research are interpreted like Upper Eocene – Priabonian.

Stratigraphical data for the section OP-1

The drill OP-1 is located in the east part of the Ovče Pole basin, approximately 1.5 km. north-east from v. Ergelija (near the town of Sv. Nikole). The drilling is deep 1910 m. The drilling cuts the complex of Paleogne sediments and ends in the base represented with jura granite. Lithological members of the drilling from the bottom to the surface are represented with sediments from the basal lithozone (lake and continental red conglomerates, aleurolites, sandstone and claystone), from the lower flysch lithozone (dark gray sandstone, aleurolite and claystone) and upper flysch lithozone (marly, aleurolites, sandstone, marly oolithic limestones and clayey).

In the section of the drilling OP-1 micropaleonological sampling was performed, and 39 samples are analyzed (Fig. 2).

Benthic foraminifers found in the section OP-1 are from the genera: *Cibicides*, *Robulus*, *Eponides*, *Gyroidina*, *Pullenia*, *Planulna*, *Quinqueloculina*, *Chysalogonium*, *Nonionella*, *Guttulina* and *Spiroplectammina*, which are in the sediment series in the drilling OP-1, have wide vertical distribution in the tercier, and because of that they are not with special stratigraphic importance.

Planktonic foraminifer fauna found in the sediments of the upper flysch lithozone, represented with the following representatives: *Globorotalia pseudoscitula* (Glaes), *Globigerina bulloides* d'Orbigny, *Globigerina corpulenta* Subbotina, *Globigerina eocaenica* Terquem, *Globigerina sp.*, *Globigerina venezuelana* Hedberg, *Globigerina triloculinoides* Plummer, *Globigerina eocaena* Gümbel, *Turborotalia pomeroli* (Toumarkine & Bolli), *Globigerina officinalis* Subbotina, *Catapsydrax dissimilis* (Cushman & Bermudez), *Globigerinatheka tropicalis* (Blow & Banner), *Globigerina triloculinoides* Plummer and *Globigerinatheka index rubriformis* Subbotina.

If analyses are made to the micropaleontologic section in whole, the maximal frequency and contents of plankton of foraminifera is showing in the upper flysch lithozone on deepness interval from 550 to 20 m (samples 28 – 39), i.e. in the upper parts of the section of the drill-hole, and under the deepth interval from 565 m (sample 27) plankton foraminifer fauna disappears.

Litostratigraphic unit	Samples	Depth (m)	Globorotalia pseudoscitula	Globigerina bulloides	Globigerina corpulenta	Catapsydrax dissimilis	Globigerina venezuelana	Globigerina sp.	Globigerina triloculinoides	Globigerina eocaena	Turborotalia pomeroli	Globigerina officinalis	Globigerina eocaenica	Globigerinatheka tropicalis	Globigerinatheka index rubriformis	Geological age
Upper flysch lithozone	39	20							*					*	*	Upper Eocene
	38	65		*							*			*	*	
	37	100		*	*			*	*	*	*			*		
	36	125		*		*			*	*	*	*	*	*		
	35	170					*	*	*	*	*	*	*			
	34	255			*		*	*	*	*						
	33	290		*	*	*	*									
	32	370		*	*	*										
	31	415		*	*											
	30	445	*													
	29	540	*													
	28	550	*													
	1–27	1270–565	no planktonic foraminifers													

Fig. 2. Distribution of planktonic foraminifers in the section OP-1

The middle part of the section, which is the bottom flysch lithozone on deepness from 782–1200 m is characterized with poor microfosill contents, which does not have stratigraphic value, and the bottom part of the profile (basal lithozone), on deepness from 1270–1798 m, is characterized with absence of microfossils.

As an index – fossils in the plankton foraminifer association, are taken the taxa: *Catapsydrax dissimilis* (Cushman & Bermudez) and *Globigerinatheka tropicalis* (Blow & Banner), which by their chronostratigraphic meaning could be classified as Upper Eocene – Priabonian, in the hidnest parts of the section.

Stratigraphical data for the section KR-1

The drill KR-1 is located in the valley of Kurjacka River, approximately 500 meters west from the village of Sopot, with deepness of 2703 m (north-east from the town Kavadarci). The drilling cuts the complex of the Paleogene sediments, which is interrupted, without reaching the paleorelief. Lithological members of the drilling on the bottom to the surface are represented with sediments from the basal lithozone (clastic material, marly sandstones, clayey and sandston-aleurolites and brecciated conglomerates material) and sediments on the upper flysch lithozone (sandy-marly, marly-clays, marly and sandstones, which alternately change, with rear pro-layers conglomerates, clayey-aleurolites, and marly sandstones).

In the section KR-1 micropaleontologic sampling was made and 19 samples were analyzed (Fig. 3).

Based on the data from the micropaleontologic analyses, the foraminifer fauna from the section KR-1 (Tikveš basin) is characterized with association of benthic and planktonic foraminifers.

Litostratigraphic unit	Samples	Depth (m)	*Catapsydrax dissimilis*	*Globigerina venezuelana*	*Globigerina sp.*	*Globigerina officinalis*	*Globigerinatheka tropicalis*	*Turborotalia pomeroli*	*Globigerina triloculinoides*	*Globigerina bulloides*	*Globigerina eocaenica*	Geological age
Upper flysch lithozone	19	10–130			*	*	*	*	*	*	*	Upper Eocene
	18	150–530			*							
	17	540–1250			*	*						
	16	1270–1325		*	*							
	15	1335–1400		*								
	14	1410–1505	*									
	13	1610–1670	*									
	1–12	1710–2700	no planktonic foraminifers									

Fig. 3. Distribution of plankton of foraminifers in the section KR-1

The planktonic foraminifers association is represented with the following representatives: *Catapsydrax dissimilis* (Cushman & Bermudez), *Globigerina venezuelana* Hedberg, *Globigerina sp.*, *Globigerina officinalis* Subbotina, *Globigerinatheka tropicalis* (Blow & Banner), *Turborotalia pomeroli* (Toumarkine & Bolli), *Globigerina triloculinoides* Plummer, *Globigerina bulloides* d'Orbigny, *Globigerina eocaenica* Terquem.

Most common representatives of the benthic foraminifers is from the genus *Cibicides* with the species: *Cibicides* cf. *dutemplei* (d'Orbigny), *Cibicides ungerianus* d'Orbigny and than as second most common is comming the genus *Robulus* with the species: *Robulus orbicularis* (d'Orbigny), *Robulus limbatus* (Bornemann), *Robulus* cf. *inornatus* (d'Orbigny), *Robulus cultratus* (Montfort), *Robulus* cf. *pseudovortex* Cole. Several samples from the genera are found also: *Vaginulinopsis,. Karreriella, Bathysiphon, Glandulina, Cyclammina sp., Textularia, Clavulinoides szaboi, Gyroidina, Nonion, Marginulina, Chrysalogonium, Uvigerina, Bulimina, Eponides*. Porcelaneous foraminifera is represented with representatives of the species: *Trilocu-*

lina, Quinqueloculina and *Pyrgo* which were found in several samples, and are usually tiny, with more dimentions and badly conserved. The discovered fauna material derives from aleurolite- marly-sandy sediments.

If analyses are made to the macro-paleontologic section in whole, most interesting is the upper part of the section of the drilling, deepness interval from 1670 – 10 (samples 13–19) where by percentage of involvement the planktonic foraminifers are dominating.

The midle and bottom part of the sediment series is practicaly sterile from viewpoint of the microfosills content, with exception of some samples which have from one to two microfosills and does not have stratigraphic value.

The association of the planktonic foraminifers and vertical distribution of separate taxa, contained in the KR-1: *Catapsydrax dissimilis* (Cushman & Bermudez), *Globigerina venezuelana* Hedberg, *Globigerina sp., Globigerina officinalis* Subbotina, *Globigerinatheka tropicalis* (Blow & Banner), *Turborotalia pomeroli* (Toumarcine & Bolli), *Globigerina triloculinoides* Plummer, *Globigerina bulloides* d'Orbigny, *Globigerina eocaenica* Ter-

quem, gave us the chance to identify one local biostratigraphic zone *Catapsydrax dissimilis – Globigerinatheka tropicalis* in the Tikveš basin. The highest parts (samples 13 – 19) of the profile KR – 1 belong to the local biostratigraphic zone *Catapsydrax dissimilis – Globigerinatheka tropicalis,* and the sediments of the upper flysch lithozone are belonging to the Upper Eocene – Priabonian geological age.

The biostratigraphic zone *Catapsydrax dissimilis – Globigerinatheka tropicalis* is characterized with the species *concurrent zone – zone* of vertical distribution of at the same time for first time occurrence of the species *Catapsydrax dissimilis* (Cushman & Bermudez), till the last disappearance of the species *Globigerinatheka tropicalis* (Blow & Banner). The bottom border of the zone is defined with the first occurrence of the index species *Catapsydrax dissimilis* (Cushman & Bermudez), and the upper border is positioned to the last disappearance of the index species *Globigerinatheka tropicalis* (Blow & Banner). The borders of the zone represent the interval on the midle P 15 to the end of P 17 and are belonging to the Upper Eocene – Priabonian geological age (Fig. 4).

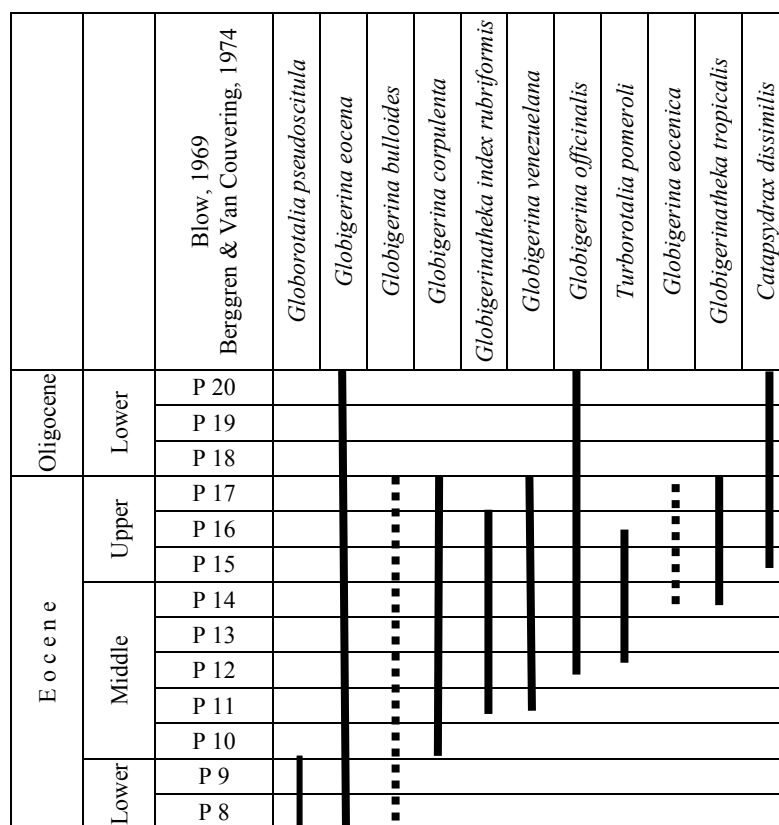| Epoch	Sub	Blow, 1969 / Berggren & Van Couvering, 1974	Globorotalia pseudoscitula	Globigerina eocena	Globigerina bulloides	Globigerina corpulenta	Globigerinatheka index rubriformis	Globigerina venezuelana	Globigerina officinalis	Turborotalia pomeroli	Globigerina eocenica	Globigerinatheka tropicalis	Catapsydrax dissimilis
Oligocene	Lower	P 20		█					█				█
		P 19		█					█				█
		P 18		█					█				█
Eocene	Upper	P 17		█	┊	█		█			┊	█	█
		P 16		█	┊	█	█	█		█	┊	█	█
		P 15		█	┊	█		█		█	┊	█	█
	Middle	P 14		█	┊	█		█		█	┊		
		P 13		█	┊	█		█		█			
		P 12		█	┊	█		█		█			
		P 11		█	┊	█		█					
		P 10		█	┊	█							
	Lower	P 9	█	█	┊								
		P 8	█	█	┊								

Fig. 4. Stratigraphic distribution of selected planktonic foraminifers from the Paleogene (Toumarkine & Bolli, 1985)

The main characteristic of the zone is the presence of other benthic foraminifer species in the profile:

– species which are found only in the zone *Catapsydrax dissimilis* (Cushman and Bermudez) and *Globigerinatheka tropicalis* (Blow & Banner).

– species which come from the older levels and disappear in within zone: *Globigerina venezuelana* (Hedberg), *Globorotalia pseudoscitula* (Glaesner), *Globigerina inflata* (d'Orbigy), *Globorotalia triloculinoides* (Plummer), *Robulus arcuatostriatus* (Hantken), *Robulus pseudovortex* Cole, *Robulus inornatus* (d'Orbigy), *Globigerina bulloides* (d'Orbigy);

– species that are found in the zone, but continue later *Spiroplectammina nuttalli* Lal, *Karreriella brady* (Cushman);

– species which are transitional for the zone: Globigerina eocaena Gűmbel, *Globigerina officinalis* (Subbotina), *Globigerina eocaenica* Terquem, *Quinqueloculina juleana d'Orbigy*, *Guttulina problema d'Orbigy*, *Giroidina soldani* (d'Orbigy), *Giroidina girardana* (Reuss), *Eponides umbonatus* (Reuss), *Eponides pygmeus* (Hantken), *Pullenia quadriloba* (d'Orbigy), *Pullenia bulloides* (d'Orbigy), *Anomalina grosserugosa* (Gűmbel), *Planulina costata* (Hantken), *Cibicides ungerianus d'Orbigy*, *Cibicidoides mexicanus Nuttal*, *Cibicides dutemplei* (d'Orbigy), *Elpphidium advenum* (Cushman).

The highest levels of the section OP-1, the interval between the samples 35 – 39 belong to the local biostratigraphic zone *Catapsydrax dissimilis* (Cushman and Bermudez) – *Globigerinatheka tropicalis* (Blow & Banner), are characterized by Upper Eocene – Priabonian geological age.

The sediments of the upper flysch lithozone on depth of 1670–10 m (samples from 13–19) from the section KR-1 of the Tikveš basin belong to the local biostratigraphic zone *Catapsydrax dissimilis* (Cushman and Bermudez) – *Globigerinatheka tropicalis* (Blow & Banner), to the Upper Eocene – Priabonian geological age.

Stratigraphic correlation between sections OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin)

For the stratigraphic correlation between the sections OP-1 and KR-1, is started from the mutually included elements connected for several Paleogene beds, i. e. from zones that have most of the paleontology data – foraminifers (Fig. 5).

In such a case, for correlation betwen drill-holes OP-1 and KR-1, as standard horizons were taken zones with planktonic foraminifers.

Considering drill-hole OP-1 as marker bed was determined the depth range 32 – 39 with most common presence of planktonic foraminifers: *Globorotalia pseudoscitula* (Glaes), *Globigerina bulloides* (d'Orbigny), *Globigerina corpulent* (Subbotina), *Globigerina eocaenica* Terquem, *Globigerina sp.*, *Globigerina venezuelana (*Hedberg), *Globigerina triloculinoides* (Plummar), *Globigerina eocaena* (Gümbel), *Turborotalia pomeroli* (Toumarkine), *Globigerina officinalis* (Subbotina), *Catapsydrax dissimilis* (Cushman & Bermudez), *Globigerinatheka tropicalis* (Blow & Banner), *Globigerina triloculinoides* (Plummer) и *Globigerinatheka index rubriformis* (Subbotina). The bottom stratigraphic level of the profile is represented with association of planktonic foraminifers which are included in the sample 32. The upper stratigraphic level is represented with the association of the foraminifers in the sample 39.

Paleogene beds of the drill hole represents the depth interval between samples 13 and 19 in association of planktonic foraminifers.

And in the section KR-1, the bottom startigraphic level is represented with the association of planktonic foraminifers in the sample 13, and the upper level is represented with the Foraminifera association in sample 19. From the correlation can be concluded that of the KR-1 drill-hole, between the samples 13 – 19, are on the same stratigraphical level with the layers from the drilling OP-1, in the depth interval between the samples 32 – 39 (directly under the surface). In this horizont are included the leading planktonic species *Catapsydrax dissimilis* (Cushman and Bermudez) and *Globigerinatheka tropicalis* (Blow & Banner), which have the shortest vertical distribution from the zone P15 to the zone P17. This elements gave us the chance to define the Upper Eocene, which directed us to its highest Upper part – horizont (P17), and the horizont which represents the base of preabon (P15), determines the border of the Upper Eocene in relation with the older Paleogene.

The joint of plankton foraminifer fauna in the Upper Eocene sediments of the section OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin) shows us the similar bionomic conditions and existence of relations between this basins during the sedimentation of the sediments.

This kind of similarities probably exist with the other paleofaunistic association in the Eocene in the Mediterranean area.

Depth OP-1   Depth KR-1
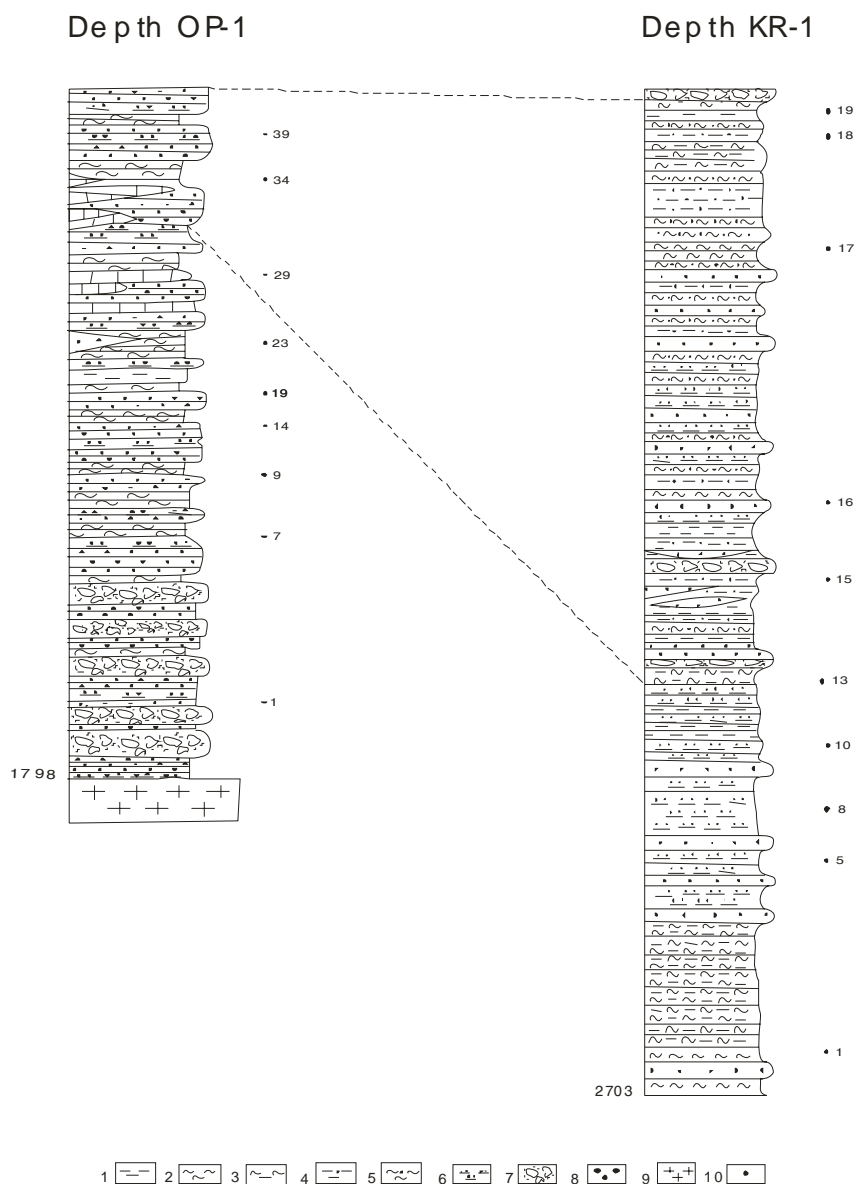
Fig. 5. Correlation of Paleogene beds in OP-1 and KP-1 well sections by planktonic Foraminifera
1 – marly, 2 – clayey, 3 – marly-clayey sediments , 4 – marly sandstones, 5 – clayey sandstones, 6 – aleurolites,
7 – conglomerates, 8 – sandstones, 9 – granites, 10 – samples

CONCLUSION

Based on the results of the stratigraphic distribution of the plankton of foraminifers species in the sections OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin), is identify *Catapsydrax dissimilis* (Cushman and Bermudez) – *Globigerinatheka tropicalis* (Blow & Banner) local biostratigraphic zone of the Upper Eocene – Priabonian geological age.

With this finding, the geological age of the Paleogene sediments from the upper flysch lithose of the Ovče Pole and Tikveš basins categorically belong to the Upper Eocene–Priabonan geological age.

In relation to this, correlation was made to the biostratigraphic zones between the Ovče Pole and Tikveš paleogenic basin. The joint of plankton foraminifer fauna in the Upper Eocene sediments of the sections OP-1 (Ovče Pole basin) and KR-1 (Tikveš basin) shows the similar bionomic conditions and existence of relations between this basins during the sedimentation of the sediments.

After the formation of this sediments the sedimentation stopped, most probably as a result of tectonic impulses, which in that time were very intense in the frames of the Alpic orogenic cycle.

REFERENCES

Arsovski M., Dumurdžanov N., 1995: Alpine tectonic evolution of the Vardar zone and its place in the Balcan region. *Geologica Macedonica*, **9**, 1, 15–22.

Grűnig A., 1985: Systematical description of Eocene benthic foraminifera of Possagno (Northern Italy), Sansoain (Northern Spain) and Biarritz (Aquitaine, France) – *Memorie di Sc. Geolog.*, **37**, 251–302, Fig. 2, Tab. 1, Padova.

Джуранов С., 1992: *Стратиграфия на Еоцена в Бургаско*. – Сп. Бълг. геол. д-во, 53.

D'Orbigny A., 1846 : *Foraminiferes fossiles du bassin tertiere de Vienne*. – Gide et Comp., 1 – 303.

Dumurdžanov N., Petrov G., Tuneva V., 1997: *Evolution of Lacustrine Neogenne – Pleistocene in the Vardar zone in Republic of Macedonia*. Symposium – Dojran.

Juranov, S., 1983: Planctonic foraminiferal zonation of the Paleocene and the Lower Eocene in part of East Balkan Mountains. *Geol. Balc.*, **13**, 2, 59–73.

Kaasschieter J., 1961: Foraminifera of the Eocene of Belgium. *Mem. Inst. Sci. Nat. Belgique*, 147, 1–271.

Колективен труд на членовите на САН, 1954: Геолошки состав и тектонска структура једног дела Овчег Поља и Тиквеша са палеонтолошком документацијом. *Трудови на Геолош. завод*, Скопје. фасц. 4.

Lőeblich A., and Tappan H., 1988: *Foraminiferal Genera and their Classification: plates New York*, Van Nostrand Reinhold, 900 p.

Pozaryska K., 1977: Upper Eocene Foraminifera of Poland and their paleographical meaning. *Acta Paleont. Pol.*, **22**, 1, 3–54.

Proto Decima, F., H. Bolli, 1978: Southeast Atlantic DSDP leg 40 Paleogene benthic foraminifers. In: *Init. Repts. DSDP*, 40, 783–809.

Stainforth R., and Lamb J., Luterbacher H., Beard J., Jeffords R., 1975: Cenozoik Planctonic foraminiferal Zonation and index forms. *The Univ. of Kansas, Paleontol. Contr.*, 62, 425 p.

Субботина Н., 1953: Верхнеэоценовые лягениды и булиминиды юга СССР. *Тр. ВНИГРИ, н. сер.*, 69, 115 – 255.

Temkova V., 1985: Проблем на границата помеѓу горен еоцен и олигоцен во Македонија. *Geol. Glasnik*, **28**, projekt 174, Sarajevo.

Toumarkine M., and H. Luterbacher, 1985: *Paleocene and Eocene planktic foraminifera*. In: Bolli, H. & (Eds.) "Plankton stratigraphy", Cambridge Univ. Press, 87–154.

Cavelier C., and Pomerol C., 1986: Stratigraphy of the Paleogene. *Bull. Soc. geol. France*, **II**, 2, 255–265.

Cushman J., and Jarvis P., 1928: Foraminifera from Trinidad. *Contr. Cush. Lab. Foram. Res.*, **4**, 85–103, 12–14.

Čanovič M., 1969: *Rezultati od mikropaleontoloških ispitivanja sedimentne serije u bušotini Ovče Polje – 1 (Makedonija)*. Nafta Gas. Novi Sad.

Čanovič M., 1969: *Mikrobiostratigrafsko proučavanje sedimentne serije u profilu bušotini Kurjačka reka – 1 (Makedonija)*. Nafta Gas. Novi Sad.

Р е з и м е

КОРЕЛАЦИЈА НА СТРАТИГРАФСКА ФОРАМИНИФЕРНА РАСПРОСТРАНЕТОСТ ВО ОВЧЕПОЛСКИОТ И ТИКВЕШКИОТ ПАЛЕОГЕНСКИ БАСЕН ВО РЕПУБЛИКА МАКЕДОНИЈА

Виолета Стојанова, Гоше Петров

Универзитет „Гоце Делчев", Факултет за природни и технички науки, Катедра за геологија и геофизика, Гоце Делчев 89, МК-2000 Штип, Република Македонија
violeta.stojanova@ugd.edu.mk // gose.petrov@ugd.edu.mk

Клучни зборови: палеоген; бентосни и планктонски фораминифери; биостратиграфска зона; овчеполски басен; тиквешки басен

Овчеполскиот и тиквешкиот палеогенски басен претставуваат големи седиментни маси и припаѓаат на источниот и централниот дел од вардарската зона на територијата на Македонија.

Според досегашните истражувања, староста на палеогените седименти (на база на многубројни фосилни остатоци од макрофосилните групи) во овчеполскиот и тиквешкиот басен е одредена како горноеоценска.

Во трудот ги презентираме резултатите од микропалеонтолошките истражувања на планктонската фораминиферна фауна, пронајдена во горната флишна литозона на дупчотините ОП-1 (овчеполски басен) и КР-1 (тиквешки басен). Биостратиграфската вредност на планктонската фораминиферна фауна во дупчотините ОП-1 и КР-1 овозможи да издвоиме една локална биостратиграфска зона во овчеполскиот и во тиквешкиот басен.

Во контекс со тоа, направена е корелација на биостратиграфските зони помеѓу овчеполскиот и тиквешкиот палеогенски басен.

NEW DATA ON THE HYDROTHERMAL ALTERATIONS IN THE PLAVICA DEPOSIT (EASTERN MACEDONIA)

Orce Spasovski, Vojo Mirčovski

The "Goce Delčev" University, Faculty of Natural and Technical Sciences,
Goce Delčev 89, MK-2000, Štip, Republic of Macedonia
orce.spasovski@ugd.edu.mk

A b s t r a c t: The data presented in the paper were obtained based on analyses carried out on samples collected from various depths along the entire length of drill-hole no. 4. The drill-hole was the last one made in the area of the Plavica deposit by the Rio Tinto Company.

The samples analyzed point out the presence of subvolcanic to volcanic rocks, presumably dacites and dacite-andesites, that can be distinguished based on the presence of primary quartz. An exception is sample no. 6 which, most probably, represents one of the vein rocks.

The alterations seen under a microscope include silicification (with several quartz generations), argillitisation, sericitisation, epidotisation, K-metasomatism and, presumably, zeolitization.

X-ray examinations determined the alterations as follows: silicification, alunitisation, argillitisation, sericitisation, K-feldspatisation, fluoritisation, propylitisation and hematisation.

Key words: Plavica deposit; hydrothermal alterations; dacites; andesites; ignimbrites; drill-hole;
microscopic examinations; x-ray examinations

INTRODUCTION

The Plavica deposit is situated in the eastern parts of the large Kratovo–Zletovo volcanic district, some 5 km north from Probištip. It is located in the middle parts of the Plavica volcanic apparatus which is charcaterized by complex composition and intense hydrothermal alterations of the volcanic rocks in an area of more than 6 km^2.

From metallogenetic point of view, the Plavica deposit occupies the central parts of the Kratovo–Zletovo ore region.

The polymetallic mineralization of the Plavica deposit and the wider vicinity have been subject matter of investigation and exploitation as early as the Roman period. Intensive investigations and exploitation activities were carried out from 1936

to 1941. Systematic geophysical and geochemical investigations including large drillings with distance between points were carried out from 1977 to 1979.

Data regarding the structural-geologic and metallogenetic characteristics of the deposit can be found in the works of Мијалковиќ and Пешиќ (1966), Стојанов (1974 and 1980), Иванов and Денковски (1978 and 1980), Ракиќ (1978), Мудриниќ (1986), Богоевски and Ракиќ (1985), Серафимовски (1990) et al.

The deposit is well investigated and studied. It can be said that it is an important polymetallic copper deposit.

SURROUNDING ROCKS

The geological composition of the immediate vicinity of the Plavica–Zlatica deposit consists mostly of volcanic and volcanogene-sedimentary

rocks whose determination is difficult (particularly in the central parts of the deposit) due to the large presence of hydrothermal alterations. However, the

large number of lithostratigraphic and petrologic examinations discovered that the geological composition of the deposit consists of ignimbrites, stratified volcanic tuffs and breccias, dacite-andesites and their pyroclasts most often occurring as intrusions (Figs. 1, 2).
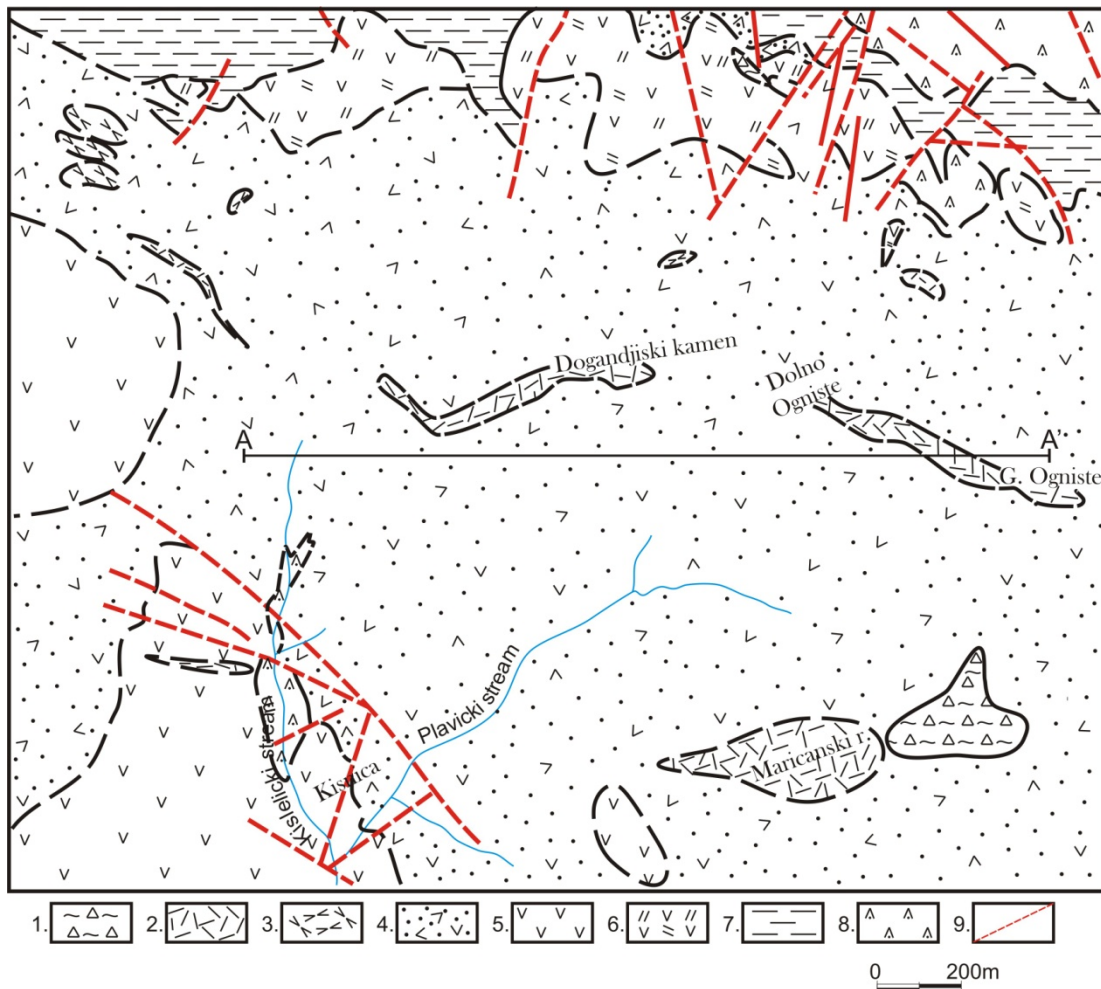
Fig. 1. Geological map of the Plavica deposit (Denkovski, 1977).
1 – Deluvium, 2 – secondary quartzites, 3 – quartzlatites, 4 – hydrothermally altered volcanics, 5 – altered dacite-andesites,
6 – propylitized dacite-andesites, 7 – stratified tuffs, 8 – ignimbrites, 9 – fault structures
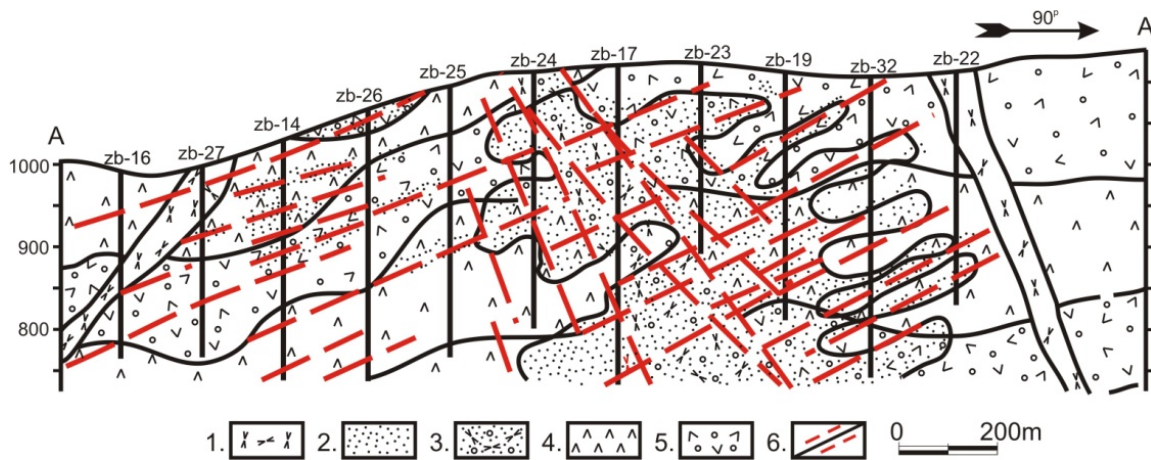
Fig. 2. Geological cross-section of Plavica (Serafimovski (1990).
1 – Quartz-latites (fresh), 2 – Si-mineralization, 3 – quartzlatites (dacites) hydrothermally altered, 4 – dacite-andesites
(hydrothermally altered), 5 – volcanic tuffs and agglomerates (hydrothermally altered), 6 – fault structures

HYDROTHERMAL ALTERATIONS

One of the most important characteristics in the Plavica deposit is the abundance of hydrothermal alterations that can be found in an area of 6 to 8 km². They have been studied before, but not in a systematic manner. The volcanic rocks that were mainly auto-hydrotactically propylitized were also affected by hydrothermal alterations. Hydrothermal alterations are most commonly found in the middle parts of the Plavica caldera as tectonically the most altered.

Investigations and examinations carried out so far determined a large number of hydrothermal alterations. The most important are silicification, sericitisation, propylitisation, argillitisation, adularisation, kaolinisation, alunitisation, turmalinisation etc. Zonal pattern can often be seen in individual alteration types, sometimes occurring discontinuously or irregularly distributed.

Hydrothermally altered rocks are whitened and macroscopically are hard to determine. Macroscopically they can be distinguished only if they contain primary quartz which allows us to say that the rock was dacite or quartzlatite.

Silicification is best pronounced along fissures that can be followed in large areas. Silicification is accompanied by alunitisation, kaolinisation, sericitisation, pyrophyllitisation etc. The most pronounced silicification zone is that between Dolno Ognište and Gorno Ognište with WNW – ESE extension.

RESULTS AND DISCUSSION

The data presented in the paper were obtained from analyses carried out on samples taken from various depths along the entire drill-hole no. 4 (Tab. 1). The drill-hole was the last drilled in the area of the Plavica by the Rio Tinto Company.

T a b l e 1

Depth of samples collected from the core of drill-hole no. 4

Sample No.	Box No.	Depth of drill-hole (m)
1	1	2.30
2	9	27.50
3	20	70.0
4	23	82.0
5	41	152.0
6	47	170.0
7	54	194.0
8	65	232.0
9	69	246.0
10	78	280.0
11	81	289.0

Samples used to make thin sections are rather intensely altered; in some parts of the thin sections relics of primary rock can not be seen.

Samples analyzed show the presence of subvolcanic to volcanic rocks (most probably dacite and dacite-andesites) that are recognizable based on the presence of primary quartz. An exception is sample no. 6 which is probably taken from a vein rock.

Alterations seen under a microscope include silicification (with several quartz generations), argillitisation, sericitisation, epidotisation, K-metasomatism and, most probably, zeolitization.

Figure 3 shows silicification and sericitisation with no visible relics of primary rock. In picture 3b a lot of vugs can be seen as relics of the places where primary minerals were located. The shape of the free spaces allows us to assume that feldspars were located there. Feldspars often occur as relics and metasomatically replaced by alunite.

Figure 3c shows silicification present as fine-grained quartz as complete replacement of the primary rock mass. Iron oxides are often intergrown with the rock mass (Fig. 3d) most commonly accompanied by silicification and argillitisation. Iron oxides often occur in association with larger quartz aggregates and pigmentise the silicium in the rock.

Figure 3 shows minerals of ring radial structure and according to their microscopic characteristics they can be classified as zeolites. X-ray examinations have not been carried out on the ring radial structures since the quantity of the material is not sufficient enough for investigations. Microscopic studies did not determine any mineral resembling epidote (Fig. 3f). However, x-ray examinations carried out later indicated that it was alunite. The sample often contains silicification with poorly pronounced kaolinisation.
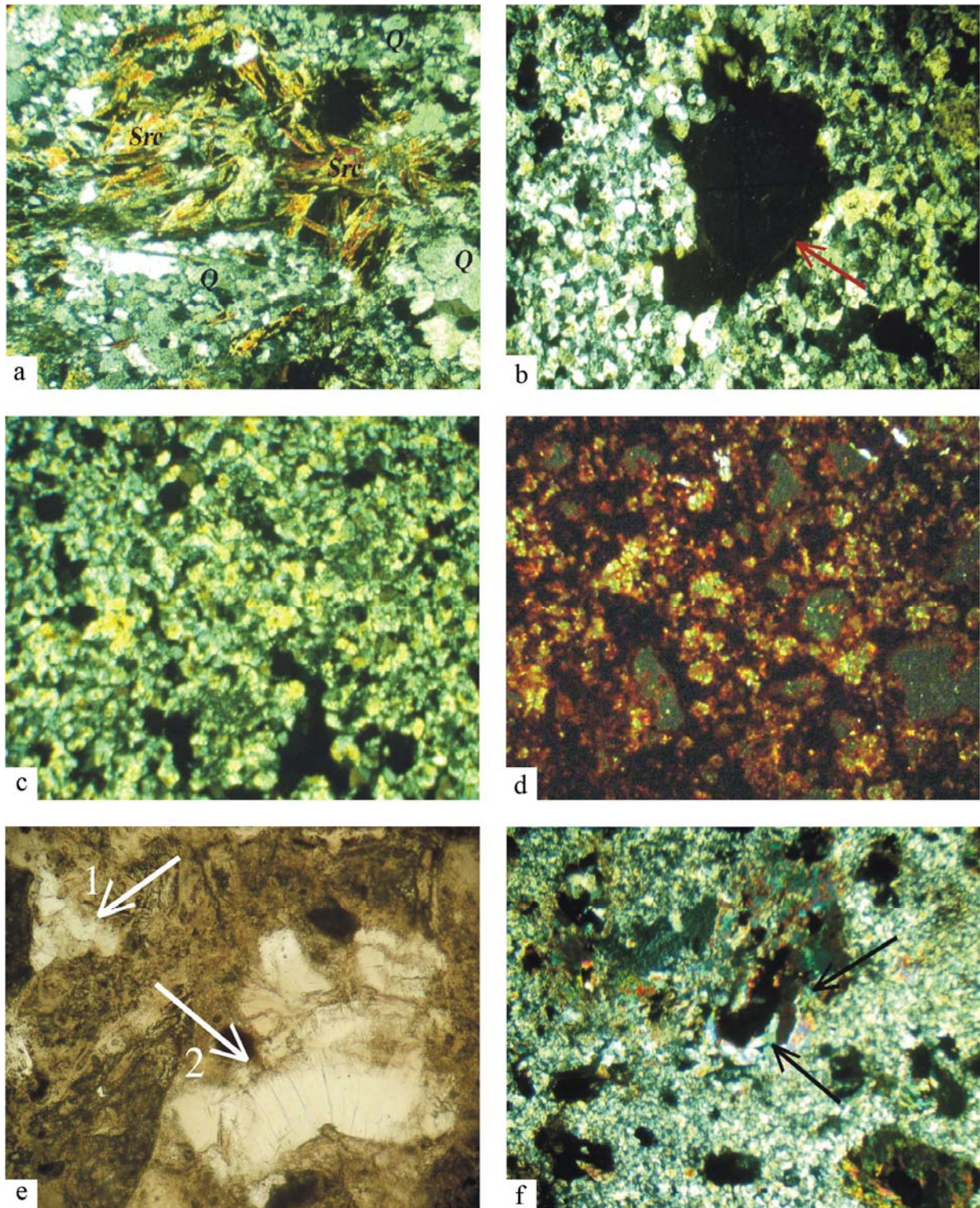
Fig. 3 Micropictures of core samples from drill-hole no. 4 of Plavica
a) Detail of pronounced sericitisation and silicification; b) an illustration of vugs formed due to leaching of individual minerals;
c) silicification of rock with fine-grained quartz; d) intergrowth of rock with Fe-oxides; e) an illustration of part of zeolites
(arrows 1 and 2), f) an illustration of epidotisation (shown as arrows).

The x-ray analyses carried out on samples from drill-hole 4 determined the minerals such as quartz, alunite, jarosite, feldspar, montmorilonite, kaolinite, fluorite and hematite (Table 2). The table shows that no big difference was revealed regarding their occurrence to depth. Only bigger occurrence of alunite relative to quartz can be seen in the deeper parts.

T a b l e 2

Minerals obtained by x-ray diffraction analysis carried out on samples of drill-hole no. 4, Rio Tinto

Sample No.	Depth of drill-hole (m)	Discovered minerals
5	152.00	quartz, alunite, jarosite, feldspar, fluorite?
6	170.00	quartz, alunite, fluorite? and hematite?
8	232.00	quartz, alunite, jarosite, feldspar, fluorite? and montmorilonite?
10	280.00	alunite, quartz, kaolinite, jarosite and feldspar

X-ray diffraction analyses carried out on samples taken from sample no. 5 are shown in Fig. 4. The figure shows that the values read from sample no. 5 correspond to quartz, alunite, jarosite, feldspar and fluorite. The most common mineral is quartz, whereas alunite occurs in high contents, and fluorite is uncertain since data for its determinations are insufficient.

The radiograph shown in Fig. 5 made it possible to read values that correspond to the minerals as follows: quartz, alunite, hematite and fluorite. It is clear that in this sample the minerals are the same as those found in sample 5, the only difference being that hematite was determined instead of feldspar. Quartz is the most common mineral as an indicator that silicification processes had a dominant role and that fluorite and hematite are hypothetical.
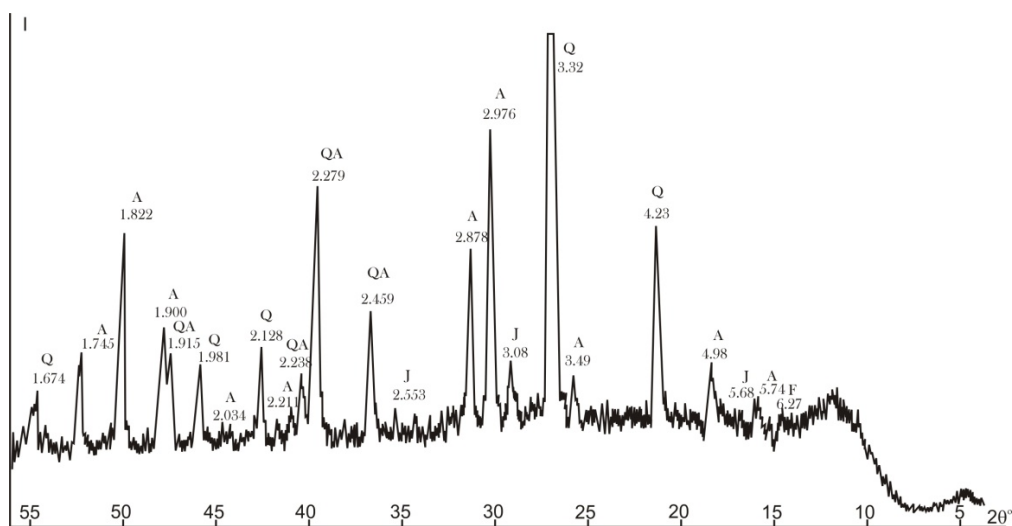
Fig. 4. Radiograph with results of x-ray analysis carried out on sample 5.
Q – quartz, A – alunite, J – jarosite, F – feldspar, f – fluorite
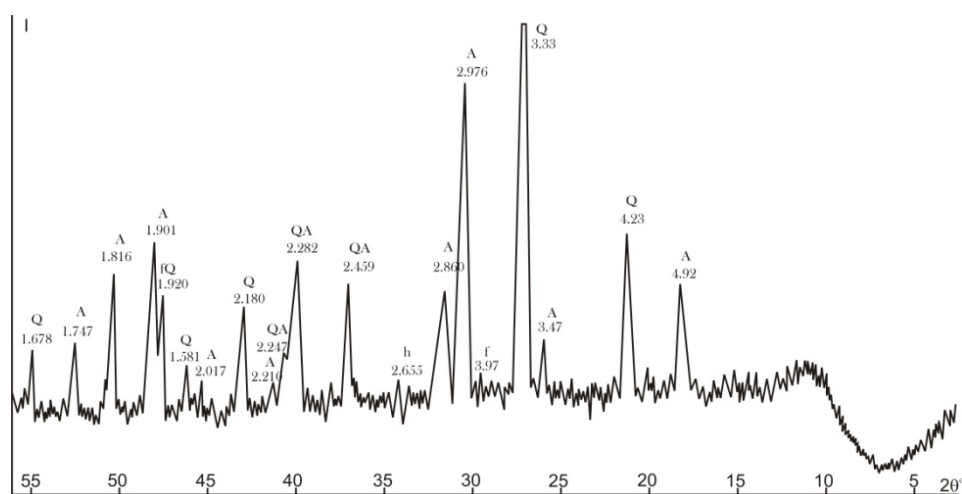
Fig. 5. Radiograph with results of x-ray analysis carried out on sample no. 6.
Q – quartz, A – alunite, h – hematite, f – fluorite

The radiograph shown in Fig. 6 shows values that correspond to the same minerals determined in sample 5 (quartz, alunite, jarosite, feldspar, fluorite and montmorilonite). This sample, unlike sample 5, shows the presence of montmorilonite. Here, like in the earlier samples described, fluorite and montmorilonite are hypothetical.

The radiograph (Fig. 7) which shows the results of x-ray analysis carried out on sample no. 10 yields values that correspond to and point out the presence of the minerals as follows: alunite, quartz, kaolinite, jarosite and feldspars. The results obtained show that the most abundant is alunite, the next most common being quartz.

Unlike earlier samples, minerals in this sample are equally well confirmed.
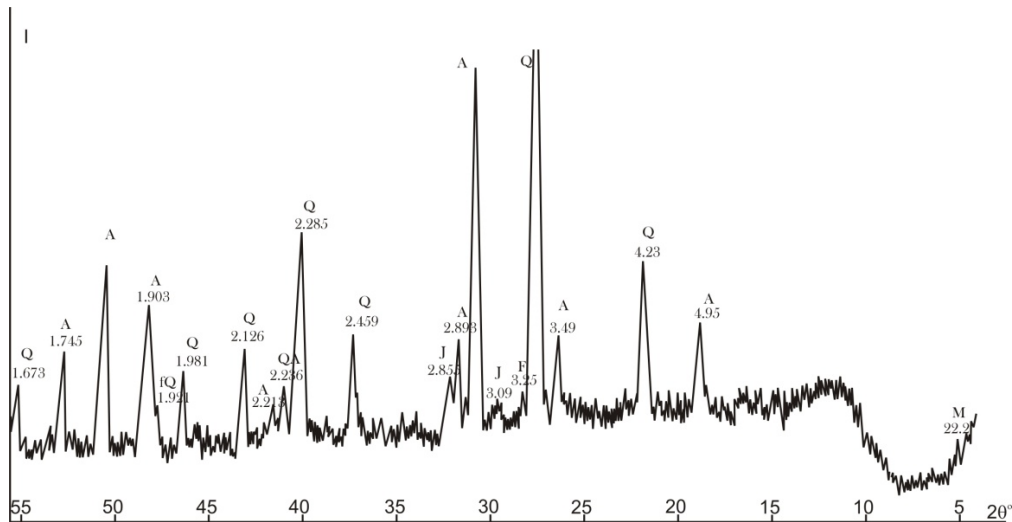
Fig. 6. Radiograph with results of x-ray analysis carried out on sample 8.
Q – quartz, A – alunite, J – jarosite, F – feldspar, f – fluorite, m – montmorilonite
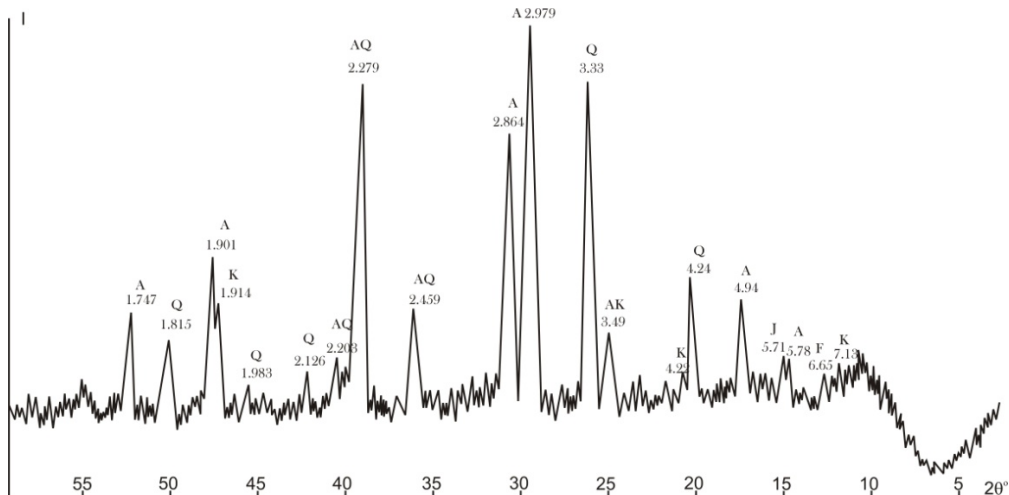
Fig. 7. Radiograph with results of x-ray analysis carried out on sample 10.
Q – quartz, A – alunite, K – kaolinite, J – jarosite, F – feldspar

The hydrothermal alteration in the Plavica deposit is of zonal pattern. Several zones can be distinguished that either cover or follow one another. An inner zone can be distinguished with secondary quartzites and alunite. The alunite is either part of the zone separating it into two subzones or goes out into the outer zones. Close to the zone of secondary quartzites there is a discontin-

ued zone of potassic metasomatism (adularisation, albitisation, hydrobiotitisation and silicification) to which the outer zone of hydrothermal alterations is added.

Silicification outside the secondary quartzites is more or less spread all over the altered zone. Still, outside the outer zone it is less abundant and disappears.

CONCLUSION

Based on the investigations carried out on the hydrothermal alterations in the Plavica deposit so far, including those of the present author, the following conclusions can be made:

The hydrothermally altered rocks were whitened and can not be ascertained macroscopically. Macroscopically they can be distinguished only if they contain primary quartz which allows us to say that the rock was dacite, dacite-andesite or quartzlatite.

Hydrothermal alterations are of zonal pattern and several zones can be distinguished that either cover or follow one another.

Hydrothermal alterations are found most in the middle parts of the Plavica caldera as tectonically most faulted. In the deeper parts of the deposit, in the propylitisation zone, the mineralization is absent, but increases in the secondary quartzite zone, in the silicification, alunatisation and in the potassic metasomatism.

In the outer zone of the hydrothermal alterations vein mineralization was found that goes outside the area under investigation. It is characterized by high contents of lead, zinc, barium, uranium and other minerals.

Plavica is a hydrothermally stock-work impregnated deposit with some traces of porphyry copper deposits.

The studied samples of rocks obtained from drill-hole 4 in the Plavica deposit, drilled by the Rio Tinto company are characterized by fairly intense hydrothermal alterations. Some of the alterations have been confirmed by microscopic and x-ray diffraction analyses.

The analyses carried out on samples collected from drill-hole 4 made it possible to determine the following alteration types: silicification, alunitisation, argillitisation, sericitisation, K-feldspatisation, fluoritisation, propylitisation and hematisation.

REFERENCES

Богоевски, К., Ракиќ, С., 1985: *Геолошке карактеристике лежишта Златица–Плавица.* Стр. фонд „Силекс“, Скопје.

Иванов, Т., Денковски, Ѓ., 1978: Геологија на металогенетскиот јазел Плавица–Златица во кратовско-злетовската област. *IX Конгрес геол. СФРЈ,* стр. 565–570, Сарајево.

Иванов, Т., Денковски, Ѓ., 1980: Хидротермални алтерации во порфирското лежиште Плавица–Златица во кратовско-злетовската вулканска област. *Симпозиум алтерација стена и минерала, 100 год. Геол. школе у Србији,* Београд.

Мијалковиќ, Н., Пешиќ, Д., 1966: Геолошке и петролошке карактеристике СИ дела кратовско-злетовске области. *Реферати VI саветовања геолога Југославије,* део II, стр. 158–170, Охрид.

Мудриниќ, Ч., 1986: Ретки и племенити метали у Cu полиметаличном лежишту Плавица–Златица (Источна Македонија), *XI Конгес геолога Југославије,* Тара.

Ракиќ, С., 1978: Неке структурне особености полиметаличног орудњења у злетовском рудном пољу, *IX Конгрес геол. СФРЈ,* стр. 565–570, Сарајево.

Серафимовски, Т., 1990: *Металогенија на зоната Леце–Халкидик,* Докторска дисертација, РГФ, Штип.

Стојанов, Р., 1974: Минералошки состав на околурудните измени на Плавица во злетовско-картовската област. *VIII југословенски геолошки конгрес,* кн. 5, стр. 42–54, Љубљана.

Стојанов, Р., 1980: Вулканската купа Плавица, полиметалните минерализации и околурудните промени во неа. *Симпозиум алтерација стена и минерала, 100 год. Геол. школе у Србији,* Београд.

Р е з и м е

НОВИ ПОДАТОЦИ ЗА ХИДРОТЕРМАЛНИТЕ ПРОМЕНИ ВО НАОЃАЛИШТЕТО ПЛАВИЦА (ИСТОЧНА МАКЕДОНИЈА)

Орце Спасовски, Војо Мирчовски

[1]*Универзитет „Гоце Делчев“, Факултет за природни и технички науки,
Гоце Делчев 89, МК-2000 Штип, Република Македонија*
orce.spasovski@ugd.edu.mk

Клучни зборови: наоѓалиште Плавица; хидротермални алтерации; дацити; андезити; игнимбрити, дупнатина; микроскопски испитувања; рендгенски испитувања

Податоците кои се презентирани во трудов се добиени врз основа на анализа на примероци земени од различни длабочини надолж целиот интервал од дупнатината број 4. Оваа дупнатина е последна издупчена на подрачјето на наоѓалиштето Плавица од страна на компанијата Рио Тинто.

Анализираните примероци укажуваат на присуство на субвулкански до вулкански карпи, најверојатно дацити и дацито-андезити, кои се препознаваат само по присуството на примарниот кварц. Исклучок претставува примерокот бр. 6, кој најверојатно е претставник на некоја од жилните карпи.

Од алтерационите промени под микроскоп се забележани: силификација – со неколку генерации на кварц, аргилитизација, серицитизација, епидотизација, К-метасоматоза и веројатно зеолитизација.

Со рендгенските испитувања се констатирани следните алтерации: силификација, алунитизација, аргилитизација, серицитизација, К-фелдспатизација, флуоритизација, пропилитизација и хематитизација.

THE COMPOSITION OF MAJOR MINERALS FROM THE BUCHIM PORPHYRY COPPER DEPOSIT, REPUBLIC OF MACEDONIA

Todor Serafimovski[1], Tadej Dolenec[2], Goran Tasev[1], Nastja Rogan[2], Matej Dolenec[2]

[1] *The "Goce Delčev" University, Faculty of Natural and Technical Sciences, Institute of Geology,*
ul. Goce Delčev 89, MK-2000 Štip, Republic of Macedonia
[2]*Faculty of Natural and Technical Sciences, Geology Department, University in Ljubljana,*
Aškerčeva 12, 1000 Ljubljana, Slovenia
todor.serafimovski@ugd.edu.mk // goran.tasev@ugd.edu.mk

A b s t r a c t: Our current study of major ore and rock forming minerals enclosed the most important minerals within the Buchim ore deposit. Rock forming minerals were represented by plagioclase, K-feldspars, biotite and amphiboles. Beside their complex formulas those minerals have shown quite uniform compositions. Amphiboles were determined as hornblende, biotites were characterized by increased Fe and Ti and decreased Mg concentrations, plagioclases were determined as sanidine while K-feldspars were represented by albites and oligoclases. We have shown that the chalcopyrite composition is highly pure without any significant presence of Ni, Co, As and Sb (<0.01%). Pyrite analyses have shown that there are increased arsenic concentrations of 0.15 ÷ 0.22 % As, such concentrations of arsenic are indicative, but are very characteristic for low temperature pyrites from porphyry copper deposits. Beside the arsenic in pyrites, there were determined increased Ni concentrations 0.45 ÷ 1.42 % Ni, while Co and Sb remain below 0.01%.

Key words: Buchim porphyry copper deposit; major minerals; composition

INTRODUCTION

First written records of the geological setting date from the turn of the 20th century (Cvijić, 1906). This deposit has been explored in late 1930, early 1940 and even during the Second World War. The most extensive ones were in the period 1955–1976, followed by extensive diamond core drillings and exploration mining drifts. Such broad exploration programme have resulted with a start mine of mine production in 1979. Since then the annual mine production rate used to be 3.8 Mt of ore processed in the concentration plant in Buchim, except during the short production break at the beginning of this century. The latter on studies were performed by Janković et al. (1980), Ivanov (1982), Čifliganec (1982, 1987, 1993), Palinkaš et al. (2008), Serafimovski (1990), Serafimovski et al. (1993, 1996, 2001, 2006), Serafimovski and Čifliganec (1996), Strasimirov et al. (1996) and others. This study was initiated by the idea to determine the exact compositions of the major ore (chalcopyrite and pyrite) and silicate (plagioclase, muscovite, biotite etc.) minerals from the ore body Central Part. Findings from this study were put in service of enhancing the ore milling and concentration process.

GEOLOGICAL SETTING

The Buchim ore deposit on a more regional scale belongs to the so called Buchim-Damjan-Borov Dol ore field, which covers an area of 65 km². This ore field consists of different lithological members of the Vardar zone and the Serbo-Macedonian massif: Precambrian amphibolites, amphibolite schists, biotite gneisses; Palaeozoic schists and granites; Jurassic ultrabasics and granites; Cretaceous and Paleogene sediments; Miocene andesites and andesite tuffs and Pliocene and

quaternary sediments. The Buchim porphyry copper deposit consists of four separate bodies: Central Part, Bunardzhik, Vrshnik and Chukar, which are occupying an area of approximately 10 km². The geological setting of the immediate surroundings of the deposit includes the following members: Precambrian gneisses (different compositions), schist and amphibolites; Palaeozoic amphibolites, serpentines and gabbros; Tertiary representatives in mineralogical and/or chemical composition correspond to latites with a transition to andesites and quartzlatites (Fig. 1).
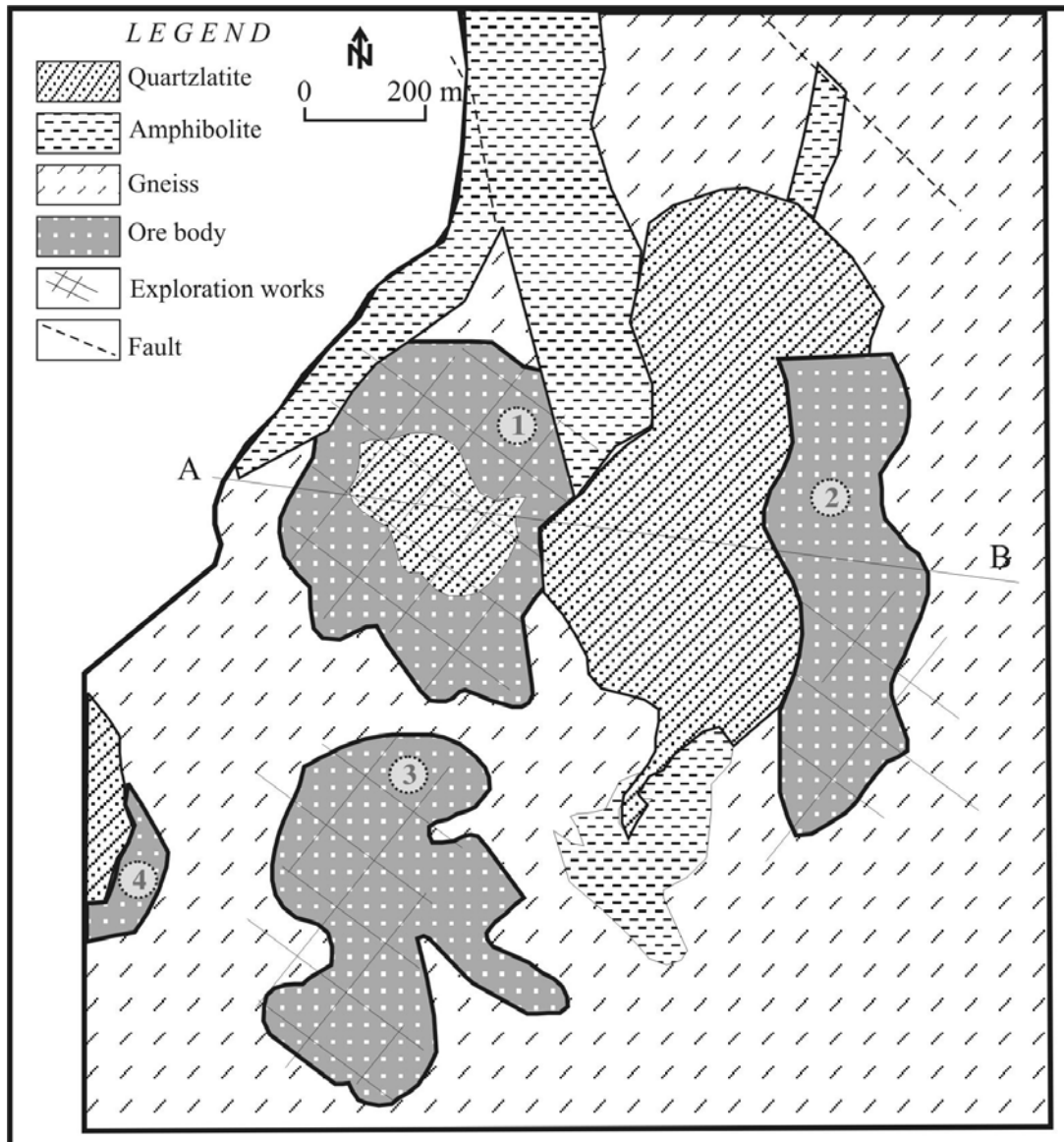
Fig. 1. Geological map of the Bučim deposit
1. Ore body Central part; 2. Ore body Vrshnik; 3. Ore body Chukar; 4. Ore body Bunardzhik

MINERAL ASSOCIATIONS

Up to date systematic studies, mostly of the Central part ore body, have identified the following minerals within the Buchim deposit: pyrite, chalcopyrite, magnetite, rutile, sphene, titano-magnetite, ilmenite, hematite, specularite, pyrrhotite, valerite, cubanite, sphalerite, galena, bismuthinite, bornite, enargite, native gold, chalcocite (Fig. 2).

Minerals	Ore forming stages			
	Metamorphic	Magmatic	Hydrothermal	Supergene
Biotite		▬		
Amphibole		▬		
Zircon		▬		
Apatite		▬		
Sphene	▬	▬		
Ilmenite	▬	▬		
Feldspar		▬		
Quartz		▬		
Sericite			▬	
Chlorite			▬	
Epidote			▬	
Anatas			▬	
Rutile	▬		▬	
Chalcedony			▬	
Calcite			▬	
Gypsum			▬	
Kaolinite			▬	
Magnetite	▬	▬	▬	
Chalcopyrite			▬	
Bornite			▬	
Pyrhotite			▬	
Cubanite			▬	
Martite			▬	
Specularite			▬	
Mushketowite			▬	
Pyrite	▬		▬	
Molibdenite			▬	
Krenerite			▬	
Native Au			▬	
Bravoite			▬	
Bismuthite			▬	
Galenobismuthite			▬	
Luzonite			▬	
Tetrahedrite			▬	
Galena			▬	
Chalcocite			▬	▬
Covellite			▬	▬
Malachite				▬
Azurite				▬
Tenorite				▬
Limonite				▬

Fig. 2. Paragenetic sequences of mineralization in the Buchim deposit (Čifliganec, 1987; modified)

Also, within the deposit were identified more rarer minerals, such is Bi-Se mineral association represented by bismuthine, galenobismuthine, fridrihite, crupcaite, emplectite, latacarite, native bismuth and cosalite (Серафимовски et al., 1990). According to the considerations of generation, time of mineral(s) formation and composition, several stages of formation were discriminated within the Buchim deposit, each in conjuction with its assemblage. The metamorphic stage has been characterized by relict Ti-Fe oxide assemblage in amphibolites and Fe-sulphide assemblages in gneiss. Magmatic stage assemblage has been represented by Fe-Ti oxides in andesites. The very complex hydrothermal stage normally have been characterized by complex mineral assemblages, such as alteration-hydrothermal assemblage, hydrothermal assemblage, high temperature Fe-Cu sulphide assemblage, lower temperature Fe-Cu-(Zn, Pb, Bi, Mo) sulphide assemblage, epithermal Fe-Cu sulphide assemblage and oxide and sulphide mineral assemblages produced during the secondary enrichment process.

METHODOLOGY

The essential stage of the study, sampling, was realized with direct coordination with an experienced mining geologists and mineral processing professionals from the Buchim mine. Samples were chosen to be representative of its kind. Sampling stage was followed by stage of preparation of samples for laboratory analyses and preparation of polished ore and thin sections. Qualitative and quantitative mineralogical examinations were performed on specialized polarizing microscopes ZEISS Axiolab Pol No. 70 and LEITZ AMPLIVAL No. 2000 with an integrated camera (for documenting the details). After the study under polarizing microscope were determined samples for analysis under the electron microprobe and scanning electron microscopy. Scanning Electron Microscope was the JEOL JSM 35 CF equiped with the XRF microprobe TRACOR NORTHERN TN-2000 in an energy dispersive system (EDS) and using standards from the manufacturer JEOL. Energy 25 keV, counting time at least 10 s for each element. Microprobe beam: $2 \cdot 10^{-9}$ A. On specimen were performed analyses on ore and silicate minerals followed by analysis at lowest magnification (scaning area of 8 mm^2). The photographs were made in a back scatered electron mode-COMPO. The results were summarized on powerful computer connected to the SEM.

The whole rock analysis followed ussual procedure. Test portion of 0,1 g is fused with LiBO$_4$ in a muffle furnace at 1000 ^{o}C. Obtained transparent melt is dissolved with diluted HNO$_3$ at heating and is transferred in a volumetric flask. All oxides are measured in the solution by ICP-AES after a previous calibrating with standard solutions. Blank sample is determined in parallel and a suitable certified reference material (CRM).

RESULTS AND DISCUSSION

The results obtained by the analysis of samples, under the state of art analytical equipment mentioned above, are given and discussed in the text below. For better understanding we have grouped analyzed minerals in two natural subgroups: silicate minerals or rock forming minerals and ore minerals. We have focused our study to these particular silicate minerals because they are participating into the composition of gneisses and amphibolites, which have hosted ore bearing andesites. Pyrite and chalcopyrite as major minerals were of special interest.

Amphiboles (%)

Analysis of amphiboles have shown quite consistent composition, either some of the analyzed compoenents have shown higher concentrations (Na$_2$O, K$_2$O, TiO$_2$ and MnO), see Table 1.

The fact that the amphiboles have the most complex chemical composition of all rock forming minerals due to high ion substitution flexibility. This was confirmed once again with our analyses. As can be seen from the Table above amphibole's composition is complex and in general belong to a hornblende group or even more precisely somewhere between the ferrohorneblende and magnesiohornblende endmost group members. The calculated structural formula could be represented as

$$Na_{(0.31-0.90)} Ca_{(1.77-2.91)} K_{(0.09-14.60)} Mg_{(2.62-4.55)} Fe_{(1.59-2.76)} Al_{(1.14-3.57)} Si_{(0.2-7.27)} O_{(22.00)} (OH)_2.$$

T a b l e   1

Quantitative x-ray spectral microanalyses of amphiboles from the Buchim porphyry copper deposit (%)

	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO	TiO$_2$	MnO	FeO
B-3	1.21	14.01	6.42	50.01	0.37	11.77	0.17	0.33	14.41
B-4	2.03	12.98	10.29	45.96	0.60	11.79	0.28	0.26	14.07
B-6	2.40	11.33	13.92	42.55	1.30	11.64	0.56	0.30	13.60
B-7	1.03	12.22	7.15	46.72	0.44	13.68	0.36	0.35	15.88
B-8	1.84	12.16	12.05	0.81	45.54	10.81	0.47	0.43	13.14
B-10	1.59	13.28	12.03	45.85	0.62	10.94	1.10	0.21	12.57

Biotites (%)

Biotite analyses under the electron micro-probe have shown interesting composition. Beside more or less standard values for K$_2$O, Al$_2$O$_3$ and SiO$_2$ were determined. Opposite to them FeO (16.06–17.62%), TiO$_2$ (1.75–2.53%) have shown increased values while the MgO was characterized by lowered values (12.49–15.76%), Table 2.

Analyzed biotites have shown quite uniform composition, more oriented to the phlogopite species. Calculated structural formula in general looks like this one: K$_{(0.95–1.23)}$ Mg$_{(1.55–1.91)}$ Fe$_{(1.09–1.20)}$ Al$_{(1.22–1.45)}$ Si$_{(3.06–3.25)}$ O$_{(10)}$ (OH)$_2$.

T a b l e   2

Quantitative x-ray spectral microanalyses of biotites from the Buchim porphyry copper deposit (%)

	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO	TiO$_2$	MnO	FeO
B-6	0.86	14.39	13.88	38.39	9.62	<0.01	1.94	0.11	17.62
B-7	<0.01	12.49	12.36	38.88	11.53	<0.01	2.53	0.09	17.05
B-10	<0.01	15.76	15.10	37.61	9.16	<0.01	1.75	<0.01	16.06

K-feldspar (%)

Very common K-feldspars were analyzed in the same manner as the previous oxide minerals. Usual concentrations were determined for Al$_2$O$_3$, SiO$_2$ and K$_2$O. Increased concentrations were determined for Na$_2$O (1.49–2.57%), FeO (0.10–2.62%), MnO (0.07–0.16%), MgO (0.36–0.79%) and TiO$_2$ (0.09–0.17%). Results from eight electron microprobe analyses are given in Table 3.

T a b l e   3

Quantitative x-ray spectral microanalyses of K-feldspars from the Buchim porphyry copper deposit (%)

	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO	TiO$_2$	MnO	FeO
B-1	2.10	<0.01	17.80	65.49	14.86	<0.01	<0.01	<0.01	0.10
B-3	2.57	<0.01	18.58	64.89	13.08	<0.01	0.09	<0.01	0.21
B-4	1.89	0.36	18.17	64.03	14.56	<0.01	0.10	<0.01	0.30
B-6	2.20	<0.01	18.49	65.47	13.05	<0.01	<0.01	0.16	0.23
B-7	2.01	<0.01	16.06	63.55	14.96	<0.01	<0.01	0.07	2.62
B-8	2.54	<0.01	18.74	64.72	13.55	<0.01	<0.01	<0.01	0.17
B-9	1.49	0.79	19.56	62.93	13.93	<0.01	<0.01	<0.01	0.83
B-10	1.87	<0.01	18.35	64.68	14.55	<0.01	0.17	<0.01	0.28

Determined compositions of K-feldspar have shown that analyzed samples are more oriented to the potassium representatives. This was supported by the calculated structural formula: $K_{(0.77-0.90)}$ $Na_{(0.13-0.23)}$ $Al_{(0.89-1.07)}$ $Si_{(2.92-3.01)}$ $O_{(8.00)}$. Composition given in the formula is in conformity to the sanidine composition $(K, Na)(Si, Al)_4O_8$.

Plagioclase (%)

Study of plagioclase minerals have resulted with more or less usual concentration of oxides (Table 4). The consistency in their composition was manifested through the concentration of Na_2O (8.04–10.49%), Al_2O_3 (19.16–24.06%), SiO_2 (60.87–68.39%), K_2O (0.24–0.51%), CaO (0.57–6.22%), MnO (0.07–0.09%), FeO (0.09–0.23%).

The structural formula calculated from the chemical composition could be written in the following manner: $Na_{(0.695-0.893)}$ $Al_{(0.992-1.264)}$ $Si_{(2.713-}$ $_{3.01)}$ $O_{(8.00)}$. The composition as this fits quite fine in a idealized plagioclase (albite) formula $NaAl-SiO_3O_8$, with an exception of B-4, which shows composition close to the oligoclase. Occasionally in a structural formula occur $K_{\leq 0.297}$ and $K_{\leq 0.027}$.

From the tables above it can be concluded that the analyzed major ore forming minerals are direct represents of the major components that are building up gneisses (plagioclase and K-feldspars) and amphibolites (amphiboles and chlorites). Also, it can be seen that the minerals are relatively fresh and without significant signs of transformation into sericite and kaolinite, which could cause problems in the ore processing. However, these results are within the frame usual for rocks that have hosted hydrothermal ore mineralization.

By analogy to study of rock forming minerals we have performed analyses, under the electron microprobe, of major ore minerals present in the Buchim deposit (pyrite and chalcopyrite).

T a b l e 4

Quantitative x-ray spectral microanalyses of K-feldspars from the Buchim porphyry copper deposit (%)

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO
B-1	10.49	<0.01	19.16	68.39	0.24	0.75	<0.01	0.09	0.21
B-4	8.04	0.24	24.06	60.87	0.51	6.22	<0.01	<0.01	0.09
B-6	10.28	<0.01	20.75	68.06	0.48	0.57	<0.01	0.07	0.23

Pyrite

The goal of the performed study of pyrites was to determine the exact composition of this mineral within the Buchim porphyry copper deposit. First of all, collected ore, concentrate and waste samples were studied under the polarizing microscope. After this preliminary study and selection we have proceeded to analysis under the electron microprobe. We have analyzed different morphological types of pyrites trying to determine the concentration of certain representative metals, which usually occur in porphyry deposits. All pyrites analyzed under the electron microprobe are shown on the Figure 3.

From the photographs can be seen that were analyzed representative, individual and compact pyrite grains, either sometimes some of them were tectonicaly deformed. Trying to determine is the composition within a single pyrite grain permanent or changes we have analyzed central and rim parts of pyrite grains. By the exprience we knew that the major changes in composition, concerning certain elements such is arsenic, occur exactly within the rim parts of mineral grains. Also, that is why we have analyzed pyrite grains from concentrate and waste, since they have direct influence on the quality of the semi-final product from the Buchim Mine. The results obtained under the electron microprobe are given in Table 5.

From 14 performed anlyses of pyrite it was confirmed that it shows the usual composition with around 52–53 % S and 47 % Fe. Only in few samples was determined presence of nickel and cobalt which substitute the iron in the mineral structure. Opposite to them were determined increased concentrations of arsenic in pyrites from samples B-1, B-4 and B-7. This, once again have confirmed that in pyrites from particular parts of the Buchim deposit there are increased concentrations of As. They have to be monitored closely in the technological process and should be expected increased As concentration in concentrates, also. The struc-

tural formula calculations have shown that the pyrite formula could be written as $Fe_{(0.98-1.05)}$ $[Ni_{(0.002-0.02)}$ $Co_{(0.01-0.09)}$ $As_{(0.002-0.004)}]$ $S_{(1.95-1.98)}$, which is very close to the idealized one FeS_2.
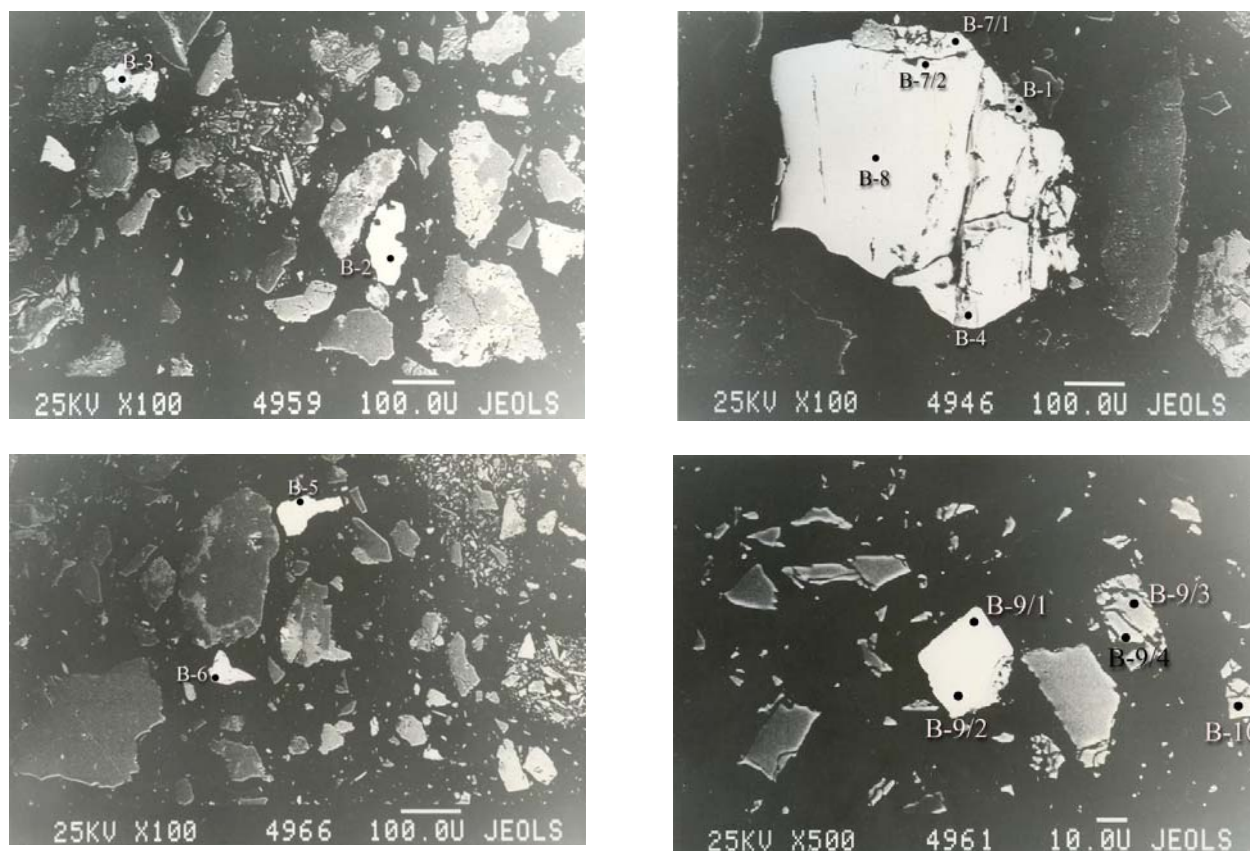

Fig. 3. Microprobe photographs of typical pyrites from the Buchim porphyry copper deposit with locations of microprobe analyses

T a b l e 5

Quantitative x-ray spectral microanalyses of pyrite from the Buchim porphyry copper deposit (%)

	S	Fe	Cu	Ni	Co	As	Sb
B-1	52.31	46.73	<0.01	0.15	<0.01	0.18	<0.01
B-2	52.52	47.24	<0.01	<0.01	<0.01	<0.01	<0.01
B-3	52.70	46.83	<0.01	0.17	<0.01	<0.01	<0.01
B-4	51.93	47.14	<0.01	0.15	<0.01	0.22	<0.01
B-5	52.13	47.73	<0.01	<0.01	<0.01	<0.01	<0.01
B-6	52.56	46.81	<0.01	0.09	<0.01	<0.01	<0.01
B-7	51.34	47.99	<0.01	0.10	<0.01	0.19	<0.01
B-7	51.87	47.80	<0.01	0.17	<0.01	0.15	<0.01
B-8	52.59	47.33	<0.01	<0.01	<0.01	<0.01	<0.01
B-9	52.14	44.95	<0.01	0.75	1.64	<0.01	<0.01
B-9	52.31	46.21	<0.01	1.03	0.27	<0.01	<0.01
B-9	52.38	46.29	<0.01	0.45	0.42	<0.01	<0.01
B-9	52.25	45.83	<0.01	1.42	0.45	<0.01	<0.01
B-10	52.24	47.76	<0.01	<0.01	<0.01	<0.01	<0.01

Chalcopyrite

Beside the pyrites from the Buchim deposit, we have analyzed chalcopyrites from this deposit. We also aimed to find out are there any increased concentrations of other elements, particularly As. In the process of analysis we have run chalcopyrites from ore, concentrate and waste. That approach gave us an unique opportunity to study chalcopyrites, which have passed through the whole technological process of the Buchim Mine. Some of the analyzed chalcopyrite grains are given on the Figure 4.

From the Figure 3 can be seen numerous individual chalcopyrite grains, while eight of them were analyzed under the electron microprobe. The results from the electron microprobe are given in Table 6.

Opposite to the pyrite composition above, the composition of chalcopyrite is highly pure. Its composition is in conformity with those given by Criddle and Stanley (1986), while the structural formula calculations have shown that the chalcopyrite formula could be written as $Cu_{(0.99-1.06)}$ $Fe_{(0.99-1.03)}$ $S_{(1.91-2.02)}$, which is equal with the idealized one $CuFeS_2$.
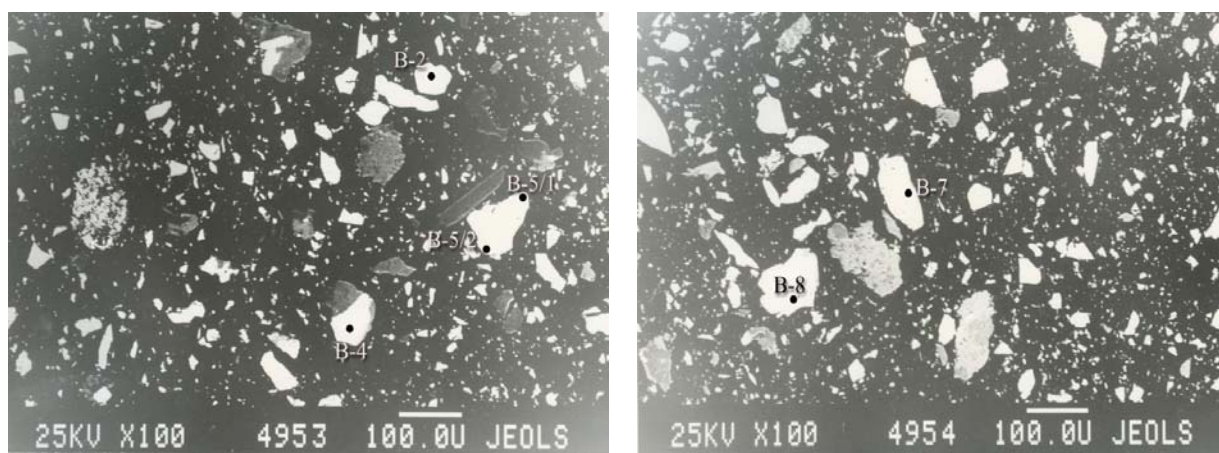

Fig. 4. Microprobe photographs of typical pyrites from the Buchim porphyry copper deposit
with locations of microprobe analyses

T a b l e 6

Quantitative x-ray spectral microanalyses of chalcopyrite from the Buchim porphyry copper deposit (%)

	S	Fe	Cu	Ni	Co	As	Sb
B-2	35.33	30.23	34.32	<0.01	<0.01	<0.01	<0.01
B-4	33.21	30.61	36.19	<0.01	<0.01	<0.01	<0.01
B-5	34.37	30.46	34.75	<0.01	<0.01	<0.01	<0.01
B-5	33.40	30.85	35.57	<0.01	<0.01	<0.01	<0.01
B-7	32.97	30.89	36.02	<0.01	<0.01	<0.01	<0.01
B-8	34.36	29.80	34.93	<0.01	<0.01	<0.01	<0.01
B-9	33.66	31.02	35.03	<0.01	<0.01	<0.01	<0.01
B-9	33.78	30.72	35.50	<0.01	<0.01	<0.01	<0.01

CONCLUSION

From the presented facts above it can be concluded that the major minerals in the mineral association determined within the Buchim ore deposit are feldspar, amphibole, biotite, quartz and chlorite as rock forming minerals and chalcopyrite and pyrite as ore minerals. Their presence, beside under

the polarizing microscope, was confirmed with x-ray structural analysis and electron microprobe. The results of the rock forming minerals have shown quite uniform compositions. Amphiboles were determined as hornblende, biotites were characterized by increased Fe and Ti and decreased Mg concentrations, plagioclases were determined as sanidine while K-feldspars were represented by albites and oligoclases.

Calculated structural formulas confirmed the analytical results and clearly defined the distinctions between measured and theoretical values of studied minerals.

The study of major ore minerals (chalcopyrite and pyrite) have shown that these two minerals are the most common ones within the Buchim ore deposit. Chalcopyrite as the major Cu-bearing mineral have shown high permanency of its composition. Opposite to chalcopyrite, pyrite have shown increased concentrations of As, which have been related with substitutions of sulfur. Increased arsenic concentrations ranged $0.15 \div 0.22$ % As. Such concentrations are indicative and demand detailed analysis of pyrite phases and quantitative determination of As-bearing pyrite phases in the whole ore mass within the Buchim deposit. All other determined minerals have shown more or less standard features.

REFERENCES

Criddle, A. J. and Stanley, C. J., 1986: *The Quantitative Data File for Ore Minerals of the Commission on Ore Microscopy of the International Mineralogical Association*. Second Issue, British Museum (Natural History), 420 p.

Cvijić, J., 1906: *Osnove za geografiju i geologiju Makedonije i Stare Srbije*. Knj. I, Beograd, 392 str.

Иванов, Т., 1982: *Металогенетска студија на рудниот реон Бучим-Дамјан-Боров Дол*. Фонд стр. док. Рудника, Бу им.

Janković, S., Petković, M., Tomson, I. N. and Kravcov, V., 1980: Porphyry copper deposits in the Serbo-Macedonian Province, Southeastern Europe. Janković, S. and Sillitoe, R. H. (eds.): *European Copper Deposits*, UNESCO-IGCP Projects Nos 169 and 60, Belgrade, pp. 96–102.

Palinkaš, A. L., Strmić-Palinkaš, S., Bermanec, V., Serafimovski, T. and Vincetić, I., 2008: Fluid inclusions in quartz from the Buchim Cu-porphyry deposit, Eastern Macedonia. *Прв конгрес на геолозите на Република Македонија*, Охрид, Зборник на трудови, стр. 193–200.

Pavičević, M., Rakić, S., Gržetić, I., Golijanin, D., 1982: *Studija pojavljivanja zlata i srebra kao i drugih pratećih elemenata u rudama centralnog dela „Bučim"*. ULEMA. Rud.-geol. fak., Beograd, 165 str.

Petrunov, R., Serafimovski, T., Dragov, P., 2001: New finding of PGE-mineralisation in porphyry-copper environment the Buchim deposit, Macedonia: preliminary microscope and microprobe data. *ABCD-GEODE 2001 workshop Vata Bai,* Romania. Vol. **79**, suppl. 2, pp 79–80.

Serafimovski, T., 1990: *Metalogenija na zonata Lece-Halkidik*. Dokt. Disertacija, Rud.-geol. fak., Štip, 391 str.

Серафимовски, Т., Манков, С., Чифлиганец, В., 1990: Бизмутско-селенската минерализација во бакарното наоѓалиште Бучим, Радовиш. *XII конгр. геол. Југ., III*, Охрид, pp 73–85.

Serafimovski, T., Čifliganec, V., Janković, S., Boev, B., 1996: Genetic Model of the Buchim Porphyry Copper Deposit, Republic of Macedonia. Proceedings of the Annual Meeting, UNESCO-IGCP Project 356, Vol. 1, 63–75, Sofija.

Serafimovski, T. and Čifliganec, V., 1996: The Buchim ore District: Geological Setting and Types of ore Mineralization. Terraines of Serbia, The Formation of the Geologic Framework of Serbia and the Adjacent Regions. Editors: Vera Knežević-Djordjević and Branislav Krstić, 341–346, Belgrade.

Serafimovski, T., Čifliganec, V., Tasev, G., 2001: The porphyry Cu-Au mineral deposits related with small volcanic intrusions in the Republic of Macedonia. *ABCD-GEODE 2001 workshop Vata Bai*, Romania. Vol. **79**, suppl. 2, pp 114a.

Serafimovski, T., Tasev, G. and Lazarov, P., 2006: Au-Ag-Te-Bi-Se minerals associated with porphyry copper mineralization in the Buchim copper mine, Republic of Macedonia. Au-Ag-Te-Se deposits IGCP Project 486, *Field Workshop*, Izmir, Turkey, pp. 154–158.

Strasimirov, S., Serafimovski, T., Kovačev, V., 1996: Temperatures of the Ore-Forming process in the Buchim Porphyry Copper Deposit (Macedonia) – Data from Fluid Inclusion Studies. *Геология рудных месторождений*, Том **38**, N. 1, 373–377, Moskva.

Čifliganec, V., 1982: *Prateće korisne komponente porfirskog ležista bakra Bučim i mogućnosti njihove valorizacije*. Mag. tez, Rud.-geol. fak., Beograd.

Čifliganec, V., 1987: *Metalogenetske karakteristike ležista bakra Bučim u srpsko-makedonskoj metalogenetskoj provinciji*. Dok. disertacija, Rud.-geol. fak., Beograd.

Чифлиганец, В., 1993. *Рудишта и појави на бакар во Република Македонија: типови и реонизација со посебен осврт на порфирското рудиште на бакар Бучим*. Рударско-геолошки факултет, Штип. 303 стр.

Р е з и м е

СОСТАВ НА ГЛАВНИТЕ МИНЕРАЛИ ОД ПОРФИРСКОТО БАКАРНО НАОЃАЛИШТЕ БУЧИМ, РЕПУБЛИКА МАКЕДОНИЈА

Тодор Серафимовски[1], Тадеј Доленец[2], Горан Тасев, Настја Роган[2], Матеј Доленец[2]

[1]*Универзитет „Гоце Делчев“, Факултет за природни и технички науки, Институт за геологија,*
ул. Гоце Делчев 89, МК-2000 Штип, Република Македонија
[2]*Факултет за природни и технички науки, Оддел за геологија, Универзитет во Љубљана,*
Ашкерчева 12, 1000 Љубљана, Словенија
todor.serafimovski@ugd.edu.mk   //   goran.tasev@ugd.edu.mk

Клучни зборови: порфирско бакарно наоѓалиште Бучим; главни минерали; состав

Нашето тековно проучување на главните рудни и силикатни минерали ги вклучуваше најважните минерали во рамките на наоѓалиштето Бучим. Силикатните минерали беа претставени од плагиокласи, К-фелдспати, биотити и амфиболи. И покрај комплексните формули тие минерали покажаа прилично уедначени состави. Амфиболите беа одредени како хорнбленда, биотите се карактеризираа со зголемени концентрации на Fe и Ti и намалени концентрации на Mg, плагиокласите беа одредени како санидини, додека К-фелдспати беа претставени од албити и олигоклас.

Покажавме дека составот на халкпиритот е со висока чистота и без некое значително присуство на Ni, Co, As и Sb (<0,01%). Анализите на пиритите покажаа зголемени концентрации на арсен (0,15 ÷ 0,22 % As). Таквите концентрации на арсен се индикативни, но и се многу карактеристични за нискотемпературните пирити од порфирските бакарни наоѓалишта. Покрај арсенот во пиритите беа одредени зголемени концентрации на никел од 0,45 до 1,42 % Ni, додека Co и Sb покажаа концентрации под 0,01 %.

MINERAL RESEARCHES OF THE EXAMPLES OF THE ARCHEOLOGICAL LOCALITY "STOBI" USING THE METHOD OF THE X-RAY DIFFRACTION

Blažo Boev[1], Tena Šijakova-Ivanova[1], Lidija Robeva-Čukovska[2], Ivan Boev[1]

[1]*The "Goce Delčev" University, Faculty of Natural and Technical Sciences, Institute of Geology,
ul. Goce Delčev 89, MK-2000 Štip, Republic of Macedonia*
[2]*Republic Institute for Conservation, Skopje, Republic of Macedonia*
blazo.boev@ugd.edu.mk // tena.ivanova@ugd.edu.mk

A b s t r a c t: In this paper examples data is presenting from the mineral researches on couple of examples from moulding decoration (archeological finding) which is found on the Kockarnica at the ancient city Stobi.

Point of the moulding fragments researches is specify if they are all natural stones from mineral origin or parts of them are synthetic. It is very important to give information for their geological origin, more specifically to give information about where we can find them.

Results will serve first for making this artifact, but also for receiving information about its origin. With other words, we need to know whether the artifact is produced in Ancient Macedonia or it is brought from further places. Given results show that the biggest part of the examples originates from Macedonia only beryl appears as an exception.

Key words: moulding; x-ray researches; thermic researches

INTRODUCTION

Stone examples, which were subject of examination, are part of moulding decoration which represents mosaic technique made above wooden base. Moulding is archeological founding from the excavations in 2006–2007 in frames of the conservatoire-researching on the object Kockarnica at the ancient city Stobi.

Stobi, which is one of the most researched locality in Republic of Macedonia is in the middle of the Vardar region between Crna Reka (Erigon) and the river Vardar (Agious) and it is assumed that it takes area about 20 hectares.

According to the oldest historical information met in the records of Roman history professor Tit Livij, Stobi originates from Hellenistic period 197 BC (Wiseman, 1971, 1973). According to archeological data from the researches this city settlement is raised 3–2 century BC although many ceramic findings show on a much early period 7–5 century BC. (Mikulčić, 2003, Project elaborat, 2004).

Because of its perfect position on the road "Via Ignacia" that leads from Danube to the Aegean this city settlement represented significant strategic, military, economical and cultural centre (Aleksova, 1997).

In the researched part of Stobi, many architectonic object are found and studied till now and they represent profane and sacral constructions with public function, palaces, baths, antique theatre, parts of city palisade, streets, forum, main entrance of the city and the casino where the artifact that we are talking about is found. The casino represents a hall which floor was covered with mosaic made of geometrical motives. In the middle there was an octagonal fountain covered with marble and above there were three tables for gambling. In the casino there were also a bath with places for seating, and a little pool for drinking water for the guests (Fig. 1, Fig. 2).

Fig. 1. Moulding of the object Kockarnica
at the ancient city Stobi

Fig. 2. Part of the mosaic of the object Kockarnica
at the ancient city Stobi

METHODS OF EXAMINATION

The analyses are made with scanning electronic microscope JEOL JSM 35CF X-ray micro-analyzer TRACOR NORTHEPN TN – 2000 and we used etalons from JEOL.

X-ray researches are made on the diffractometer Simens D 500 with computer support of Cu monochromatic radiation of 40 KB/30 mA with automatic changeable input shutter. Determination of the mineral phases is made by program package DIFRAK 11 in programs EVAL and IDR.

Quantitative presence of the mineral phases is made by Peter and Kelman's method with already defined coefficients for some mineral phases.

Preparations made for x-ray diffraction are pictured in $2\theta = 3 – 60°$.

Thermal researches are made on derivatograph Q-1500 D under these conditions:
– weight of the experiment 500 mg,
– sensitivity of TT 200 mg,
– sensitivity of DTA 250 μB, DTT 500 μB,
– speed of warming up 10 C/min,
– temperature interval of the measuring from 15–20 C° to 1000 °C,
– inert material Al_2O_3,
– centre in the oven-air without turbulence.

RESULTS AND DISCUSSION

Subject of examine are 12 samples. In the Tables 1 and 2 chemical compositions are presented of all 12 samples.

T a b l e 1

*Chemical composition
of the samples 1, 2, 3, 4, 5, 6 and 7 (in %)*

	1	2	3	4	5	6	7
SiO_2	93.45	91.16	62.21	93.36	99.36	0.86	2.42
Al_2O_3	3.38	0.99	5.97	1.19	0.30	<0.01	1.43
Na_2O	1.26	<0.01	<0.01	<0.01	<0.01	<0.01	
K_2O	<0.01	0.09	1.10	0.20	<0.01	0.14	0.45
CaO	1.09	<0.01	1.04	1.02	<0.01	1.52	5.00
FeO	0.74	7.77	8.12	2.84	<0.01	0.12	0.35
TiO_2		<0.01	0.05	0.08	<0.01	0.08	0.09
MnO		<0.01	0.14	<0.01	<0.01	0.11	
MgO					<0.01	51.14	1.45
SO_3							1.18

T a b l e 2

*Chemical composition
of the samples 8, 9, 10, 11 and 12 (in %)*

	8	9	10	11	12
SiO_2	0.78	65.49	37.35	98.74	0.86
Al_2O_3	0.36	16.96	2.12	<0.01	<0.01
Na_2O		0.44	1.74	0.53	<0.01
K_2O	0.15	0.08	1.72	0.14	0.24
CaO	0.44	0.03	8.56	0.08	3.36
FeO	0.14	0.16	3.97	0.07	0.27
TiO_2	<0.01			<0.01	<0.01
MnO				0.07	0.09
MgO	1.05	0.83		<0.01	57.30
SO_3	<0.01				
PbO			32.08		
CuO			11.45		

In *sample 1* we have presence of the following minerals: quartz, albite and calcite. On Fig. 3 we have crystal of quartz.

On Fig. 4 x-ray diagram of sample 1 is given. Quartz is based under these d-values: 4.24, 3.34, 2.45, 2.27; 2.23; 2.12; 1.97; 1.81; 1.66.

The four most intense d-values for albite are: 3.20; 3.78; 6.39; 3.68, and for calcite are: 3.03, 1.87; 3.85; 2.09

The presence of the minerals is following: quartz 96%, albite 1% and calcite 1%

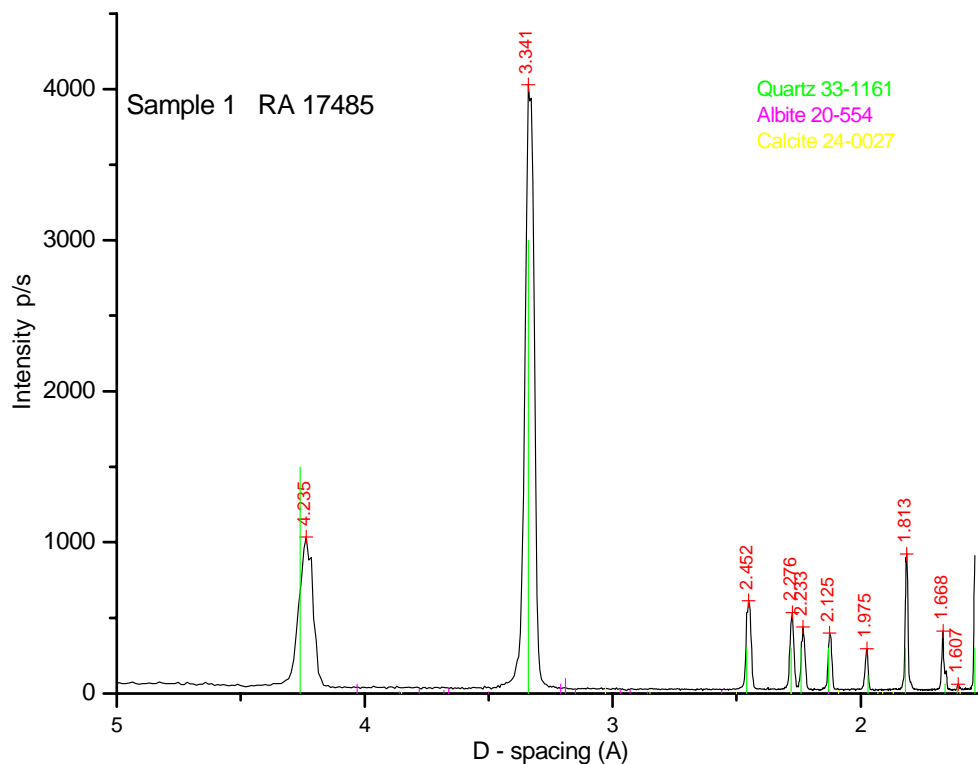**Fig. 3.** Quartz crystal used in sample number 1

Fig. 4. The powder x-ray diagram of sample 1

Sample number 2: In this sample we have presence of the minerals quartz and hematite. On Fig. 5 we have quartz with hematite. Hematite is based on the following d-values: 2.70; 2.52; 1.69; 1.84 (Fig. 6 and Fig. 7). These values are in accordance with JCPDS 33-664. We have quartz with 90% presence and hematite 9%.

Sample number 3: We have presence of these minerals: magnetite, quartz, dolomite, albite, and muscovite (Fig. 10). Percentage of the minerals is next: quartz 45%, magnetite 41%, dolomite 7%, muscovite 4%, albite 3%. The x-ray diagram is given on the Figs. 8 and 9.

Characteristic d-values for magnetite are 2.53-1.48-2.97-1.62, for dolomite 2.89-2.19-1.79-2.02, for albite 3.20-3.78-6.39-3.68 and for muscovite 4.50-9.91-2.56-3.62.

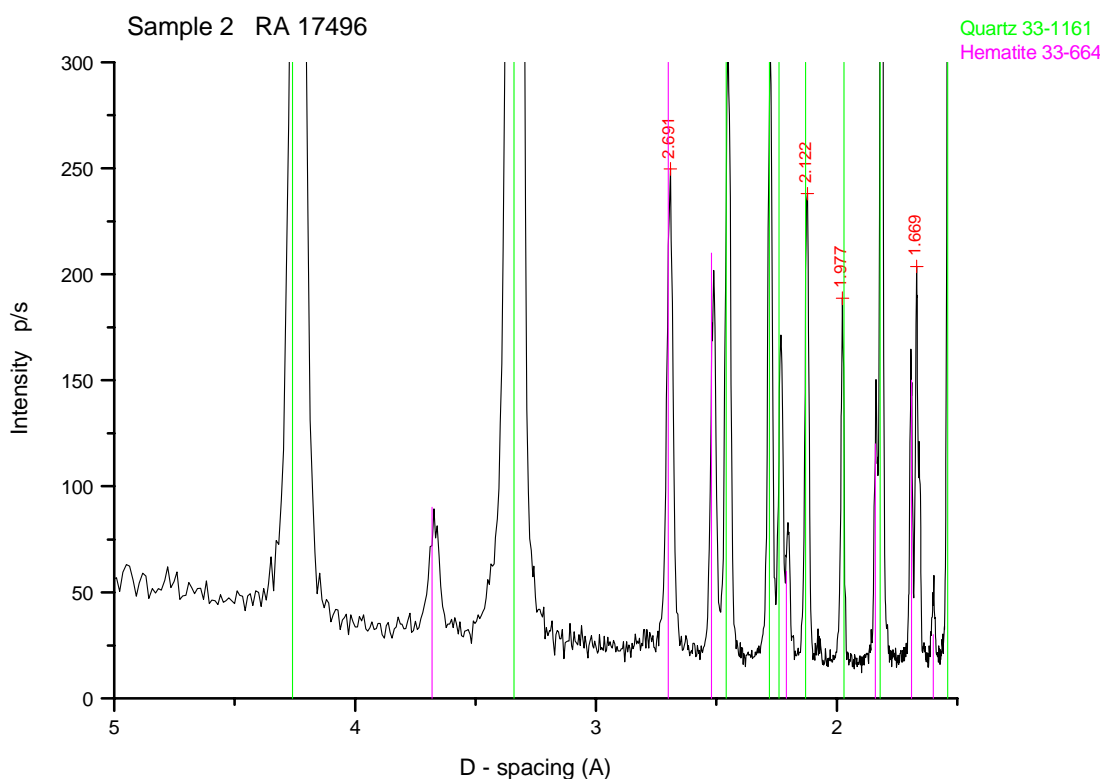**Fig. 5.** Quartz with hematite from moulding in Stobi
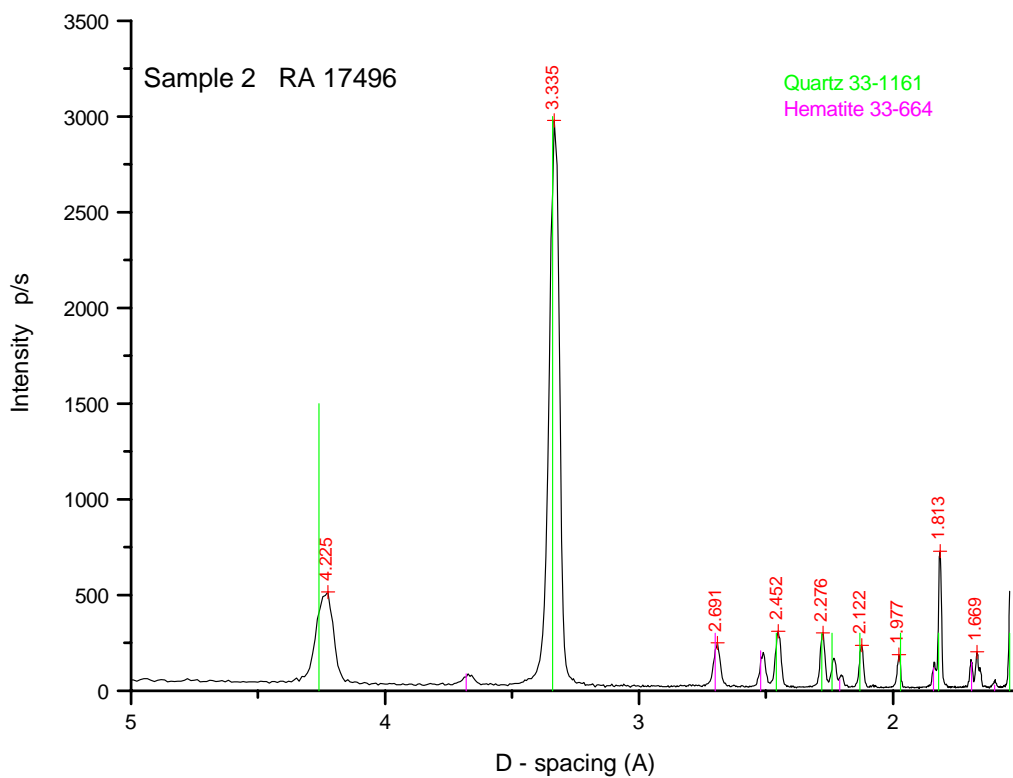

Fig. 6. The powder x-ray diagram of sample 2-1

Fig. 7. The powder x-ray diagram of sample 2-2
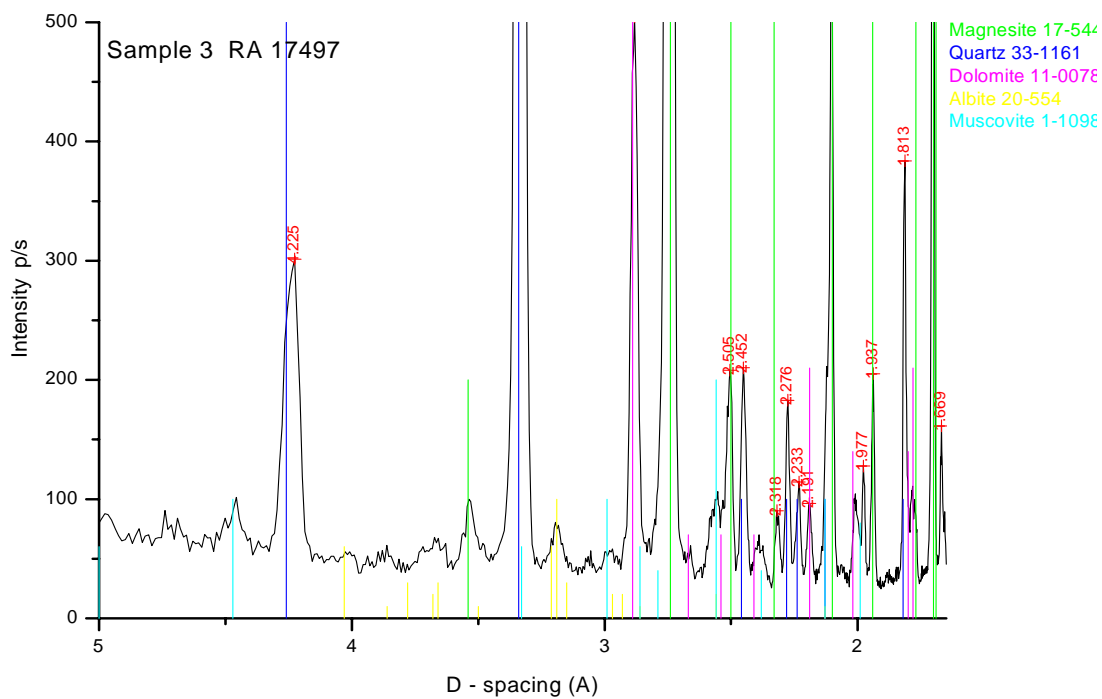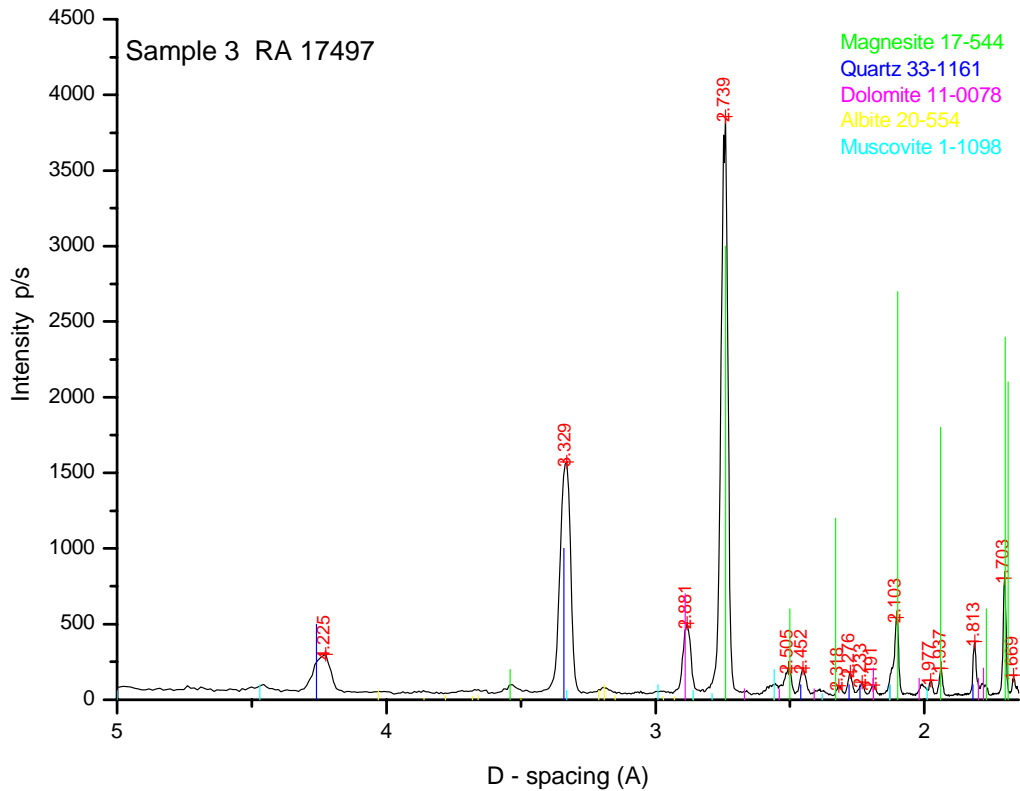

Fig. 8. X-ray diagram of sample 3-1

Fig. 9. X-ray diagram of sample 3-2

Fig. 10. Photo of sample number 3

Sample number 4: In this sample we have quartz 76%, dolomite 16%, hematite 3%, calcite 2 %, halloysite 2 %. We can see some of these minerals on Fig. 11. The x-ray diagram of sample number 4 is given on Fig. 12.

Sample number 5: In this sample we have 99 % quartz and dolomite 1 % (Fig. 13). X-ray diagram is given on Fig. 14.

Sample number 6: We have the minerals magnesite and dolomite. On (Fig. 16) magnesite is shown. Its presence is 98% and dolomite 1%. The x-ray diagram is given on Fig. 15.

Fig. 11. Photo of sample 4
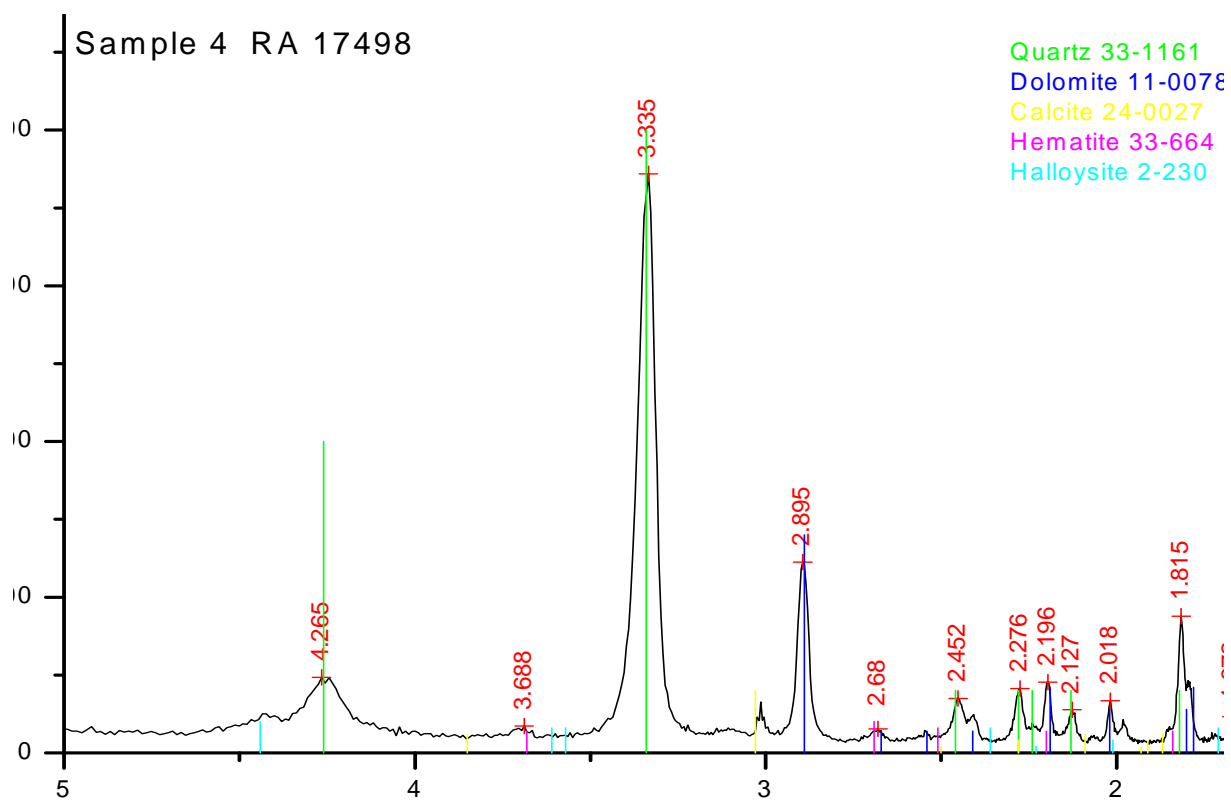
Fig. 12. X-ray diagram of sample 4
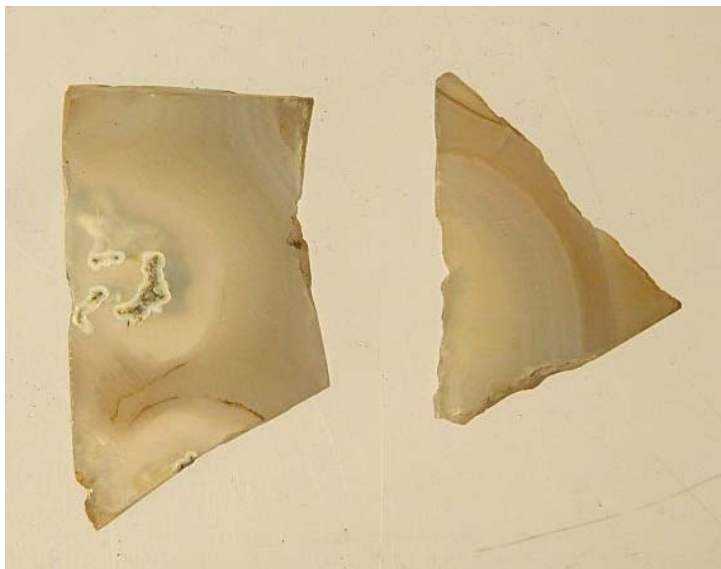
Fig. 13. Achate of sample 5
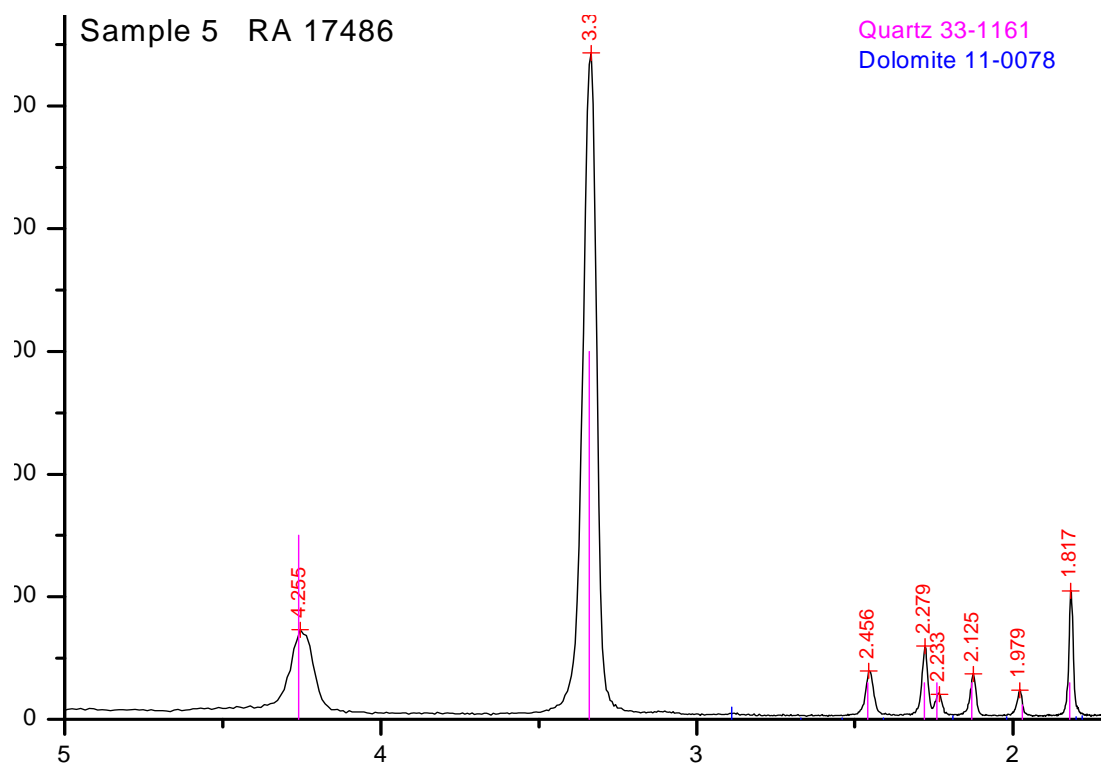
Fig. 14. X-ray diagram of sample number 5
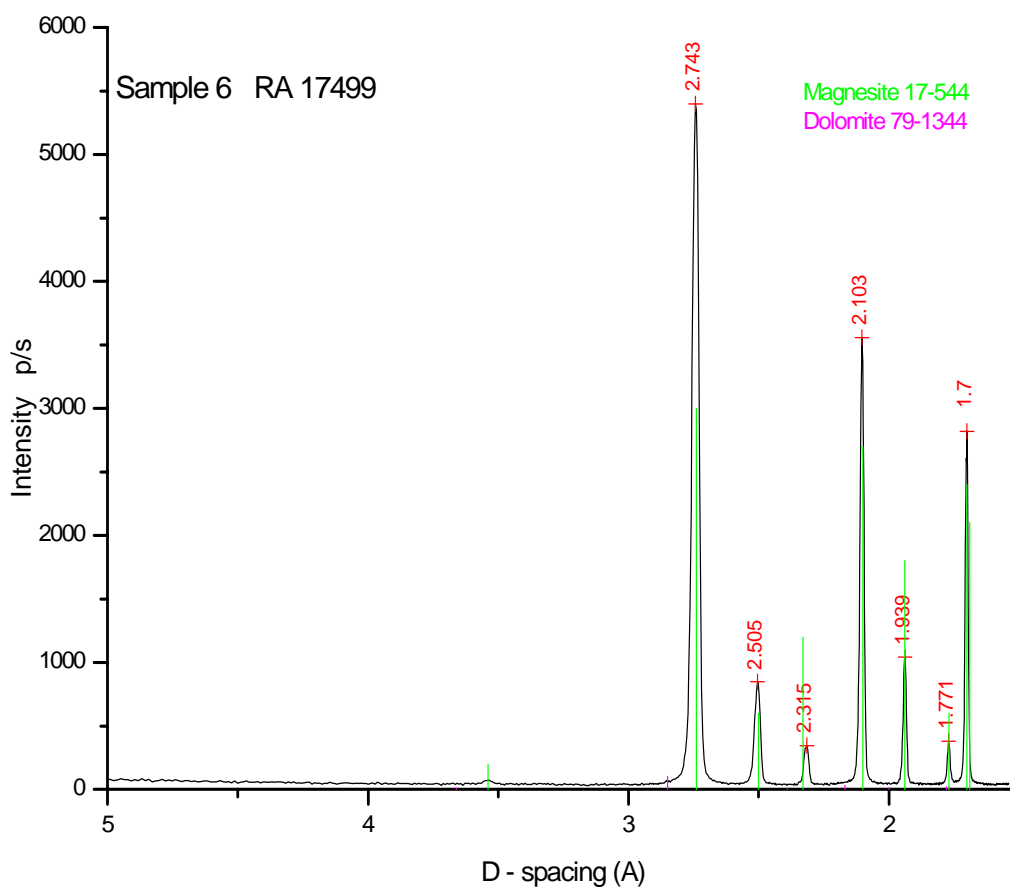
Fig. 15. X-ray diagram of sample number 6
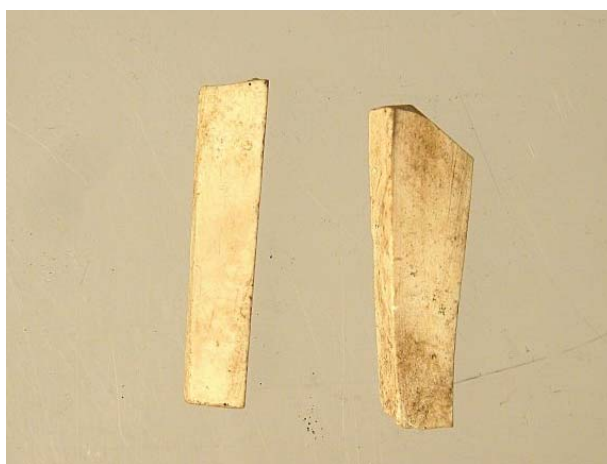
Fig. 16. Magnesite of sample 6

Sample number 7: From the x-ray diagram shown on Fig. 18 we can see that it is about amorphous phase most probably organic material, with little presence of quartz, calcite and olivine. We have two examples of the sample on Fig. 17.

Fig. 17. Organic material with presence of olivine, calcite and quartz
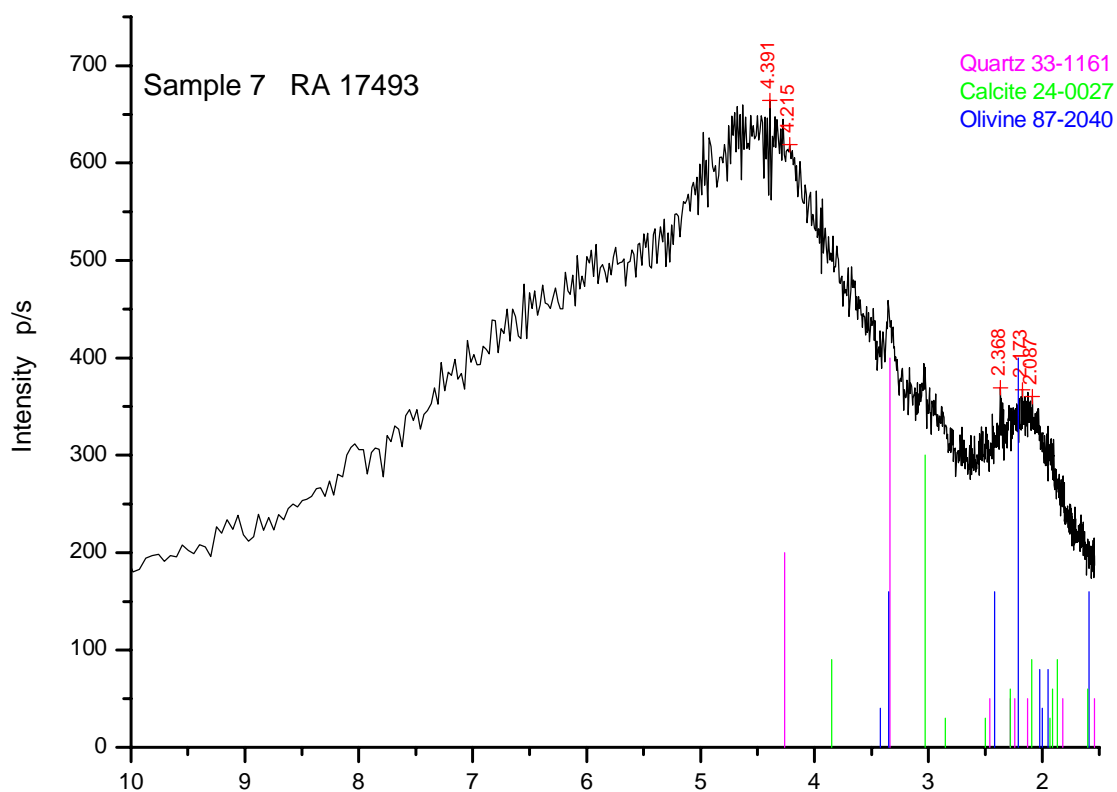
Fig. 18. X-ray of sample 7

Sample number 8: We have amorphous phase with presence of olivine (Fig. 19). The x-ray diagram is given on Fig. 20. For olivine we have these d-values 2,49-2,41-2,24-1,73 that are in full agreement with JCPDS standards 87 – 2040.

Fig. 19. Amorphous material with presence of olivine
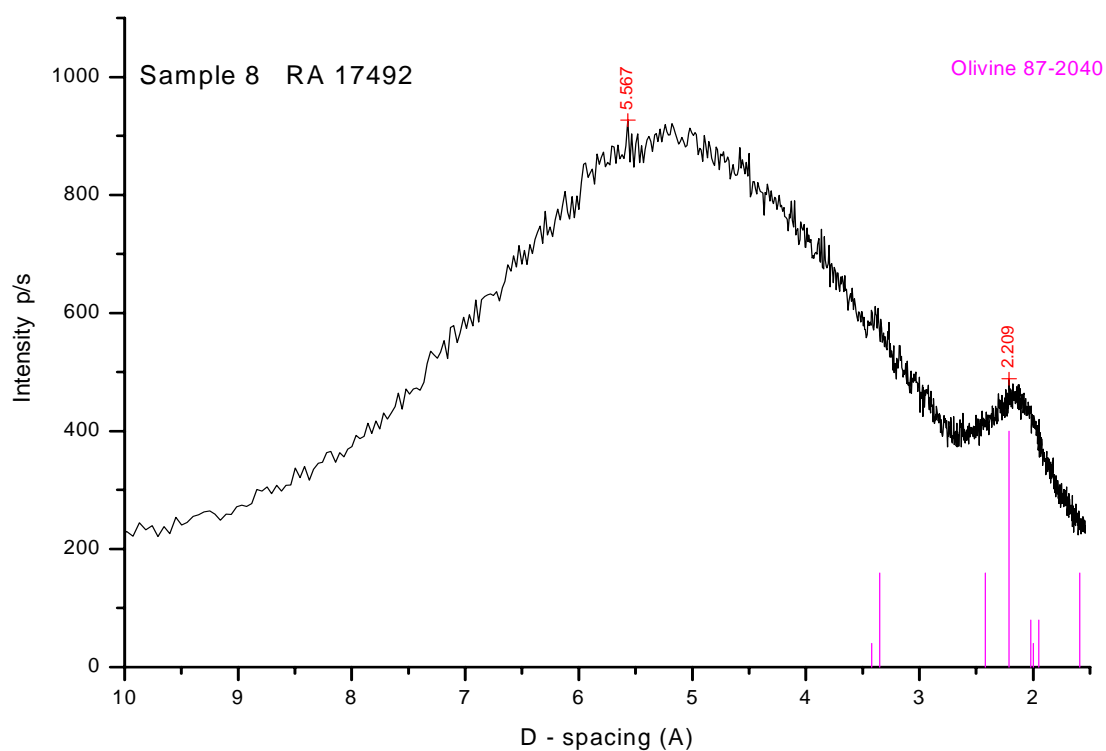
Fig. 20. X-ray of sample 8

Sample number 9: From the x-ray diagram shown on Fig. 22 we can see that it becomes a word about the mineral beryl. The following d-values are given: 7.998; 4.593; 3.982; 3.263; 2.872; 2.529; 2.158; 1.995; 1.744; 1.631. These values are in complete agreement with the data given in JCPDS. On Fig. 21 we have crystals of beryl.

Fig. 21. Crystals of beryl
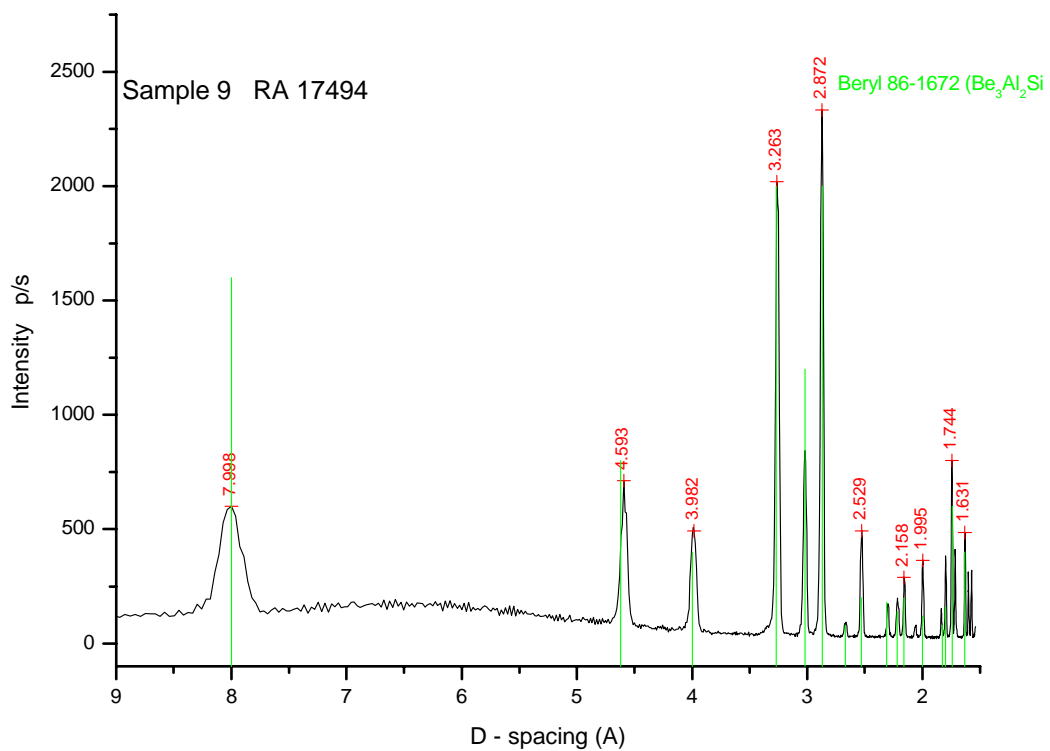
Fig. 22. X-ray diagram of sample 9

Sample number 10: We have amorphous SiO_2 (Fig. 23). From the x-ray diagram (Fig. 24) we can see a presence of cuprites and massicot. d-Values for cuprites are 2.47-2.14-1.51-1.29. Characteristic d-values for massicot are 3,07-2,95-2,75-2,38. The d-values that we have for cuprites and massicot are in full agreement with the data of JPDS 78-2076 and 77-1971.

Fig. 23. Amorphous SiO_2 with cuprite and massicot
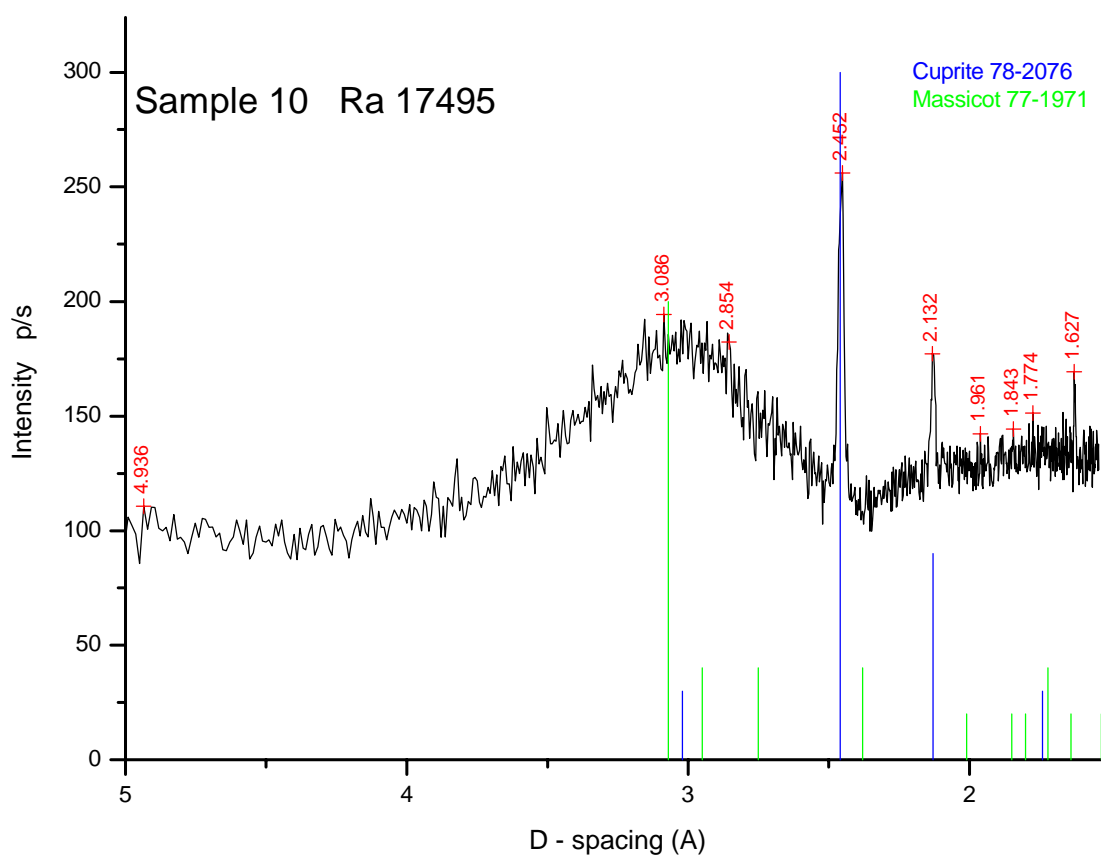
Fig. 24. X-ray diagram of sample 10

Sample 11: In this sample we have quartz with 99%, and muscovite 1%. x-ray diagram is given on Fig. 25.

Sample 12: We have magnesite. Its presence is 99%. From the x-ray diagram we can see that besides magnesite there is 1% of quartz and dolomite. Most intense d-values for magnesite are 2,74-2,10-1,70-2,50 (Fig. 26)
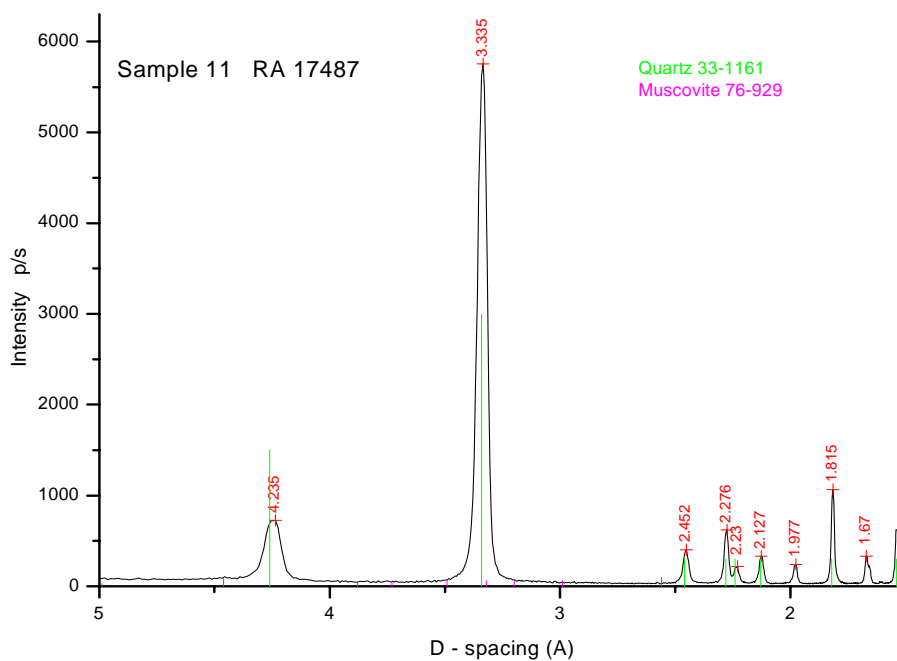
Fig. 25. X-ray diagram of sample 11
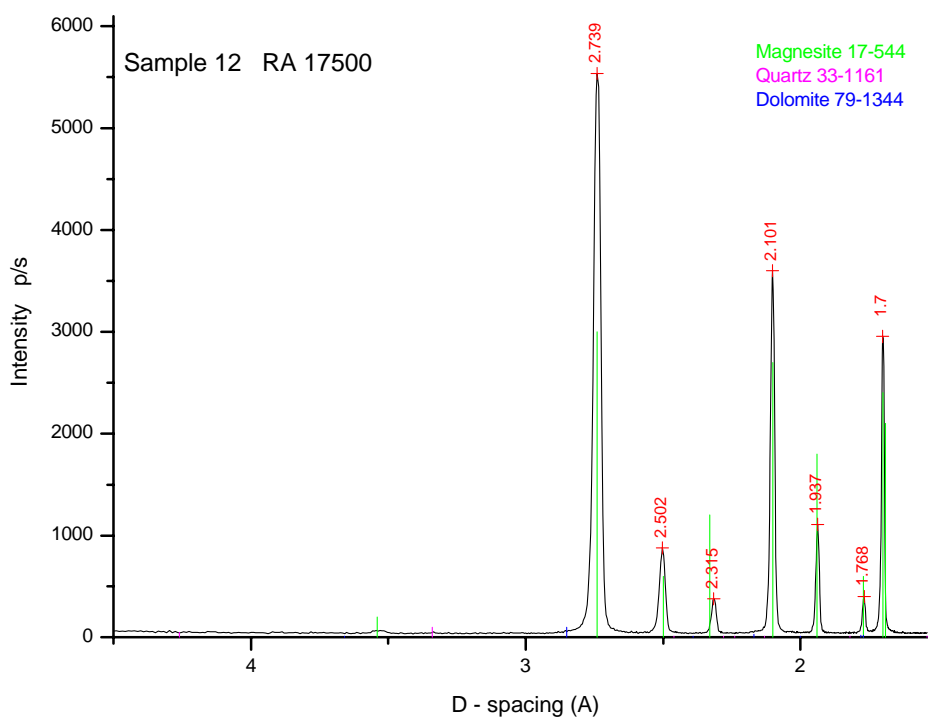
Fig. 26. X-ray diagram of sample 12

CONCLUSION

Making researches that were taken on the moulding examples from the locality Stobi using the method of x-ray diffraction confirmed the presence of monomineral phases (quartz, beryl, magnesite) and also presence of the polymineral associations which in base represents magmatic rocks from the places of the Republic of Macedonia. With these researches it is confirmed that the biggest part of the minerals used in moulding decoration in the old casino in Stobi is taking origin from Macedonia. Only beryl which is found in the examples of this locality can be said that definitely is not coming from this region of Macedonia. Beryl as a mineral is brought from the east parts of the previous Macedonian Empire.

RFERENCES

1. Aleksova, B., 1997: *Loca Sanctorum Macedoniae*, Institute for Old Slav Culture, Macedonian civilization, Skopje.

2. Mikulčić. N., 2003: *Stobi, the ancient city*, Skopje.

3. Project elaborat for conservation and restauration works on the object "Kockarnica" in Stobi (IV phase), arh. br. 07-166/39, INDOK-NKC, Skopje, 2004 (in Macedonian).

4. Wiseman, J., 1971: Excavations at Stobi, *American Journal of Archaeology*, **76**, p-p 407–424.

5. Wiseman, J. R., 1973: Stobi: A Guide to the excavations, Beograd.

Р е з и м е

МИНЕРАЛОШКИ ИСТРАЖУВАЊА НА ПРИМЕРОЦИ ОД АРХЕОЛОШКИОТ ЛОКАЛИТЕТ „СТОБИ" СО ПРИМЕНА НА РЕНДГЕНСКА ДИФРАКЦИЈА

Блажо Боев[1], Тена Шијакова-Иванова[1], Лидија Робева-Чуковска[2], Иван Боев[1]

[1]*Универзитет Гоце Делчев, Факултет за природни и технички науки,*
ул. Гоце Делчев 89, МК-2000 Штип, Република Македонија
[2]*Републички институт за конзервација, Скопје, Република Македонија*
blazo.boev@ugd.edu.mk // tena.ivanova@ugd.edu.mk

Клучни зборови: рендгенски истражувања; термички истражувања

Врз основа на извршените минералошки испитувања во неколку примероци од архитектонската декорација на објектот Коцкарница во античкиот град Стоби е одредено присуство на минералите кварц, берил и магнетит. Исто така е одредено и присуство на минерални асоцијации кои се репрезентативни магматски карпи кои потекнуваат од територијата на Р. Македонија.

Со овие испитувања е констатирано дека поголем дел од минералите кои се употребени за декорација на коцкарницата во Стоби потекнуваат од територијата на Р. Македонија.

Само за минералот берил, кој е најден во примерокот бр. 9, може дефинитивно да се каже дека не потекнува од територијата на Р. Македонија. Берилот е најверојатно донесен од источните делови на некогашната Македонска Империја.

DETERMINATION OF TRACE ELEMENTS IN HEMATITE'S IRON REFERENCE MATERIAL JSS-804-1 USING k_0-INAA

Milena Taseska[1], Petre Makreski[1], Vekoslava Stibilj[2], Radojko Jaćimović[2], Trajče Stafilov[1]

[1]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, SS. Cyril and Methodius University, P.O. Box 162, MK-1001 Skopje, Republic of Macedonia*
[2]*Jožef Štefan Institute, P.O. Box 3000, SI-1001 Ljubljana, Slovenia*
trajcest@iunona.pmf.ukim.edu.mk

A b s t r a c t: Different trace elements in hematite's iron ore reference material (JSS-804-1) were investigated using k_0-instrumental neutron activation analysis (k_0-INAA). To avoid the interference of iron as matrix elements, a method for its separation was applied. Namely, a liquid-liquid extraction procedure by diisopropyl ether (DIPE) in hydrochloric acid solution and determination of trace elements in the aqueous phase was undertaken. The k_0-INAA method was applied to determine the content of the investigated elements thus making it possible to follow the distribution of 39 elements (with intermediate/medium and long half-lived radionuclides) in the studied referent material. An important advantage of the proposed method is the possibility to determine the content of several trace elements after Fe separation. Additionally, the elimination of the matrix element also lowered the detection limit for some trace elements compared to their corresponding values determined by k_0-INAA and certified values for some elements.

Key words: k_0-INAA; k_0-RNAA; trace elements; reference material; hematite

INTRODUCTION

For the calibration of different types of instruments, as well as for method validation in the analysis of major and trace elements, iron ore reference materials are used as very important materials in the analytical chemistry of quality control of raw and final products in mining and metallurgy. However, there are many iron reference materials without certified values for the content of many trace elements present that could be very important in validating methods used for process control in the iron and steel production industry. Therefore it is very important to extend the list of certified elements in these types of reference materials.

A number of studies have been carried out concerning the determination of trace elements in iron ore materials directly from dissolved samples by atomic absorption spectrometry (AAS) and atomic emission spectrometry with inductively coupled plasma (AES-ICP), (Schrön et al., 1983; Castillo et al., 1988; Barros , 1989; Stafilov, 2000; Makreski et al., 2004) or after the separation and concentration of the elements of interest (Viets, 1984; Eidecker & Jackwerth, 1988; Stafilov et al., 1993; Kabil et al., 1996; Lazaru & Stafilov, 1998;

Zendelovska & Stafilov, 2001; Stafilov & Zendelovska, 2002). Radioanalytical instrumental methods (instrumental neutron activation analysis – INAA, x-ray fluorescence spectrometry – XRF, and particle (proton) induced x-ray emission – PIXE) are rarely used to determine trace elements due to matrix and inter-element interferences and background effects (Palme et al., 1988; Suzuki & Hirai, 1995; Tomura & Tomuro, 1999; Jaćimović et al., 2002; Tomuro & Tomura, 2002; Nečemer et al., 2003, Taseska et al., 2006; Jaćimović et al., 2008; Makreski et al., 2008).

Iron as the matrix of the investigated materials has such nuclear characteristics (cross-section, abundance, resonance integral) that the induced radionuclide ^{59}Fe ($T_{1/2}$ = 44.5 d, with mean gamma energies at E_γ = 1099.3 keV and E_γ = 1291.6 keV) is moderately activated and interferes with the determination of many trace elements by INAA (Tomura & Tomuro, 1999; De Soete et al., 1972). In this work a method is presented for simultaneous measurement of 39 elements in hematite's iron reference material JSS 804-1 using k_0-INAA after the extraction of Fe by diisopropyl ether (DIPE).

EXPERIMENTAL

Sample

JSS 804-1 (Iscor Hematite), iron-based reference material was supplied by the Iron and Steel Institute of Japan.

Extraction of iron from matrix

The powder sample of JSS 804-1 (~100 mg) was dissolved on a hot plate by successively adding freshly prepared aqua regia. After evaporation to dryness, 1 mL of 2 mol L^{-1} HNO_3, 0.8 mL of redistilled water and 3.2 mL conc. HCl were introduced (7.7 mol L^{-1} HCl solution). Iron was removed by extraction with 4 mL of DIPE (5 times, 30 s each). The organic layer was removed using a Pasteur pipette. After the phase separation, the aqueous part was evaporated almost to dryness and transferred in a polyethylene ampoule with 2 mL of 2 mol L^{-1} HNO_3 and irradiated in the carousel facility (CF) of the TRIGA Mark II reactor of the Jožef Štefan Institute in Ljubljana, Slovenia. In the same way, two blank samples were prepared and irradiated together with the aqueous phase of the reference material.

k_0-Instrumental neutron activation analysis

The iron reference material was analyzed by k_0-INAA as follows: Powder (0.1 g) was sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). Sample and standard (Al–0.1%Au IRMM-530 disc of 6 mm in diameter and 0.2 mm high) were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated for 20 hours in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor at a thermal neutron flux of $1.1 \cdot 10^{12}$ cm^{-2} s^{-1} (Jaćimović et al., 2008).

Trace elements in aqueous phaze were analyzed by k_0-INAA (Fig. 1) in four repetitions. The aqueous phase (3–4 g) was transferred in a pure polyethylene ampoule and irradiated for 18 hours at the CF at a thermal flux of $1.1 \cdot 10^{12}$ n cm^{-2} s^{-1} for intermediate/medium and long lived isotopes.
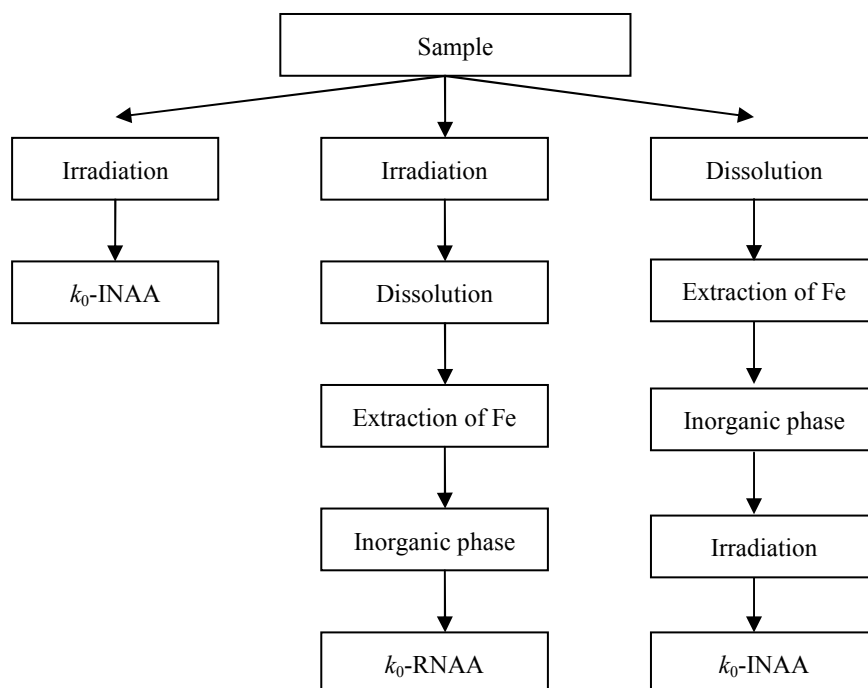

Fig. 1. Scheme of the separation and determination of the element contents of iron reference material using k_0-INAA and k_0-RNAA

After long irradiation, the samples were transferred in clean polyethylene ampoules and measured after 3, 8–10 and 30–35 days cooling time on an absolutely calibrated HPGe detector.

The HyperLab (HyperLab 2002 System, 2002) program was used for peak area evaluation, whereas for determination of f (thermal to epithermal flux ratio) and α (epithermal flux deviation from the ideal 1/E distribution), the "Cd-ratio" method for multimonitor was applied (Jaćimović et al., 2003). The values $f = 28.6$ and $\alpha = -0.001$ were used to calculate the element concentrations. The elemental concentrations and effective solid angle calculations were carried out on the software package Kayzero for Windows (User's Manual Kayzero for Windows Version 2, 2005).

RESULTS AND DISCUSSION

A comparison between the results obtained in the inorganic phase after iron extraction with DIPE and in the powdered sample by k_0-INAA for the reference material JSS-804-1 is presented in Table 1. It is evident that after extraction, iron was practically removed (98.5%). The results of the analysis of the extracted sample show that 18 elements remained in the acidified solution (As, Ba, Ce, Co, Cr, Cs, Eu, K, La, Nd, Sc, Sm, Sr, Tb, Th, U, W and Yb), i.e. they are not removed by DIPE. As can be seen, the rare-earth elements (REE) e.g. Ce, Eu, La, Nd, Sm, Tb and Yb fit into this group (the ratio between k_0-INAA in the powdered sample and after iron extraction is near 1). The limit of detection (LOD) for numerous elements (Ag, Rb, Se, Sn, Ta, Te, Zn and Zr) was much lower after iron extraction compared to the corresponding values obtained by k_0-INAA measurements in powdered sample which means that they could be analyzed in the inorganic phase after iron removal. This could be explained by either their low content in the iron materials or the presence of ^{59}Fe ($T_{1/2} = 44.5$ d) in the gamma spectrum. Comparing the results obtained in the powdered sample and inorganic phase after iron extraction, it could be concluded that Br, Mo and Sb are also extracted by DIPE (Tables 1).

It should be pointed out that these results and the previously published results for the same reference material obtained by radioanalytical procedure (Jaćimović et al., 2008) are in good agreement (see Table 1). The samples were irradiated firstly and then digested and iron was extracted by DIPE and the trace elements were determined in aqueous phase by k_0-radiochemical instrumental neutron activation analysis, k_0-RNAA (Fig. 1). Using k_0-RNAA the contents of the elements in blank sample are negligible, but it not in the case when we did first extraction and then irradiation. The contents of elements in blank samples are presented in Table 1. So, we should emphasize that the proposed method could eliminate the necessity of using the irradiated samples and radioanalytical laboratory for majority of investigated elements. The disadvantage of this procedure is that some elements like As, Au, Ba, Hf, K, Na, Zn and Zr are introduced into the sample during iron extraction with DIPE especially when dealing with relatively small element quantities.

The data obtained by k_0-INAA for the content of the elements in the studied iron reference material is in agreement with certified values given in the last column of Table 1. Taking into account that the JSS 804-1 standard gives certified values for only 4 elements, the results obtained provide useful additional information on the content of the other elements in the standard.

CONCLUSIONS

The proposed method enabled the measurement of 39 elements in the studied sample. The ratios between the k_0-INAA values obtained before and after iron extraction were near 1 for 18 elements (As, Ba, Ce, Co, Cr, Cs, Eu, K, La, Nd, Sc, Sm, Sr, Tb, Th, U, W and Yb) including REE. This shows that DIPE is not selective for these elements. Also, after Fe extraction, the limit of detection for many elements was lowered. Taking into account that certified values in the studied iron ore reference standard are given only for few elements, the obtained results provide important information on the content of many other elements.

T a b l e 1

Results obtained by k_0-INAA in the powdered sample and in the aqueous phase after iron extraction with DIPE for the reference material JSS-804-1. All results are in mg kg^{-1}

El.	k_0-INAA$^\$$ (Powder) Cont.±Unc.*	k_0-RNAA$^\$$ (Inorganic) Cont.±Unc.*	R#	k_0-INAA$^{\$\$}$ (Inorganic) Cont.±Unc.*	n	R##	k_0-INAA** (Inorganic-Blank) Cont.±Unc.*	n	JSS 804-1 Cert.±Unc.
Ag	<0.6	<0.3		0.22±0.01	2		0.050±0.003	1	
As	24.6±0.9	20.3±0.7	0.824	25.0±1.9	4	1.013	1.96±0.09	2	20±4
Au	<0.003	<0.001		0.008±0.009	2		0.019±0.020	2	
Ba	171±7	147±6	0.862	179±7	4	1.046	14.2±0.7	2	
Br	1.25±0.06	<0.1		0.26±0.20	2	0.206	0.065±0.004	2	
Ca	<1097	450±67		<245	4		71.8±23.6	2	277±10
Cd	<3.2	<0.5		<1.7	4		<0.2	2	
Ce	21.6±0.8	24.1±0.9	1.115	21.8±1.2	4	1.009	0.91±0.03	2	
Co	3.89±0.14	3.55±0.13	0.912	4.17±1.10	4	1.071	0.0089±0.0004	2	
Cr	37.9±1.5	42.0±1.5	1.108	30.7±5.8	4	0.810	0.598±0.038	2	40±2
Cs	0.29±0.03	0.40±0.02	1.362	0.41±0.02	4	1.426	0.021±0.001	2	
Cu	<305	<283		<2837	4		<500	2	<10
Eu	0.32±0.04	0.35±0.02	1.112	0.30±0.02	4	0.954	0.0068±0.0002	2	
Fe	671751±23513	5734±201	0.009	9980±5573	4	0.015	3.62±1.48	2	662610±340
Ga	<3.2	<18		<9.4	4		<1.7	2	
Hf	0.29±0.04	0.30±0.01	1.037	1.28±0.21	4	4.384	0.485±0.017	2	
Hg	<2.3	<0.1		0.19±0.01	2		<0.016	2	
K	1282±57	<2123		1941±370	4	1.515	469±16	2	
La	10.3±0.4	11.8±0.4	1.143	9.42±0.94	4	0.916	0.49±0.04	2	
Mo	2.97±0.21	0.56±0.04	0.187	1.64±0.61	4	0.552	0.34±0.01	2	
Na	154±5	156±6	1.015	4524±1358	4	29.35	2255±82	2	
Nd	8.0±0.9	11.1±0.4	1.382	8.54±0.62	4	1.066	0.38±0.03	2	
Rb	<7.1	4.5±0.2		4.65±0.52	4		0.33±0.03	2	
Re	<0.03	<0.005		<0.04	4		<0.02	2	
Sb	1.28±0.05	0.18±0.01	0.138	0.53±0.06	2	0.411	0.030±0.006	2	
Sc	3.36±0.12	3.29±0.12	0.981	2.81±0.13	4	0.837	0.018±0.001	2	
Se	<0.7	<0.3		1.08±0.06	1		<0.05	2	
Sm	1.45±0.05	1.52±0.05	1.048	1.40±0.13	4	0.970	0.080±0.007	2	
Sn	<44.8	<8.9		12.9±2.2	1		<2.5	2	<10
Sr	113.1±10.7	121.7±4.9	1.076	107.9±18.8	4	0.953	<1.7	2	
Ta	<0.03	0.11±0.01		0.12±0.06	3		0.0035±0.0002	2	
Tb	0.16±0.01	0.16±0.01	0.991	0.17±0.02	4	1.024	0.0083±0.0005	2	
Te	<2.4	<0.4		<0.88	4		<0.08	2	
Th	0.97±0.4	0.66±0.02	0.681	1.37±0.15	4	1.419	0.26±0.01	2	
U	0.61±0.03	0.57±0.02	0.929	0.72±0.06	4	1.184	0.072±0.003	2	
W	69.9±2.5	57.5±2.0	0.822	77.3±18.1	4	1.105	<0.3	2	
Yb	0.81±0.03	0.81±0.03	0.998	0.72±0.11	4	0.889	0.030±0.001	2	
Zn	<6.8	2.6±0.2		3.08±3.13	4		2.35±0.31	2	
Zr	<108	<19.0		52.9±18.2	4		22.5±0.8	2	

$^\$$ – Results from Jaćimović et al., 2008; $^{\$\$}$ – Results after blank subtraction; * – Total estimated uncertainty of the method; ** – Results in the solution of the blank samples; # – Ratio between k_0-RNAA and k_0-INAA in powder sample; ## – Ratio between k_0-INAA in the aqueous phase and k_0-INAA in powder sample; n – Number of independent measurements; < – limit of detection (LOD).

REFERENCES

Barros J. S., 1989: Determination of antimony, arsenic, bismuth, cadmium, cobalt and silver in complex sulphide minerals by flame atomic absorption spectrometry, *Analyst*, **114**, 369–373.

Castillo J. R., Mir M. J., Martinez M. L., Gomez T., 1988: Study of the composition of siliceous material by AAS, *At. Spectrosc.*, **9**, 9–12.

Eidecker R., Jackwerth E., 1988: Zur Multi-Elementanreicherung aus Reineisen und reinen Eisenverbindungen, *Fresenius' Z. Anal. Chem.*, **331**, 401–407.

HyperLab 2002 System, 2002: *Installation and quick start guide*, HyperLabs Software, Budapest, Hungary.

Jaćimović R., Lazaru A., Mihajlović D., Ilić R., Stafilov T., 2002: Determination of major and trace elements in some minerals by k_0-instrumental neutron activation analysis, *J. Radioanal. Nucl. Chem.*, **253**, 427–434.

Jaćimović R., Smodiš B., Bučar T., Stegnar P., 2003: k_0-NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software. *J. Radioanal. Nucl. Chem.*, **257**, 659–663.

Jaćimović R., Makreski P., Stibilj V., Stafilov T., 2008: Determination of major and trace elements in iron reference materials using k_0-NAA, *J. Radioanal. Nucl. Chem.*, 278, 795–799.

Kabil M. A., El-Kourashy A.G., El-Hagrasy M.A., 1996: Flame atomic absorption spectrometric investigation and determination of cobalt and copper using ethanolamine and triethanolamine as chemical modifiers, *J. Anal. At. Spectrom.*, **11**, 379–387.

Lazaru A., Stafilov T., 1998: Determination of copper in sulfide minerals by Zeeman electrothermal atomic absorption spectrometry, *Fresenius' J. Anal. Chem.*, **360**, 726–728.

Nečemer M., Kump P., Rajčević M., Jaćimović R., Budič B., Ponikvar M., 2003: Determination of sulfur and chlorine in fodder by X-ray fluorescence spectral analysis and comparison with other analytical methods, *Spectrochim. Acta*, **58B**, 1367–1373.

Makreski P., Jovanovski G., Kaitner B., Stafilov T., Boev B., Cibrev D., 2004: Minerals from Macedonia. X. Separation and identification of some oxide minerals by FT IR spectroscopy, AAS, EAS-ICP and Powder XRD, *N. Jb. Miner. Abh.*, **180**, 215–243.

Makreski P., Jaćimović R., Stibilj V., Stafilov T., Jovanovski G., 2008: Determination of trace elements in iron minerals by instrumental and radiochemical neutron activation analysis, *Radiochim. Acta*, 96, 855–861.

Palme H., Pavićević M. K., Spettel B., 1988: Major and trace elements in some minerals and ore from Crven Dol, Allchar, *Nucl. Instr. Meth. Phys. Res.*, **A271**, 314–319.

Schrön W., Bombach G., Beuge P., 1983: Schnellverfahren zur flammenlosen AAS-Bestimmung von Spurenelementen in geologischen Proben, *Spectrochim. Acta*, **38B,** 1269–1276

De Soete D., Gijbels R., Hoste J., 1972: Neutron activation analysis. John Wiley & Sons, New York.

Stafilov T., Lazaru A., Pernicka E., 1993: Determination of thallium in sulfide minerals by Zeeman electrothermal atomic absorption spectrometry, *Acta Chim. Slov.*, **40**, 37–46.

Stafilov T., 2000: Determination of trace elements in minerals by electrothermal atomic absorption spectrometry, *Spectrochim. Acta*, **B55**, 893–906.

Stafilov T., Zendelovska D., 2002: Determination of trace elements in iron minerals by atomic absorption spectrometry, *Turk. J. Chem.*, **26**, 271–280.

Suzuki S., Hirai S., 1995: Determination of trace elements in high grade pure iron and iron ore certified reference materials by instrumental NAA, *Bunseki Kagaku*, **44**, 209–215.

Taseska M., Stafilov T., Makreski P., Jaćimović R., Stibilj V., Jovanovski G., 2006: Liquid-liquid extraction and determination of trace elements in iron minerals by atomic absorption spectrometry, *Geologica Macedonica*, **20**, 33–38.

Tomura K., Tomuro H., 1999: Determination of trace manganese in high-purity iron by instrumental neutron activation analysis using a thermal column, *J. Radioanal. Nucl. Chem.*, **242**, 147–153.

Tomuro H., Tomura K., 2002: Neutron activation analysis of manganese in Japanese iron reference standard materials, with large amounts of manganese, *J. Radioanal. Nucl. Chem.*, **254**, 241–248.

User's Manual Kayzero for Windows, Version 2, 2005: *For reactor neutron activation analysis (NAA) using the k_0 standardization method*, Software developed by DSM Research, Geleen (NL), developed at the INW-RUG, Gent (B) and the AEKI, Budapest (H).

Viets J. G., O'Leary M. R., Clark R. J., 1984: Determination of arsenic, antimony, bismuth, cadmium, copper, lead, molybdenum, silver and zinc in geological materials by atomic-absorption spectrometry, *Analyst*, **109**, 1589–1592.

Zendelovska D., Stafilov T., 2001: Extraction separation and electrothermal atomic absorption spectrometric determination of thallium in some sulfide minerals, *Anal. Sci.*, **17**, 425–428.

Р е з и м е

ОПРЕДЕЛУВАЊЕ НА ЕЛЕМЕНТИ ВО ТРАГИ ВО ХЕМАТИТЕН РЕФЕРЕНТЕН МАТЕРИЈАЛ JSS-804-1 СО ПРИМЕНА НА k_0-INAA

Милена Тасеска[1], Петре Макрески[1], Векослава Стибиљ[2], Радојко Јаќимовиќ[2], Трајче Стафилов[1]

[1]*Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“,*
п. фах 162, МК-1001 Скопје, Република Македонија,
[2]*Институт Јожеф Штефан,*
п. фах 3000, 1001 Љубљана, Словенија
trajcest@iunona.pmf.ukim.edu.mk

Клучни зборови: k_0-INAA; k_0-RNAA; елементи во траги; референтен материјал; хематит

Извршено е определување на различни елементи во траги во хематитен железен референтен материјал (JSS-804-1) со примена на k_0-инструменталната неутронска активациона анализа (k_0-INAA). За да се избегне влијанието на железото како матричен елемент, воведен е метод за негово сепарирање. Имено, применета е течно-течната екстракција со диизопропилетер (DIPE) во раствор од хлороводородна киселина и потоа определување на елементите во траги во водната фаза. k_0-INAA е применета за определување на содржината на испитуваните елементи, при што има можност за следење на дистрибуцијата на 39 елементи (со кратко и долго полувреме на распаѓање на радионуклидите) во испитуваниот референтен материјал. Важна предност на предложениот метод е можноста за определување на содржината на повеќе елементи во траги по отстранувањето на железото. Освен тоа, елиминацијата на матричниот елемент доведува до намалување на границите на детекција за некои елементи во траги споредени со соодветните вредности добиени со k_0-INAA и со сертифицираните вредности за некои елементи.

CONTAMINATION AND PROTECTION OF GROUND WATERS IN THE ALLUVIAL SEDIMENTS OF THE BREGALNICA RIVER IN THE DELČEVO REGION, DEPENDING ON THEIR HYDROGEOLOGICAL CHARACTERISTICS

Vojo Mirčovski[1], Orce Spasovski[1], Vlado Mirčovski[2]

[1]*University "Goce Delčev", Faculty of Natural and Technical Sciences,*
ul. Goce Delčev 89, MK 2000 Štip , Republic of Macedonia
[2]*Sajbie Demir 1/13 , MK 2000 Štip, Republic of Macedonia*
vojo.mircovski@ugd.edu.mk

A b s t r a c t: The alluvial sediments in the Delčevo region are a two layer porous environment built of different granulometric and filtration characteristics. The lower layer is a coarse porous water-bearing environment present as a gravel sandy series (K = 96 – 276 m/day) and finer-grained granulometric sands with clay interlayers the filtration coefficient being $K = 1.73 \cdot 10^{-2} – 17.28$ m/day, underlying a layer of rather weaker filtration characteristics made up of sandy clays ($K = 2.16 \cdot 10^{-3}$ m/day), and dusty sands the filtration coefficient being $K = 3.15 \cdot 10^{-2}$ m/day. The lithological-hydrogeological characteristics of the cover sediments do not provide sufficient protection of ground waters against contamination of the Bregalnica alluvion in the Delčevo region and pertain to the waters endangered from contamination.

Key words: ground waters; contamination; protection; cover sediments; alluvial sediments; Bregalnica; Delčevo

INTRODUCTION

The issue of environmental pollution, particularly surface and ground waters has been subject matter of concern over the past decades as a result of industrial development and the use of chemical in agriculture.

The alluvial sediments of the Bragalnica River in the Delčevo region are widespread occurring in an elongated belt from Trabotivište to Oči Pale, south of Delčevo on both sides of the river as river terraces. The sediments contain significant amounts of ground waters that are used for water supply of a number of industrial facilities or houses from excavation wells. Present day life style results in anthropogenic pollution.

GEOLOGICAL COMPOSITION OF THE WIDER AREA

The Delčevo area is composed of Cambrian, Paleozoic, Triassic, Paleogene, Neogene and Quaternary rocks (Ковачевиќ et al., 1973).

The oldest rocks are the Cambrian amphibole gabbros occurring as large or small masses with sharp margins towards the Paleozoic granites and greenschists.

The Paleozoic rocks are present as graphite-quartz schists phyllites and quartz-sericite schists, granodiorites, quartzdiorites, schistose biotite coarse-grained granites (occupying a large area of the Delčevo area) as well as Permian grey clayey sandstones.

The Triassic rocks are present as sandstones, sandy clays and conglomerates, layered and milonitized limestones occurring in a small area.

The Paleogene is present as Eocene conglomerates, sandstones, slates, marls and quartzlatite volcanic intrusions.

The Neogene is present as Pliocene sediments as a clay facies, loams and sands that comprise the

lower parts of the Pliocene as well as a gravel and sand facies comprising the upper parts.

The youngest rocks are those of the Quaternary present as proluvial and alluvial sediments extending mostly along the Bregalnica River.

HYDROGEOLOGICAL CHARACTERISTICS OF THE WIDER AREA

The structural type of porosity in the wider surrounding in Delčevo made it possible to distinguish

Boundary type of aquifer,

Fracture type of aquifer,

Karst type of aquifers, and

Conditionally waterless terrains.

A characteristic hydrogeological cross-section for the area under investigations is shown in Fig. 1.
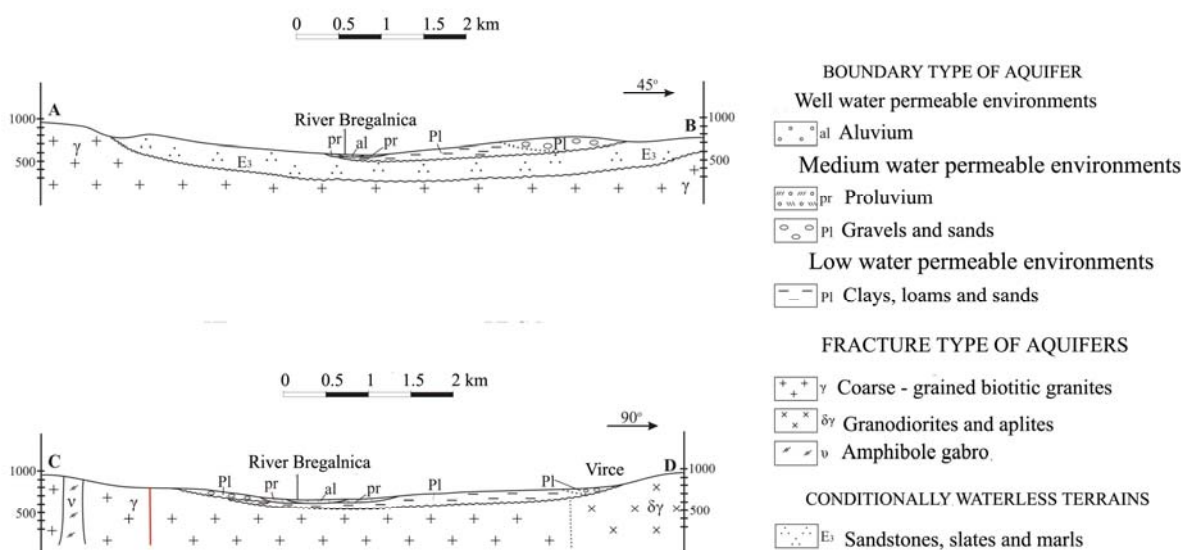

Fig. 1. Hydrogeological cross-section of the area under investigations

Boundary type of aquifers occurs in alluvial and proluvial sediments and in the Pliocene gravels, sands, clays and loams.

Based on water permeability boundary type of aquifers have been divided into

– *well water permeable environments,*

– *medium water permeable environments*, and

– *low water permeable environments*.

Well water permeable environments are made up of alluvial sediments located close to the Bregalnica River and the smaller river flows in the region.

Medium water permeable environments occupy a large area in the right side of the Bregalnica River. They are present as Pliocene sands, gravels and proluvial sediments.

Low water permeable environments are situated in the right side of the Bregalnica present as Pliocene, clays, loams and sands.

The fracture type of aquifers formed in the hard rock masses as quartzlatites, sandstones, sandy clays and conglomerates, grey clayey sandstones, schistose biotite coarse-grained granites, quartzdiorites, grandiorites, aplites, phyllites, quartz-sericite schists, graphite-quartz schists and amphibole gabbros.

The karst type of aquifers occurs in a small area in the Triassic limestones that are characterized with cavernous porosity.

Conditionally waterless terrains are made up of Eocene conglomerates, sandstones, slates and marls

STRUCTURAL-LITHOLOGICAL CHARACTERISTICS OF THE ALLUVIAL SEDIMENTS

The alluvial sediments in the region of Delčevo are located mostly along the valley of the Bregalnica, and less along other river flows. Along the Bregalnica they occur as an elongated belt on a 16 km long strike from Trabotivište to the Oči Pale locality, south of Delčevo. They occur as 100 to 600 meters wide river terraces on both sides of the river.

In the area, the alluvial sediments are a distinct geological and hydrogeological unit separated from the Pliocene and Eocene sediments in which significant amounts of ground waters have been accumulated as boundary type of aquifers.

The structural-lithological characteristics of the alluvial sediments in the Delčevo region were discovered with the hydrogeological investigations carried out for the water supply (Максимов and Ивановски, 2004**)** and the uncovered cross-sections close to the Bregalnica.

Hydrogeological investigations discovered the structural location of the alluvial sediments relative to the basal Pliocene sediments as well as their facial lithological changes.

A characteristic geological-hydrogeological cross-section revealed during drilling a drill-hole is shown in Fig. 2. The drill-hole is in the first river terrace of the Bregalnica, 100 meters from the river-bed close to the leather factory in the industrial sector of the town.

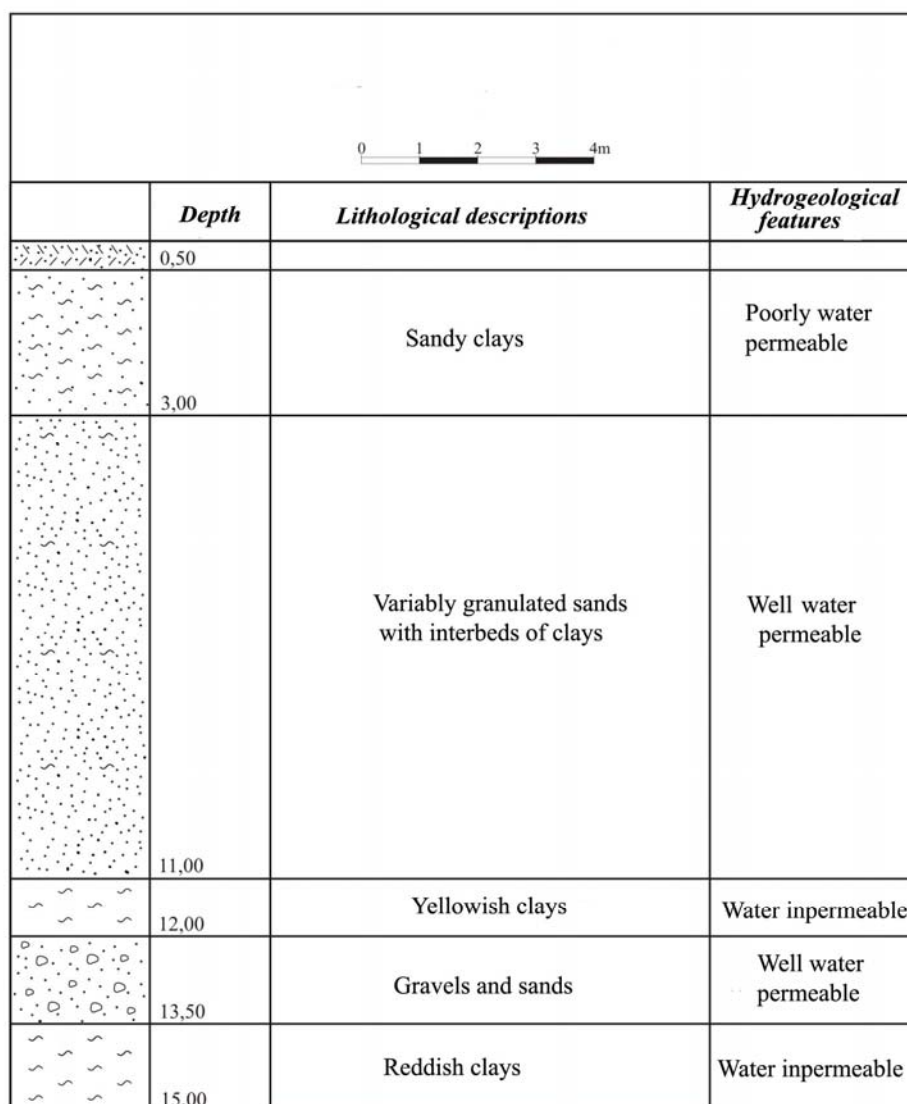|	Depth	Lithological descriptions	Hydrogeological features
	0,50		
	3,00	Sandy clays	Poorly water permeable
	11,00	Variably granulated sands with interbeds of clays	Well water permeable
	12,00	Yellowish clays	Water inpermeable
	13,50	Gravels and sands	Well water permeable
	15,00	Reddish clays	Water inpermeable

Fig. 2. Geological-hydrogeological cross-section of a drill-hole drilled in alluvial sediments

Based on this drill-hole the base of the alluvial sediments is 13.5 meters in depth. Larger porous gravels and sands have accumulated above the Pliocene clays. Clayey sediments alternate finer-grained variably granulated sands with interbeds of clays, sandy clays towards the surface. In the end the cross-section ends in dust-sandy sediments.

The lithological-hydrogeological characteristics of the alluvial sediments can be seen from the cross-sections near the Bregalnica.

Fig. 3 shows a cross-section of alluvial sediments close to the Golak dairy farm 4 km north-west of Delčevo. The cross-section is some 20 meters from the Bregalnica river-bed, formed with gravel and sand diggings. The cross-section is about 2.5 meters deep, the level of the ground water being 2 meters in depth. Two lithological units can clearly be distinguished in the cross-section: a cover made up of 40 to 50 cm dusty sands overlying alluvial sediments made up of gravel and sand whose thickness has not been determined and can not be assessed.
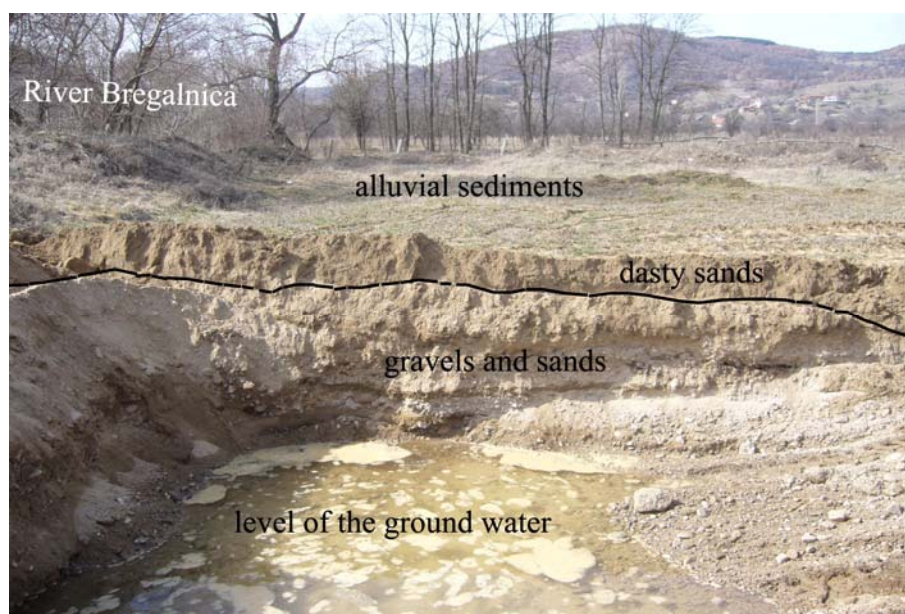

Fig. 3. Cross-section of alluvial sediments near the Bregalnica River, close to the Golak dairy farm 4 km north-west from Delčevo

A well discovered cross-section of alluvial sediments can be seen 6 km south-east from Delčevo, in close proximity to the Bregalnica near the pig farm (Fig. 4). In both cross-sections alluvial sediments and the cover layer can be seen clearly. The cover layer is 40 to 50 cm thick being made up of dusty sands. Right below the cover layer are the alluvial sediments present as coarse- to medium-size gravels and sands. The height of the alluvial terrace in this part amounts from 2.5 to 3 meters above the Bregalnica River level.

A well has been drilled in the Bregalnica River alluvion for the water supply of the Granite Construction Company Base when entering Delčevo from Berovo. An 8 to 9 meters thick alluvial water-bearing layer has been determined made up of gravels and sands (Ѓузелковски, 1997).

Based on the data presented so far it can be said that the alluvial sediments in the Delčevo region transgressively and discordantly overlie the Pliocene sediments made up of clays, loams and sands.

A gravel sandy series and a series of with sands with clay interbeds can be distinguished with accumulated over sediments made up of sandy clays and dusty sands.

The thickness of alluvial sediments varies from 5 to 15 meters being the thickest close to the Bregalnica, getting thinner going further from the river.

Investigations carried out so far have determined that the thickness of the gravel-sandy series amounts to 9 meters, and that of the cover sediments from 0.4 to 4 meters.

The thickness of the cover sediments is smallest close to the river amounting from 0.4 to 0.5 meters and increases going further from the river-bed on the left and the right sides being 4 meters thick in some parts.
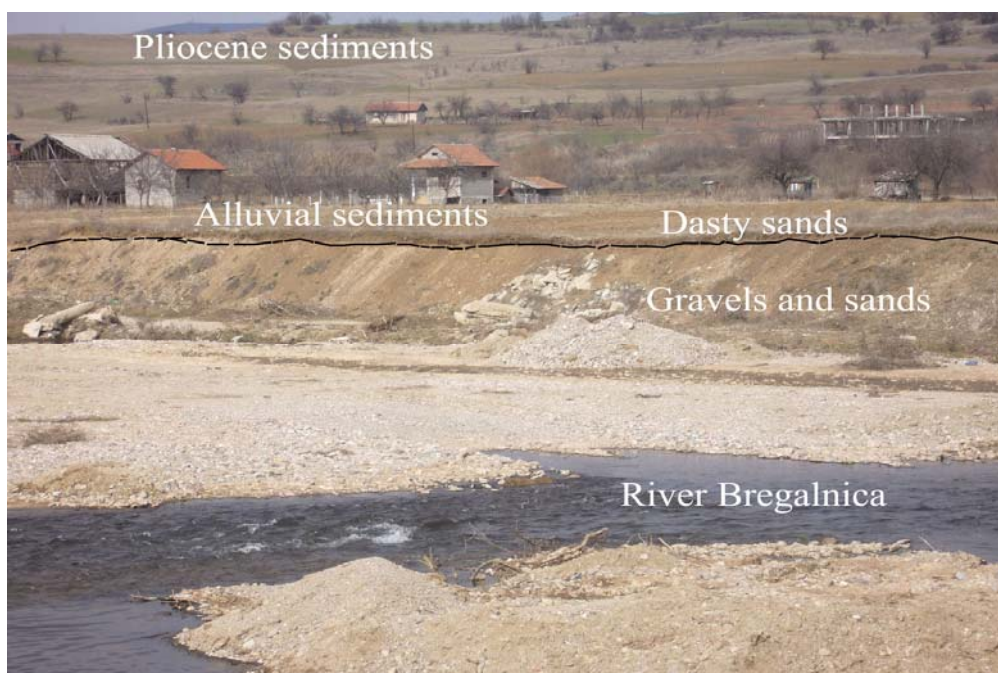
Fig. 4. Cross-section of alluvial sediments near the Bregalnica River, close to the pig farm 6 km south-east of Delčevo

GRANULOMETRIC COMPOSITION AND FILTRATION FEATURES OF THE LITHOLOGICAL MEMBERS

The base of the alluvial sediments is built of a series of gravels and sands and various granule sands with clay interbeds of supercapilar intergranular porosity creating a coarse porous environment. This coarse porous environment transgressively and discordantly is overlain by settled sediments of sandy clays and dusty sands of fine porosity. It is characteristic for both zones that they are horizontally spread in a large area with identical lithological and granulometric composition, whereas vertically they largely vary as is the case with the 0.4 to 4 meters thick cover sediments.

The filtration features of the cover sediments that are important for the protection of ground waters against contamination have been determined based on granulometric analyses. Samples were collected from uncovered cross sections shown in Figs 3 and 4 according to furrow method up to 0.5 meters in depth. Determination of filtration coefficient (K) was done according to USBR and Slichter methods in the Institute for Civil Engineering, Skopje. The results obtained have been given in Table 1.

Data obtained by both methods made it possible to calculate the mean filtration coefficient of cover sediments made up of dusty sands that amounts to $K = 3.15 \cdot 10^{-2}$ m/day.

From the results obtained it can be said that the cover sediments are of low to very low permeability.

The thickness of cover sediments that amounts to 0.4 to 0.5 meters for the areas near the river banks helped calculate the transmission coefficient or water permeability of the cover. If the mean thickness of the cover layer at the river bank amounts to 0.45 meters, transmissivity coefficient will amount to $T = 1.42 \cdot 10^{-2}$ m²/day.

T a b l e 1

Values of filtration coefficient (K) according to the USBR and Slichter methods

	d_{10} (mm)	d_{20} (mm)	USBR (m/day)	Slichter (m/day)	Mean value for K (m/day)
Sample 1	0.003	0.008	$4.12 \cdot 10^{-3}$	$6.38 \cdot 10^{-4}$	$2.38 \cdot 10^{-3}$
Sample 2	0.008	0.018	$3.14 \cdot 10^{-2}$	$5.46 \cdot 10^{-4}$	$1.60 \cdot 10^{-2}$
Sample 3	0.007	0.02	$3.54 \cdot 10^{-2}$	$4.76 \cdot 10^{-3}$	$2.01 \cdot 10^{-2}$
Sample 4	0.012	0.04	$1.87 \cdot 10^{-1}$	$1.41 \cdot 10^{-3}$	$9.42 \cdot 10^{-2}$
Sample 5	0.009	0.02	$4.21 \cdot 10^{-2}$	$7.84 \cdot 10^{-3}$	$2.48 \cdot 10^{-2}$
					$3.15 \cdot 10^{-2}$

The filtration coefficient for the water-bearing gravel sandy series was determined based on data obtained with well testing drilled for water supply. According to this data the filtration coefficient is in the span of $K = 96 - 276$ m/day. The filtration coefficient for the finer-grained variably granulated sands with interbeds of clays according to Domenico & Schwarts (1990) is $K = 1.73 \cdot 10^{-2} - 17.28$ m/day.

Based on studies carried out it can be said that the alluvial sediments in the Delčevo region are two layer porous environment built of two layers of different granulometric and filtration characteristics.

The lower part is a coarse porous water-bearing environment with good filtration features overlain by a cover layer of significantly lower filtration features.

In order to understand the level of protection against contamination of the cover sediments of ground waters accumulated in the alluvial sediments it is necessary to assess the percolating speed of possible contaminants from the surface through the cover layer to the gravel sandy water-bearing layer as well as the time necessary for contamination through the cover layer to reach ground waters.

Since two cover layers have been found with different lithological composition and filtration features, the above parameters will be calculated for each layer individually.

Percolating speed through cover sediments can be determined by the equation

$$V_z = -\frac{K}{n_{ef}} i$$

V_z – percolating speed (m/day),
K – vertical filtration coefficient (m/day),
i – hydraulic gradient,
n_{ef} – effective porosity.

The vertical movement of liquid particles can, in the least possible case, approximate with the flow through empty cover semi porous layer of hydraulic gradient 1. According to the formula above the percolating speed through the cover layer made up of dusty sands amounts to $V_z = 7.87 \cdot 10^{-2}$ m/day; $K = 3.15 \cdot 10^{-2}$ m/day; $n_{ef} = 0.4$ mean value of fine-grained sand and dust according to Domenico & Schwartz (1998).

Percolating time through the cover layer to the water-bearing gravels and sands can be calculated by the formula $t = \dfrac{m}{V_z}$ amounting to 5.72 days,

t – time in days,
m – thickness of low permeable cover layer = 0.45 meters,
V_z – percolating speed = $7.87 \cdot 10^{-2}$ m/day.

Possible contamination will pass through the cover layer in 5.72 days which indicates that the dusty sands of the cover sediments near the river banks provide litle protection to the ground waters accumulated in the water-bearing layer.

The following results have been obtained for the sandy clays of the cover sediments above the water-bearing layers made up of sands and clay interbeds, gravels and sands in the parts far from the river beds: filtration coefficient according to Domenico & Schwartz (1990). $K = 2.16 \cdot 10^{-3}$ m/day; coefficient of effective porosity according to Domenico & Schwartz (1998), $n_{ef} = 0.4$.

The value for percolating speed obtained amounts to $V_z = 5.4 \cdot 10^{-3}$ m/day. In 4 meter thick sediments contamination will pass in a time period of 185 days.

This fact points out that the cover sediments are a better protection relative to ground waters near the river banks.

GROUND WATERS FORMING IN THE ALLUVIAL SEDIMENTS

The geological and hydrogeological structural location of the alluvial sediments in the Delčevo area made possible the accumulation of significant amounts of ground waters. Ground waters have accumulated in a boundary type of water bearers in the alluvial layers made up of gravels and sands with clay interbeds. The water-bearing layer pertains to the open to semiclosed water-bearing layers or hydrogeological structures.

Recharge of the water-bearer with water is done mostly by the Bregalnica River waters, water falls, and waters from water flows in higher hypsometric level.

The general strike of ground water flow is towards and parallel to the Bregalnica River bed.

CONTAMINANTS OF GROUND WATERS IN THE ALLUVIAL SEDIMENTS
OF THE BREGALNICA RIVER

The biggest active and possible contaminants of ground waters in the alluvial sediments of the Bregalnica in the Delčevo area are: the waters of the river, agricultural cultivable areas, animal farms, industrial facilities, landfills, waste waters discharged from settlements, petrol stations and oils depots, regional and local roads and cemeteries. The location of contaminants is given in the map in Fig. 5.

The map clearly shows that most of the contaminants are near the Bregalnica River, on the alluvial terraces or in their immediate surrounding.
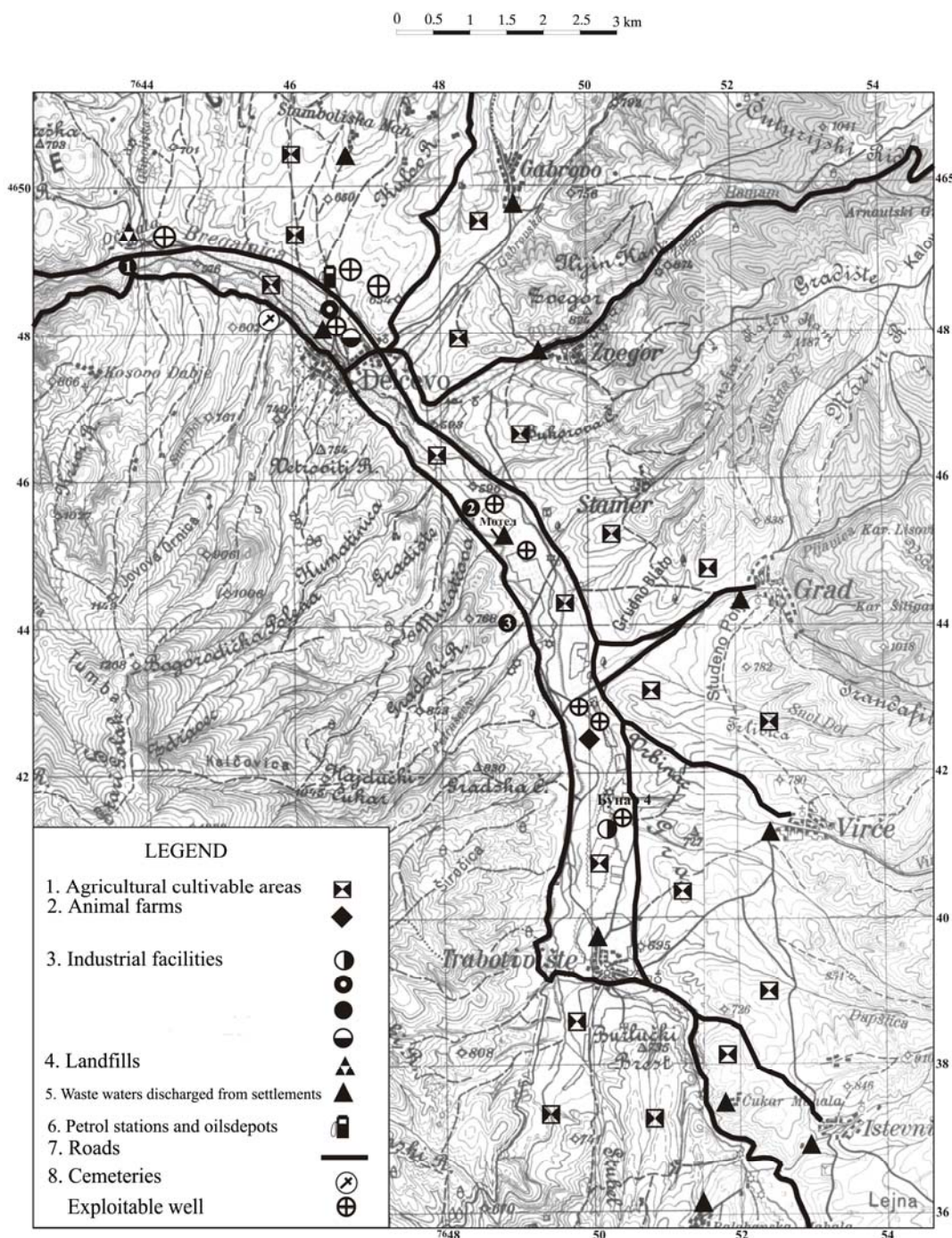

Fig. 5. Map of surface and ground waters contaminants of the wider vicinity of Delčevo

Waste from all contaminants, without any filtering or purification, directly or via discharge pipes flow into the Bregalnica River waters, in some cases into underground of the geological environment and further on into ground waters.

Based on the hydrogeological characteristics of the alluvial sediments and the location of the bigger contaminants it can be said that the ground waters in the alluvial sediments in the Delčevo area are ground waters endangered from contamination. This means that the production of contaminating materials in the area endanger ground waters in the alluvial sediments.

MEASURES FOR THE PROTECTION OF GROUND WATERS IN ALLUVIAL SEDIMENTS

The protection of the natural quality of ground waters in the alluvial sediments along the Bregalnica River in the Delčevo area call for undertaking the activities as follows:

– waste waters discharged from the town of Delčevo and the bigger settlements must join a sewer system and purified before discharge into the Bregalnica,

– waste waters from industrial facilities and animal farms must join a sewer system and be purified before discharge into the river,

– the landfill and industrial waste from Delčevo and the bigger settlements must be dumped in the right constructed waste dump,

– to construct protection zones round the structures that supply drinking water for the population (well, water captures etc.),

– to compile a detailed inventory of pollutants and their impact on the environment,

– in the future, the vulnerability map of ground waters must be taken in consideration when constructing facilities that may endanger the environment. The map is part of the hydrogeological map of the Republic of Macedonia the scale 1 : 100 000,

– to compile a pisiometric net and measure points for the monitoring of surface and ground waters quality.

CONCLUSION

Water-bearing layers made up of gravel with sand and sands with clay interbeds in the basement with cover sediments accumulated above them (made up of sandy clays and dusty sands) have been distinguished in the alluvial sediments along the Bregalnica River.

The thickness and filtration characteristics of the cover sediments do not provide sufficient protection to ground waters accumulated in them against contamination coming from the area. In that regard, it can be said that the ground waters in the alluvial sediments in the Delčevo area belong to the endangered ground waters by contamination.

In order to protect the natural quality of ground waters it is necessary to undertake adequate preventive measures.

REFERENCES

Domenico, P. A. & Schwartz, F. W., 1990: *Physical and Chemical Hydrogeology*. 1-824, John Wiley & Sons.

Domenico, P. A. & Schwartz, F. W. 1998: *Physical and Chemical Hydrogeology*. 1-506, John Wiley & Sons.

Ковачевиќ, М., Петковски, П., Темкова, В., 1973: *Толкувач за основната геолошка карта 1:100 000 за листот Делчево*. Геолошки завод, Скопје.

Максимов, Д., Ивановски, Л., 2004: *Технички извештај за резултатите добиени од пробно експлоатациониот бунар ПЕКБ-1, изработен за ДППУ Матис – Делчево*. КОИНГ ДОО, Штип.

Ѓузелковски, Д., 1997: *Подземните води (издан) за решавање на водоснабдувањето во Р. Македонија и нивната заштита*. Геохидропроект, Скопје. Геолошки завод, Скопје.

Р е з и м е

ЗАГАДУВАЊЕ И ЗАШТИТА НА ПОДЗЕМНИТЕ ВОДИ ВО АЛУВИЈАЛНИТЕ СЕДИМЕНТИ НА РЕКАТА БРЕГАЛНИЦА ВО РЕГИОНОТ НА ДЕЛЧЕВО, ВО ЗАВИСНОСТ ОД НИВНИТЕ ХИДРОГЕОЛОШКИ КАРАКТЕРИСТИКИ

Војо Мирчовски[1] , Орце Спасовски[1], Владо Мирчовски[2]

[1]*Универзитет „Гоце Делчев“, Факултет за природни и технички науки,*
Гоце Делчев 89, МК-2000 Штип, Република Македонија
[2]*Сајбие Демир 1/13, МК-2000 Штип, Република Македонија*
vojo.mircovski@ugd.edu.mk

Клучни зборови: подземни воид; загадување; заштита; покривни седименти; алувијални седименти; Брегалница; Делчево

Алувијалните седименти од регионот на Делчево претставуваат двослојна порозна средина изградена од два слоја со различни гранулометриски и филтрациони карактеристики.

Долниот слој претставува грубо порозна водоносна средина претставена со чакалесто песоклива серија (K = 96 – 276 m/ден) и со поситно зрнести разно гранулирани песоци со прослојки од глини со коефициент на филтрација K = 1,73·10^{-2} – 17,28 m/ден. Над него се наоѓа покривен слој со значително послаби филтрациони карактеристики, изграден од песокливи глини (K = 2,16·10^{-3} m/ден), и правливи песоци со коефициент на филтрација K = 3,15·10^{-2} m/ден.

Литолошко-хидрогеолошките карактеристики на покривните седименти не овозможуваат доволна заштита од загадување од површината на теренот на подземните води од алувионот на Брегалница во регионот на Делчево и затоа тие спаѓаат во групата води загрозени од загадување.

INSTRUCTIONS TO AUTHORS

The *Geologica Macedonica* is an official publication of the "Goce Delčev" University, Faculty of Natural and Technical Sciences, Štip, Republic of Macedonia. It is published a year. The journal publishes **original scientific papers, short communications, reviews, professional** and **educational papers** from all fields of Mining, Geology, Petrology, Mineralogy and Geochemistry....

The journal also publishes, continuously or occasionally, the bibliographies of the members of the Faculty, book reviews, reports on meetings, information on future meetings, important events and dates, and various heading which contribute to the development of the corresponding scientific field.

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.

SUBMISSION OF MANUSCRIPTS

The authors bear the sole responsibility for the content of the contributions. It is assumed that by submitting their paper the authors have not violated any internal rules or regulations of their institutions related to the content of the contributions. Submission of a paper implies that it has not been published previously, that it is not under consideration for publication elsewhere, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the Publisher.

For the first submission, please send two hard copies of the manuscript and an identical electronic copy of the manuscript on a disc (in MS Word) to the Editor-in-Chief of Geologica Macedonica, the "Goce Delčev" University, Faculty of Natural and Technical Sciences, Goce Delčev 89, MK 2000 Štip, Republic of Macedonia. Electronic version of the manuscript can be also sent by email at todor.serafimovski@ugd.edu.mk

A cover letter must accompany every new submission. It should contain full names of all authors and their affiliation, the manuscript title and the name and contact information for the corresponding author. Please provide a mailing address, email address, and phone and fax numbers. Authors are requested to submit, with the manuscript, the names and full contact details (including email addresses) of 3 potential referees.

PREPARATION OF MANUSCRIPTS

Prepare the entire manuscript in double-space typing, on numbered pages of A4 format with margins of 2.5 cm on each side. Do not use footnotes.

The papers should be written in the shortest possible way and without unnecessary repetition. The original scientific papers, short communications and reviews should be written in English. Abstract and key words in Macedonian, must accompany each manuscript.

Manuscript should contain: title, authors names and addresses, abstract, key words, introduction, experimental or theoretical background, results and discussion, acknowledgement (if desired) and references.

Title. It should be brief and informative but should define the subject of the manuscript. It should include most of the key words.

Authorship. List the first and last name of each author. Omit professional and official titles. Give the complete mailing address of each author. For the corresponding author include an email address and a phone and fax numbers. The name of the corresponding author should carry an asterisk.

Abstract. Each manuscript should be pro-

vided with an abstract of about 100–150 words. It should give the aim of the research, methods or procedures, significant results and conclusions. Define any abbreviations used in the abstract.

Key words. Up to 5 key words or phrases should be given to facilitate indexing and online searching.

Introduction. The most important previous results related to the problem in hand should be reviewed avoiding a detailed literature survey, and the aim and importance of the research should be clearly stated.

Experimental section. This section should contain a description of the materials used and methods employed in form which makes the results reproducible, but without detailed description of already known methods.

Manuscripts that are related to theoretical studies, instead of experimental section should contain a subheading **theoretical background** where the necessary details for verifying the results obtained should be stated.

Results and discussion. The authors should discuss their findings, postulate explanations for the data, elucidate models and compare their results with those of other works. Irrelevant comparisons and speculations unsupported by the new information presented in the manuscript should be avoided. The conclusions should be not given separately but included in this section.

Tables. They should be given with a suitable caption and should be numbered consecutively with Arabic numerals. Footnotes to tables should be typed below the table and should be referred to by superscript lowercase letter. Each table should be typed on a separate sheet. The correct position of the tables should be marked on the manuscript.

Figures. Figures (photographs, diagrams and schemes) should be numbered consecutively with Arabic numerals in order to which they referred. They should accompany the manuscript but should not be imbedded in the text. Each figure should be clearly marked with the figure number and the first author's name. All figures should have captions that should be supplied on a separate sheet. Correct position of the figures should be marked on the manuscript. The size of the symbols for the physical quantities and units as well as the size of the numbers and letters used in the reduced figures should be comparable with the size of the letters in the main text of the paper. Each figure or group of figures should be planned to fit, after appropriate

reduction, into the area of either one or two columns of text. The maximum finished size of a one column illustration is 8.0 cm and that of a two column illustration is 17.0 cm width. Make sure you use uniform lettering and sizing of your original artwork. All figures should be printed on a high quality graphics plotter. Figures should be also sent in electronic form as TIFF or JPG files with minimum 300 dpi or higher resolution.

Color illustrations in print can be included only at the author's expense.

Units. The SI (Systeme Internationale d'Unites) for quantities and units should be used throughout the whole text. If nomenclature is specialized, nomenclature section should be included at the end of the manuscript, giving definitions and dimensions for all terms.

The **names of chemical substances** should be in accordance with the IUPAC recommendations and rules or *Chemical Abstract* practice.

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

REFERENCES

Literature references should be numbered and listed in order of citation in the text. They should be selective rather than extensive with the exemption to review articles. Avoid references to works that have not been peered-reviewed. Citation of a reference as "in press" implies that it has been accepted for publication.

The surname of one or two authors may be given in the text, whereas in case of more than two authors they should be quoted as, for example, Julg *et al.* [1]. References should be cited as follows:

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 Rzanovo–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.

For the web references, as a minimum the full URL should be given. Any further information, if available (author names, dates, reference to a source publication, etc.) should also be given.

EDITORIAL PROCESS

Receipt of manuscripts. Receipt of each manuscript is acknowledged by email to the corresponding author within three working days. The manuscript is read and examined for conformity to these Instructions to Authors. Failure to meet the criteria outlined may result in return of the manuscript for correction before evaluation.

Peer review/evaluation. Papers received by the Editorial Board are sent to two referees (one in the case of professional and educational papers). Although authors are invited to suggest reviewers who are competent to examine their manuscript, the Editorial Board is not limited to such suggestions. Identities of the reviewers will not be released to the authors. The review process is expected to be complete within 3 months, but conflicting recommendations and other unpredictable events may cause some delay.

The comments and recommendations of the referees and the Editorial Board are sent to the authors for further action. The authors are allowed 30 days to undertake revisions and return the corrected text to the Editorial Board. The final decision on acceptance or rejection is made by the Editorial Board. This decision, together with any relevant reasons, will be send to the corresponding author.

Publication process. The accepted manuscript is checked for conformation to the Instructions to Authors and to ensure that all necessary paperwork is present. Any areas that are identified as problematic will be addressed by the Editorial Board in consultation with the corresponding author. The papers will be prepared for publication by a professional copy editor responsible for ensuring that the final printed work is consistent in form and style.

Galley proofs. A galley proof is sent to the corresponding author. It should be checked very carefully and must be returned within 2 days of receipt. The proof stage is not the time to make extensive corrections, additions, or deletions.

Reprints. The corresponding author will receive, free of charge, 20 reprints of the paper published in the *Geologica Macedonica.* Additionally he will receive a complementary copy of the journal.