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Drilling rig, open pit mine "Buchim",
Radoviš, Republic of Macedonia

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

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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 $0.15 \div 0.22$ % 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 $0.45 \div 1.42$ % 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, Vršnik and Chukar, which are occupying an area of approximately 10 km². The geological setting of the immediate surroundings of the deposit includes the following mem-

bers: 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).

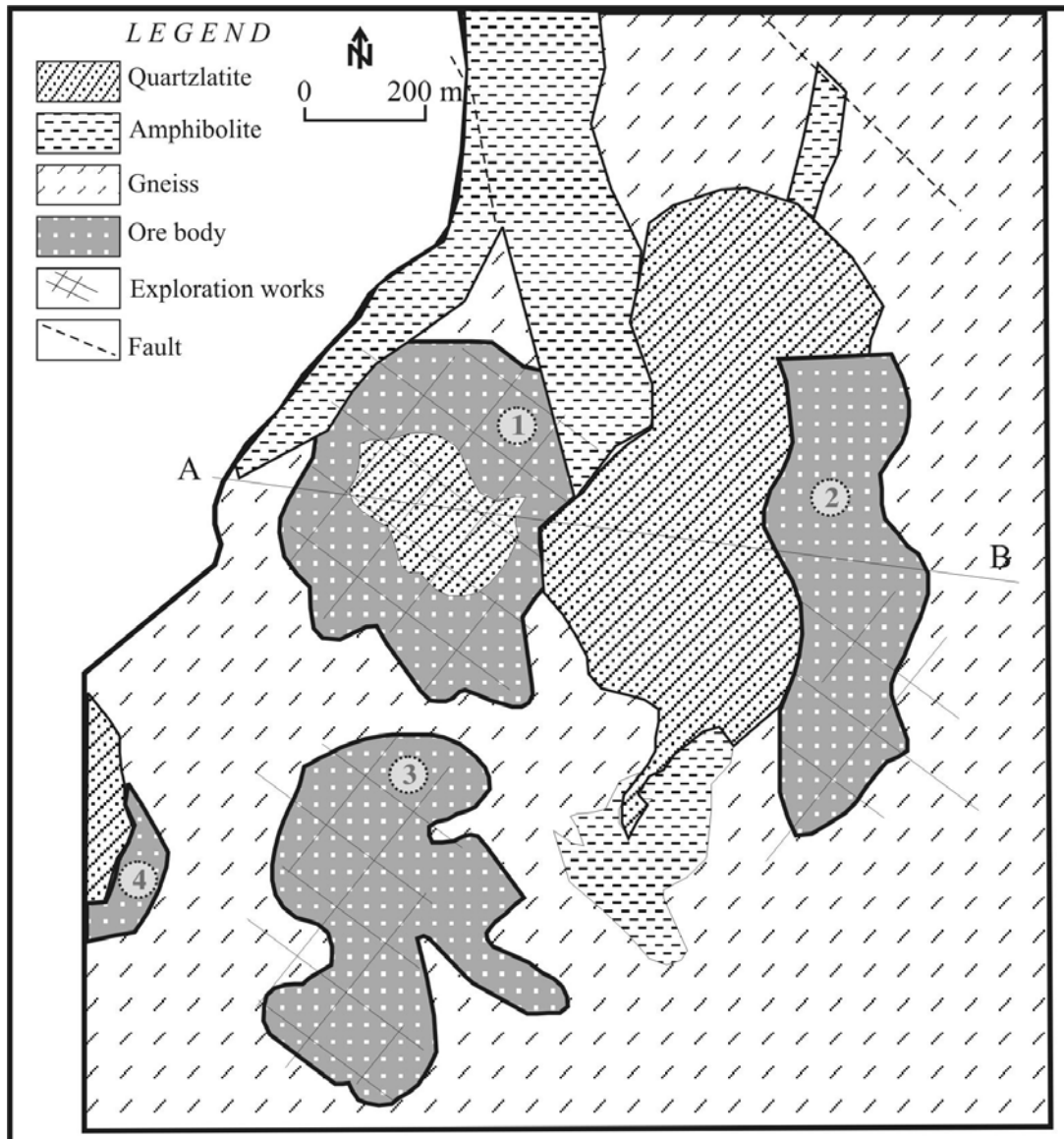


Fig. 1. Geological map of the Bučim deposit
1. Ore body Central part; 2. Ore body Vršnik; 3. Ore body Chukar; 4. Ore body Bunardzhik

MINERAL ASSOCIATIONS

Up to date systematic studies, mostly of the Central part ore body, have identified the following minerals within the Buchim deposit: pyrite, chalcocopyrite, magnetite, rutile, sphene, titanomag-

netite, 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, laticarite, 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 conjunction with its assemblage. The metamorphic stage has been characterized by relict Ti-Fe oxide assemblage in amphibolites and Fe-sulphide assemblages in gneiss. Mag-

matic 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 equipped 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 (scanning area of 8 mm²). The photographs were made in a back scattered electron mode-COMPO. The results were summarized on powerful computer connected to the SEM.

The whole rock analysis followed usual procedure. Test portion of 0,1 g is fused with LiBO₄ in a muffle furnace at 1000 °C. Obtained transparent melt is dissolved with diluted HNO₃ 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 ana-

lyzed components have shown higher concentrations (Na₂O, K₂O, TiO₂ 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 ferrohornblende 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.

Table 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 microprobe have shown interesting composition. Beside more or less standard values for K₂O, Al₂O₃ and SiO₂ were determined. Opposite to them FeO (16.06–17.62%), TiO₂ (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.

Table 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 Al₂O₃,

SiO₂ and K₂O. Increased concentrations were determined for Na₂O (1.49–2.57%), FeO (0.10–2.62%), MnO (0.07–0.16%), MgO (0.36–0.79%) and TiO₂ (0.09–0.17%). Results from eight electron microprobe analyses are given in Table 3.

Table 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 $NaAlSi_3O_8$, 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).

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).

Table 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 tectonically 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 experience 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 analyses 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 $\text{Fe}_{(0.98-1.05)} [\text{Ni}_{(0.002-0.02)}$

$\text{Co}_{(0.01-0.09)} \text{As}_{(0.002-0.004)}] \text{S}_{(1.95-1.98)}$, which is very close to the idealized one FeS_2 .

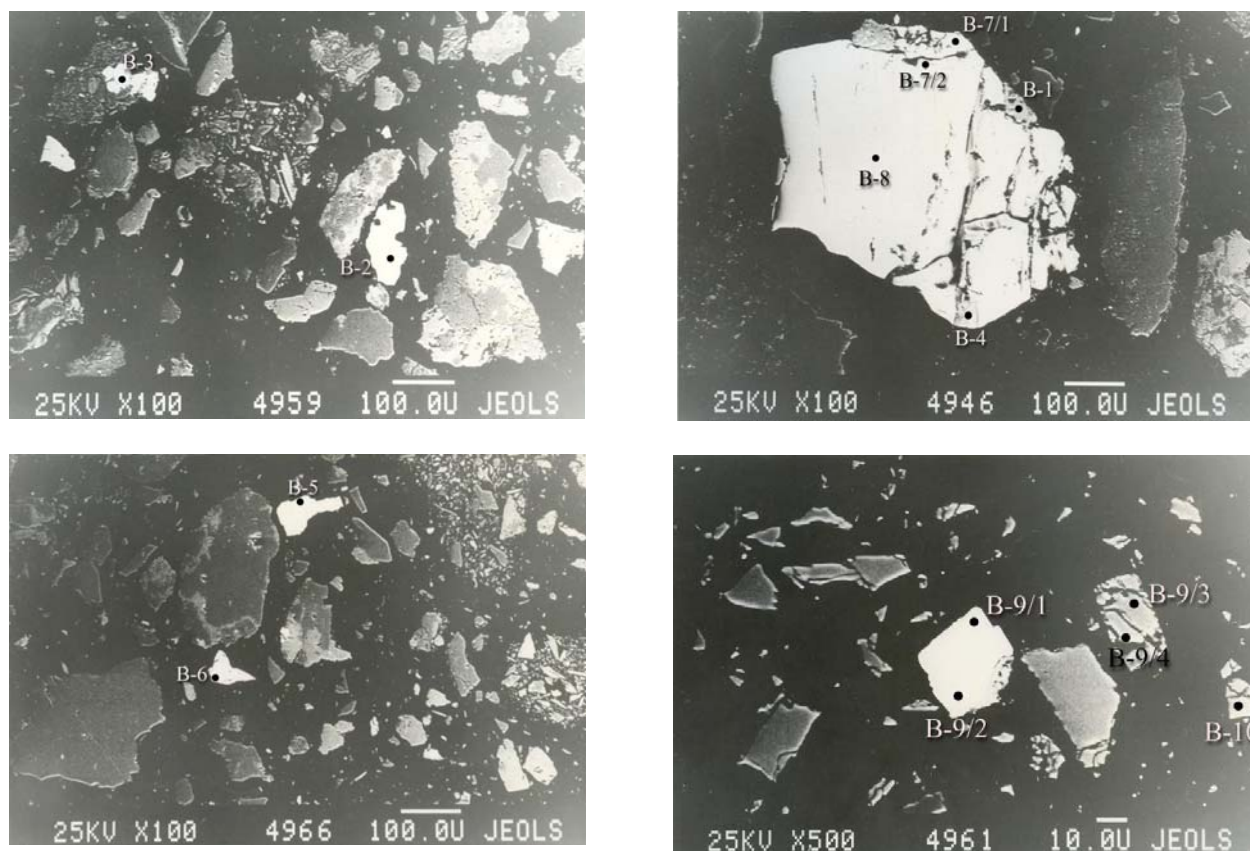


Fig. 3. Microprobe photographs of typical pyrites from the Buchim porphyry copper deposit with locations of microprobe analyses

Table 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 $\text{Cu}_{(0.99-1.06)}\text{Fe}_{(0.99-1.03)}\text{S}_{(1.91-2.02)}$, which is equal with the idealized one CuFeS_2 .

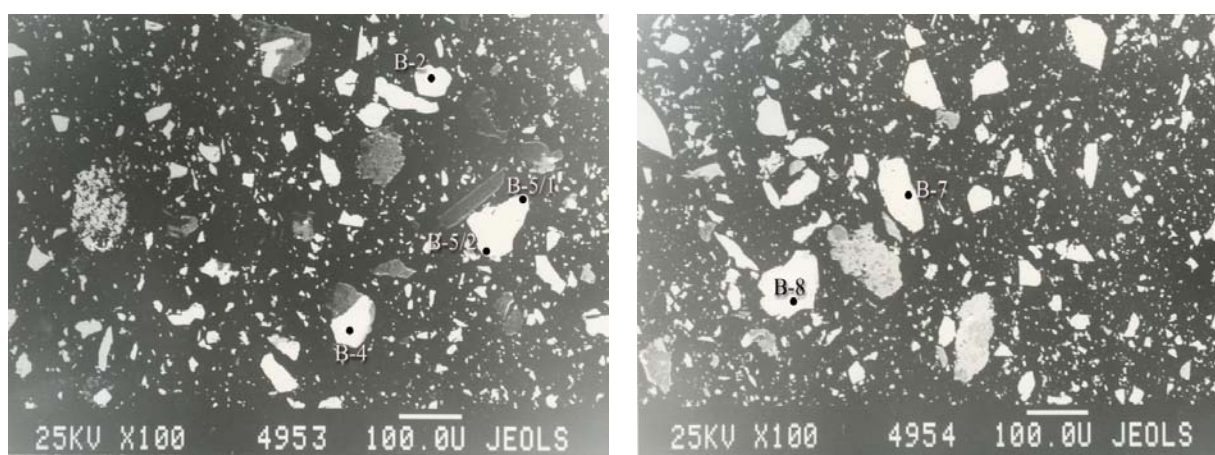


Fig. 4. Microprobe photographs of typical pyrites from the Buchim porphyry copper deposit with locations of microprobe analyses

Table 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.

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Резиме

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

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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, биотитите 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 %.