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RARE MINERAL PHASES RELATED WITH MAJOR SULPHIDE MINERALS IN THE BUČIM PORPHYRY COPPER DEPOSIT, R. MACEDONIA

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Abstract: With the latest detailed mineralogical studies with polarizing optical microscope and microprobe analysis in the Bučim porphyry copper deposit were found and determined several representative and rare mineral phases, which have been composed metals from the gold-platinum group as well as those from the Cu-Bi-Se-Te-As group. In the bismuth-selenium of rare mineral phases were confirmed bismuthinite, galenobismutite, krupkaite, friedrichite, emplectite, laitakarite and native bismuth, which represent new rare mineral phases in the Bučim porphyry copper deposit, as well as mineral phases of the Au-Pd group where clearly was confirmed presence of gold and palladium with elemental mixtures representative for these mineral phases. It should be stressed out that both types of rare mineral phases were determined in pyrite and chalcopyrite from major ore parageneses in the Bučim deposit. The bismuth-selenium mineral phases are related to the major quartz-pyrite-chalcopyrite paragenesis, while Au-Pd mineral phases are related with slightly higher temperature, oxido-sulphide parageneses such are magnetite-pyrite-chalcopyrite (Mt-Py-Cp) and pyrite-chalcopyrite (Py-Cp).

Key words: ore minerals; gold-palladium phases; rare Bi-Se mineral phases; Bučim mine

INTRODUCTION

The Bučim porphyry copper is located within the Bučim–Damjan-Borov–Dol ore region of Macedonia, which is part of the well known Lece–Chalkidiki metallogenic zone (Serafimovski, 1993), where manifestations of porphyry copper and epithermal ore are developed. On a more local scale the Bučim copper mine is located in eastern central Macedonia, 10 km west of the town of Radovis. It is the only deposit of this kind in Macedonia that is currently being exploited and up to date produced copper and significant amounts of by-product gold. The mine started production in 1980 and produced four million tonnes of ore annually with 0.25% Cu, 0.27% Au, and 1 g/t Ag. Estimated reserves are approximately 100 million tonnes of low grade Cu-Au ores with some Ag and Mo and include primary (the most important Cu-Au resources) as well as secondary (related to the zone of oxidation-cementation enrichment) and mixed types of ores. The deposit is a porphyry copper type deposit (Serafimovski et al., 1996) and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites (Čifliganec, 1993).

Basic ore paragenesis was studied by Pavičević and Rakić (1983), Čifliganec (1993), Serafimovski et al. (2006), and others. Beside the basic ore paragenesis (pyrite, chalcopyrite, magnetite, bornite, enargite, etc.), Bi-Se mineral phases and especially Au-Pd mineral phases were also determined. Petrunov et al. (2001) published preliminary microscopic and microprobe data of the occurrence of the platinum group elements (PGEs) within the Bučim porphyry copper deposit for the first time. An increased content of Pd as well as Pd-mineralization (PGM) was established in the Cu-Au ores of the deposit in Bučim, Macedonia. Thus, this is the fourth case in the territory of the Balkan Peninsula after Bor-Majdanpek, Serbia (Janković, 1990), Skouries, Greece (Tarkian et al., 1991), and Elatsite, Bulgaria (Petrunov et al., 1992) where the Cu-porphyry style of hydrothermal PGM has been found.

As an alkaline porphyry deposit, the Bučim deposit represents, beside copper, a significant gold resource for Macedonia and fits quite well into the recently reported elevated levels of PGEs, particularly Pd and Pt, described in the Cordillera of British Columbia (Copper Mountain, Galore Creek), Allard Stock, La Plana Mountains, and Copper King Mine in the USA, Skouries porphyry deposit in Greece, Elatsite in Bulgaria, and so on (Economou-Eliopoulos, 2010) and bismuth-selenium derivatives (Voudouris et al., 2013). With the latest studies, results were obtained for Au-Pd-bearing pyrite and chalcopyrite as well as Bi-Se±Au±Ag±Te minerals, which are the subject of this particular paper.

GEOLOGICAL FEATURES OF THE BUČIM PORPHYRY COPPER DEPOSIT

Geologically the Bučim deposit is located in gneiss, micaschists, and amphibolite, which make up the basement of the Serbo-Macedonian Mass (SMM). During the Neogene, tectonic and magmatic processes resulted in widespread magmatism, which at the present erosion level is represented by sub-volcanic and volcanic facies of latite and andesite in the form of dykes and necks. Detailed geological studies in the Bučim area have demonstrated the presence of subvolcanic intrusions which are of particular importance as regards the spatial distribution of the copper mineralization in the deposit.

The ore deposition is genetically connected with the intrusion of Tertiary, Oligocene-Miocene (27.5–24.5 m.y., Serafimovski, 1993, or 24.5–24.0 m.y., Barcikowski et al., 2012), subvolcanic latitic and latite-andesitic bodies within Precambrian metamorphic rocks-gneisses, micashists, and amphibolites. Primary Cu-Au mineralization occurs around the subvolcanic bodies, being most abundant amid the hosting gneisses. Four ring-shaped ore bodies (Central, Bunardžik, Vršnik, and Čukar), are located within and around the magmatic bodies (Figure 1). Three ore bodies are morphologically related to stocks, and the fourth body is presumably a fragment of a previously existing sheet-like layer of manto-type oxidized and redeposited ore (Figure 1).

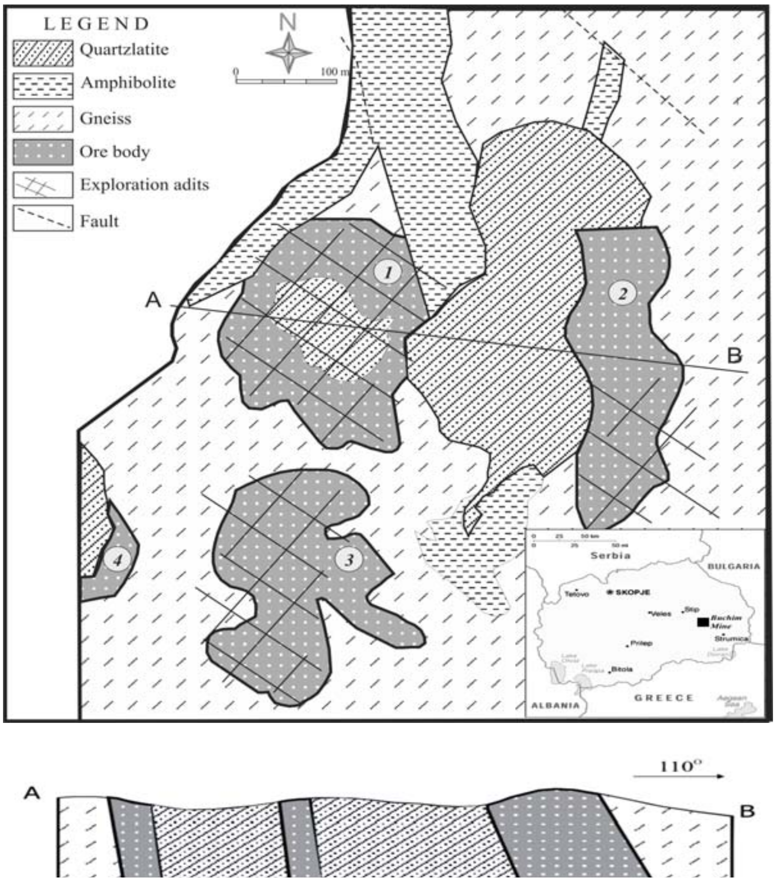


Fig. 1. Simplified geological map of the Bučim porphyry copper deposit (Serafimovski, 1993).
1. Central ore body; 2. Vršnik ore body; 3. Čukar ore body; 4. Bunardžik ore body

The main (Central) ore body is approximately 500 m in diameter and 250 m in vertical extent and has been worked in a large open pit. The ore consists of 0.25% Cu, 0.27g/t Au, 1g/t Ag, 13g/t Mo, and 1–4% pyrite. The igneous rocks have been altered to clays and micas. Important metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, haematite, and cubanite. According to the results of exploration, the copper mineralization covers an area of 1.5–2.0 km^2 and is traced to a depth of 300 m.

The country rocks adjoining the porphyry stocks are silicified, chloritized, and sericitized, and underwent argillic alteration. Early potassic alteration developed as well (Čifliganec, 1993).

MINERAL ASSOCIATIONS

More than three decades of study of this deposit have shown that it is characterized by a complex mineral assemblage and mineral paragenesis. Numerous authors have studied mineral association in the Bučim deposit: Ivanov and Jasmakovski (1970), Zarić (1974), Pavicević and Rakić (1983), Nevenić (1984), Čifliganec (1987), Serafimovski (1990, 1993); Serafimovski et al. (1990); Čifliganec et al. (1997), Tasev (2003); Serafimovski et al. (2006); Volkov (2010); Serafimovski et al. (2013); Lehmann et al. (2013) etc. According those studies of listed authors, wide variety of minerals have been recognized in the Bučim deposit – both ore-bearing and gangue ones. The mineral composition of the orebodies explored so far does not substantially differ, however there are certain peculiarities of mineral assemblages. Titanite, rutile, magnetite, hematite, chalcopyrite, pyrite, bornite, native gold, molybdenite, petzite, calaverite, and argentite were identified as ore minerals. Enargite, tetrahedrite, galena, and sphalerite are less abundant. Chalcocite and covellite are predominant in the Čukar ore body, being accompanied by pyrite, tenorite, and occasional native copper, malachite, and azurite. The ore mineralization was formed in the following sequence: titanite, rutile, and magnetite crystallized first, followed by pyrrhotite, cubanite, valleriite, and the early generation of chalcopyrite. After deposition of these minerals, the hydrothermal ore-forming solution became enriched in sulfur, giving rise to pyrite crystallization. The late chalcopyrite and galena formed at the final stage of ore deposition (Serafimovski, 1993). Recently, the presence has been confirmed of Bi-Se association representted by bismuthine, galenobismuthine, friedrichite, krupkaite, emplectite, laitakarite, native bismuth and cosalite (Serafimovski et al. 1990). This association of rare mineral phases has been studied and upgraded by Serafimovski et al. (2006) and in the present study, which results are given within this paper. Since, the majority of determined rare mineral phases have been found in the chalopyrite and pyrite from the central part orebody in Bučim deposit, in the following review we will give basic mineralogical features of these two most common minerals in the deposit.

Chalcopyrite is the most widespread ore mineral; at the same time it represents the principal ore mineral from the economic point of view. Its occurrence varies widely both in gneisses and magmatic rocks. Quantitatively it is less abundant than pyrite; exceptionally, at certain places it dominates over pyrite in the samples collected from gneisses. In andesites, chalcopyrite generally occurs in traces. It has been developed in individual dispersed grains rarer aggregates (up to 0.3 mm) and is distributed very unevenly throughout the principal host rock. Exceptionally seldom it is intergrown with pyrite or, still more seldom, with bornite.

Inside the Precambrian metamorphic complex (gneisses), chalcopyrite occurs in the form of highly non-homogeneous, diffusive-dispersive dissemination and sometimes forms nest to nest-veiny concentrations. Chalcopyrite is, most typically, concentrated in the rocks exhibiting a pronounced silicification and large proportion of femic minerals.

The size of dispersed chalcopyrite grains varies between some ten microns to 0.2 mm, exceptionally up to 0.5 mm, whereas the size of aggregates seldom exceeds 1.0 to 2.0 mm size. Chalcopyrite frequently hosts inclusions of silicates, magnetite, hematite and rutile.

The chemical composition of the chalcopyrite in the central part of orebody varies within the following limits 33.2–35.2% Cu, 29.7–31.3% Fe and 34.3–35.9% S (Pavičević and Rakić, 1983)

The chalcopyrite of the high-temperatute sulphide assemblage fraquently occurs in the form of resorbed grains (the size expressed in microns) in the meta-granular individuals of pyrite and sometimes magnetite. However, the disseminated chalcopyrite, which accompanies micro-vein and vein-nest concentrations of pyrite, locally replaces and cements pyrite and, more rarely, magnetite.

It appears, despite the microscopic investigations and the experience gained from microscopic observations, that chalcopyrite most commonly forms isolated aggregates or else occurs in the form of somewhat coarser individual grains inside quartz veins, the thickness of which ranges up to 0.5 mm, sometimes even to 2.0–3.0 cm.

The quartz veinlets often host magnetite and, at increased contents of pyrite, chalcopyrite content drops to traces. The rarest is the occurrence of nest-vein pyrite concentrations (developed within idiomorph grains up to 0.1 cm) and chalcopyrite (upto 0.5 cm) in association with calcite and a little galena. These concentrations filled subsequent cracks and fissures and can be recognized in the amphibolites hosting higher concentrations of rutile.

Microscopic investigations detected the existence of two, even more, generations of chalcopyrite, confirmed by in situ observations. The first, i.e. the oldest generation was being developed together with pyrite and occurs as a relict inside pyrite. This generation of chalcopyrite is less common in the deposit. The second generation of chalcopyrite is most widespread and represents the principal bearer of copper mineralization. The central part of orebody grades at about 1.0% chalcopyrite.

Pyrite is the most widespread mineral in the Bučim deposit and it exhibits a marked frequency of occurrence while at the same time, its proportion in the orebody varies. Most commonly it occurs in the form of unevenly distributed disseminations; in the form of a micro-jetty veiny concentration; in crystalline form of monomineral accumulations; and, in quartz veinlets, together with magnetite and chalcopyrite. The thickness of such veinlet concentrations is very variable: from parts of a millimeter to several millimeters; in quartz veins upto 1.0 cm, where pyrite is most frequently present in the form of very jagged vein-network-jetty concentrations.

Diffusion-disperssion disseminations in altered gneisses are most frequently non-homogenous, and consist of individual grains or micro-nest-like to nest-veiny pyrite aggregates. Pyrite features a high frequency of occurrence in veiny concentrations either by forming monomineral accumulations or by occurring in quartz veins together with magnetite and chalcopyrite.

Subsequently developed fractures are filled with the youngest pyrite concentrations in the form of microfilms. The size of individual pyrite grains varies from sub-microscopic to several millimeters, exceptionally up to 0.5 cm.

Most frequently, pyrite occurs in the form of irregular, jagged grains; idiomorphic grains are also common and are usually somewhat larger in size. Very often, pyrite grains host a number of inclusions of altered silicate minerals, the size of which is expressed in microns, then magnetite with hematite grains but also very frequently cements and replaces its individual grains or aggregates. Within the given orebody, in the topmost portions, pyrite has been affected by oxidation. The content of pyrite in the orebody is up to 2%.

METHODOLOGY

An intensive field sampling programme took place within the boundaries of an active Bučim open pit mine. Samples were taken from the central ore body, between levels of 580 m and 540 m, for microscopic and microprobe study. In total 40 ore samples were studied under a Zeiss Axiolab Pol reflected light polarized microscope equipped with ZEISS MC 80 DX (Databack D4) analogue camera and state of the art LEICA DMP 4500 reflected light polarized microscope equipped with digital camera LEICA DFC 450 (at magnifications within range ×100 to ×630) in the optical laboratory of the Faculty of Natural and Technical Sciences, University "Goce Delčev" – Štip, R. Macedonia. Quantitative elemental analyses of the most interesting samples were performed in two stages. First of all we used an older JEOL Superprobe 733 with the following standards; for Bi-synthetic Bi_3S_3, for Ag-synthetic Ag, for Cu, Fe and S-synthetic $CuFeS_2$, for Se-synthetic PbSe, for Pb-synthetic PbS, for As-chemically analyzed and checked for homogeneity FeAsS, $I = 0.8$ A, $U = 25$ kV. At the more advanced stage of the study we proceeded to the JEOL JXA-8200 Electron Probe Micro-Analyser WD/ED Combined Microanalyser (equipped with a SE- and BSE-detector, five-WDS crystal spectrometer and an EDS analyser) in the analytical facilities at the Institute of Geochemistry and Petrology, ETH-Zurich, Switzerland. The selected electron beam conditions were a beam current of 20 nA at an acceleration voltage of 15 kV. The X-ray studies of particular minerals were carried out using X-ray diffraction (TUR-M-60, camera RKD-57, Cu, Ni 30 hours). Beside the analysis of elements, microphotographs were taken, also.

RESULTS

In accordance to up to date mineral composition and mineral associations studies in the Bučim deposit, as well as with the latest studies of certain details major ore minerals (chalcopyrite and pyrite), were determined interesting and rare mineral phases of bismuth, bismuth-selenium mixtures on one side and gold-palladium mineral phases that are rarity in the Bučim deposit, which in the World were found in just several porphyry deposits such are Santo Thomas II – Phillipines, Skouries in Greece, Elatsite in Bulgaria, Bor in Serbia, etc. In following review first of all we will give the most important features of the particular Bi, Se and mixtures of rare Bi-Se sulphosalt mineral phases, while later we will concentrate on Au, Ag and Pd phases in the chalcopyrite and pyrite in the Bučim deposit. Description of the bismuth-selenium will be presented in order of their genetic succession. Namely, within the quartz-pyrite-chalcopyrite paragenesis, bismuth and bismuth-selenium minerals occur in the following order: quartz-pyrite-chalcopyrite-bismuthinite-galenobismutite-krupkaite-friedrichite -emplectite-laitakarite-native bismuth. As can be seen from the order of succession we may conclude that the bismuth-selenium mineralization has been related to the final stages of the main mineral assemblage that caries the major amounts of copper in the deposit.

Bismuthinite – Deposition of bismuth-selenium minerals starts with bismuthinite, which all together with friedrichite, are major representatives of that mineralization. The bismuthinite only can be seen microscopically as allotriomorphic grains (5–40 µm) within the coarse grains of chalcopyrite. Bismuthinite often corrodes chalcopyrite and is developed metasomathically along hydrothermally altered rocks of the metamorphic setting at the latite neck in the deposit. In reflected light, bismuthinite, shows similar color to galena, but differs from it by the strong anisotropy. The chemical composition of bismuthinite is given in the Table 1, columns-analyses 2 and 3. As can be seen the calculated formula of bismuthinite from the Bučim deposit is quite close to the theoretical values in mineral's formula.

Galenobismutite – This mineral classifies into secondary minerals of the bismuth-selenium mineralization. It occurs, also, in chalcopyrite in form of separate allotriomorphic grains or together with krupkaite built irregular aggregates (50–60 µm).

Table 1

Quantitative X-ray spectral analyses of bismuth and bismuth-selenium minerals in the Bučim deposit (in % wt)

Element	Sample										
	1	2	3	4	5	6	7	8	9	10	11
Bi	99.52	80.36	80.37	54.67	55.38	64.06	64.08	41.69	42.63	41.66	80.11
Pb	0.18	–	–	26.64	21.05	–	–	33.38	30.03	30.11	2.21
Cu	–	0.43	0.31	0.92	6.55	14.14	13.89	–	9.50	10.25	–
Ag	–	–	–	–	–	2.75	2.79	4.96	0.70	0.62	–
Fe	–	0.62	0.71	–	–	0.71	0.61	–	–	–	–
As	–	–	–	–	–	–	–	–	–	–	–
Se	–	–	–	–	–	1.48	2.45	0.26	–	–	13.41
Te	–	–	–	–	–	–	–	–	–	–	1.10
S	–	18.59	18.61	18.42	17.71	16.74	16.15	16.84	17.20	17.36	3.10
Σ	99.70	100.00	100.00	100.75	100.69	99.98	99.97	97.13	100.06	100.02	99.93

1. Native Bismuth [Bi]; 2. Bismuthinite [$(Bi_{1.95}Cu_{0.03}Fe_{0.05})_{2.04}S_{2.95}$]; 3. Bismuthinite [$(Bi_{1.95}Cu_{0.02}Fe_{0.05})_{2.04}S_{2.95}$]; 4. Galenobismutite [$(Pb_{0.92}Cu_{0.10})_{1.02}Bi_{1.87}S_{4.10}$]; 5. Krupkaite [$Cu_{1.1}Pb_{1.09}Bi_{2.85}S_{5.94}$]; 6. Emplectite [$Bi_{1.11}(Cu_{0.80}Fe_{0.04}Ag_{0.09})_{0.94}(S_{1.84}Se_{0.11})_{1.95}$]; 7. Emplectite [$Bi_{1.12}(Cu_{0.80}Fe_{0.04}Ag_{0.09})_{0.94}(S_{1.84}Se_{0.11})_{1.95}$]; 8. Cosalite [$(Pb_{1.55}Ag_{0.44})_{1.99}Bi_{1.92}(S_{5.05}Se_{0.03})_{5.08}$]; 9. Friedrichite [$Cu_{5.02}(Pb_{4.87}Ag_{0.21})_{5.08}Bi_{6.85}S_{18.01}$]; 10. Friedrichite [$Cu_{5.36}(Pb_{4.84}Ag_{0.19})_{5.03}Bi_{6.82}S_{17.88}$]; 11. Laitakarite [$(Bi_{4.01}P_{0.10})_{4.11}(Se_{1.78}Te_{0.09}S_{1.02})_{2.89}$]

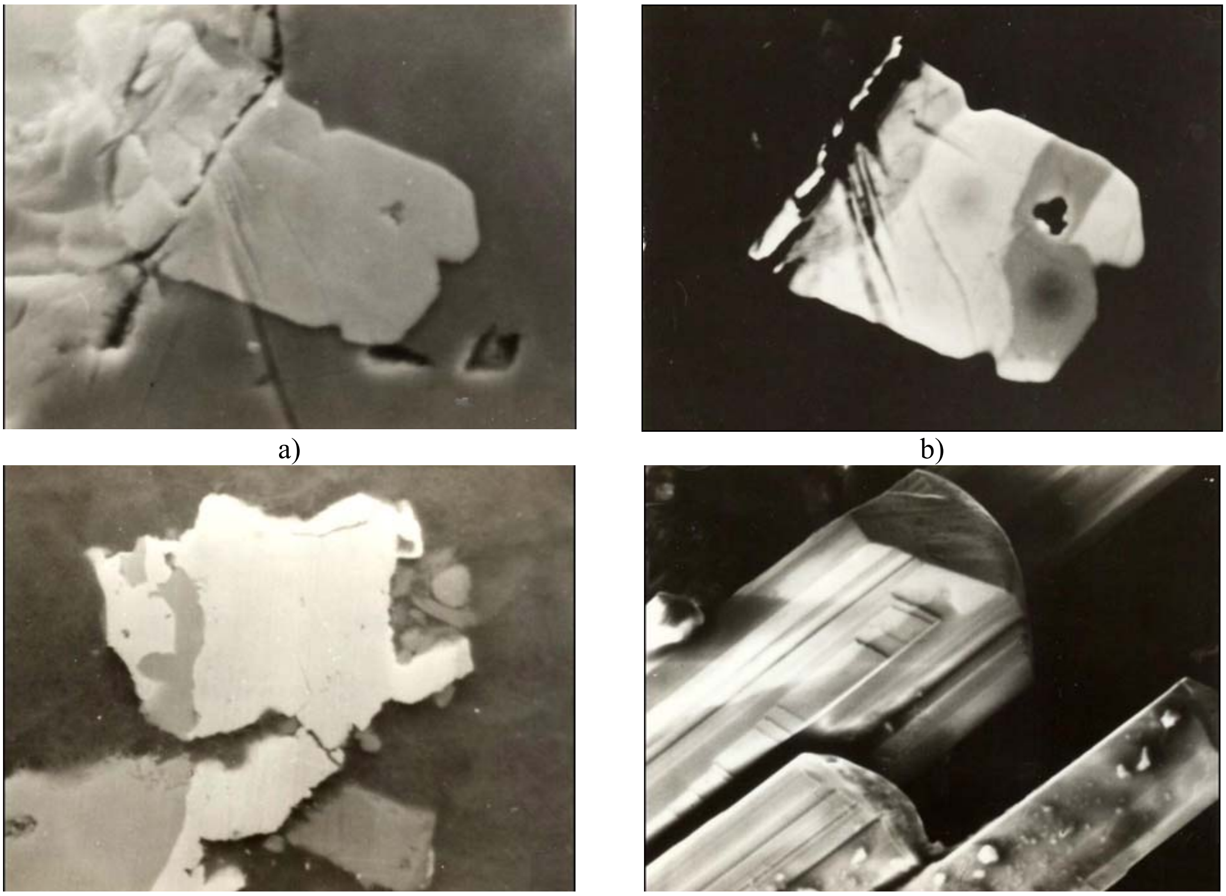
In reflected light shows similar features to galena and bismuthinite, but however it is slightly more grayish than galena. The calculated formula of galenobismutite from the Bučim deposit is quite close to the theoretical values with an exception of presence of copper up to 0.92% Cu (Table 1, analysis 4), which characterizes galenobismutite and bismuthinite from this deposit.

Krupkaite – Although very rare in the nature, this mineral was determined within the Bučim deposit. There it develops with galenobismitite in coarse grained chalcopyrite and it is characterized by copper content of up to 6.55%wt Cu. As can be seen the calculated formula of this particular mineral from the Bučim deposit is quite close to the theoretical values in its formula.

Friedrichite.– Is one of the major bearers of bismuth and and is quite widely distributed in the ore deposit. The most often it forms rod-like, ribbed crystals or sheaf-like aggregates (1–3 mm in size), which grow over coarse grained chalcopyrite. In reflected light is very similar to galena and is virtually indistinguishable from bismuthinite, galenobismutite and krupkaite. Certain optical inhomogeneity determined during reflected light microscope observations, are probably attributable to the significant content of silver (0.62÷0.70 %wt Ag) and copper (9.50÷10.25%wt Cu). The calculated formula of friedrichite from this deposit close to the theoretical values with certain small deficiency of bismuth (measured 41.66 to 42.63%wt Bi, theoretical 43.10%wt Bi).

As can be seen from the Figure 2a,b, the laitakarite-emplectite aggregate is metasomathically developed along altered rock and it has a form of a meta-aggregate. Also, we may conclude that the emplectite has been deposited prior to laitakarite and with it has corrosion-like contact.

Emplectite – The emplectite belongs to the group of rare minerals within the Bučim ore deposit and one of bismuth minerals richest with copper.



a) b)

c) d)

Fig. 2. Bismuth-selenium mineral paragenesis in the Bučim porphyry copper deposit
a) Laitakarite-emplectite aggregate (gray-white) in hydrothermally altered rock (dark), backscattered electrons, magnif. 1300×.
b) Laitakarite (white), emplectite (gray), COMPO, magnif. 1300×. **c)** Bismuthinite (white) along chalcopyrite (gray) in hydrothermally altered rock (dark), COMPO, magnif.3000×. **d)** Illustration of cosalite crystal representative morphological forms. (scanning-electron photograph, magnif. 102×)

In reflected light it is virtually indistinguishable from bismuthinite, krupkaite, laitakarite and friedrichite. Although analyses has shown crystalochemical formula close to the theoretical, we would like to stress the increased presence of selenium (1.48÷2.45 %wt Se), certain deficiency of copper which is complemented by iron (0.61÷1.90 %wt Fe) and silver (0.99÷2.85%wt Ag).

Laitakarite – This particular mineral is one of the rarest minerals in the nature, which by numerous researchers is considered as an indicator of gold-bearing endogenous mineraliations, as it is the case with the Bučim deposit as well. In the order of succession laitakarite occurs at the end, it precedes only to the bismuth. It is closely related to the emplectite. It is one of the Bi-Se minerals with highest contente of selenium (13.41 %wt Se).

Native bismuth – After the bismuthinite and friedrichite it is the most common bismuth mineral in the Bučim deposit. In reflected light it is characterized by yellowish color with strong anisotropy and very often form corrosion structures with all bismuth and bismuth-selenium minerals deposited earlier. In such corrosion structures within native bismuth were detectable laitakarite, friedrichite and bismuthinite relics. Native bismuth mineral grain sizes were in the range 5–40 μm. Chemical analyses have proven relatively high purity expressed with bismuth concentration of up to 99.52 %wt Bi.

Cosalite – In the quartz-pyrite-cosalite paragenesis, in the Bučim deposit, the major mineral is cosalite. It has been developed in form of bundle-like agregates composed of needle-like crystals. Length of individual crystals reaches 1 cm while thickness is up to 1 mm. Very often cosalite overlays chalcopyrite or pyrite and quartz. Most of the cosalite crystals are represented by very characteristic ribbed surfaces along the elongated side. From the chemical composition point of view we would like to stress out that cosalite from Bučim shows representative values for silver with up to 4.96 %wt Ag. Bismuth, sulfur and selenium in regards to their concentrations are very close to those given in theoretical formula for this particular mineral.

Preliminary microscope and microprobe investigations in our “quest” for rare minerals within Bučim porphyry copper deposit determined two main mineral assemblages: magnetite-pyrite-chalcopyrite (Mt-Py-Cp) and pyrite-chalcopyrite (Py-Cp) as major hosts of Au and Pd.

The studied pyrites are of four different generations and increased concentrations of Au and Pd were determined in so-called block pyrites or massive pyrites with emphasized crystallinity and sizes up to 0.5 mm. Au-Pd phase occurs as a separate mineral phase, which is distinguished by a special colour (gull grey to pink grey; Figure 3). That mineral phase in the composition mostly corresponds to the pyrite (Table 2), but as can be seen from the table, increased gold (7.746% Au, Table 2, analysis 10) and palladium (6.784% Pd, Table 2, Analysis 11) concentrations are directly associated with decreased concentrations of iron and sulfur as major constituents of pyrite.

From the Table 2 it can be seen that, among the 12 analyses shown, gold is present in concentrations within the range of 0.027–7.746% Au and increased gold concentrations are usually accompanied by increased concentrations of palladium, except in analysis No. 3.

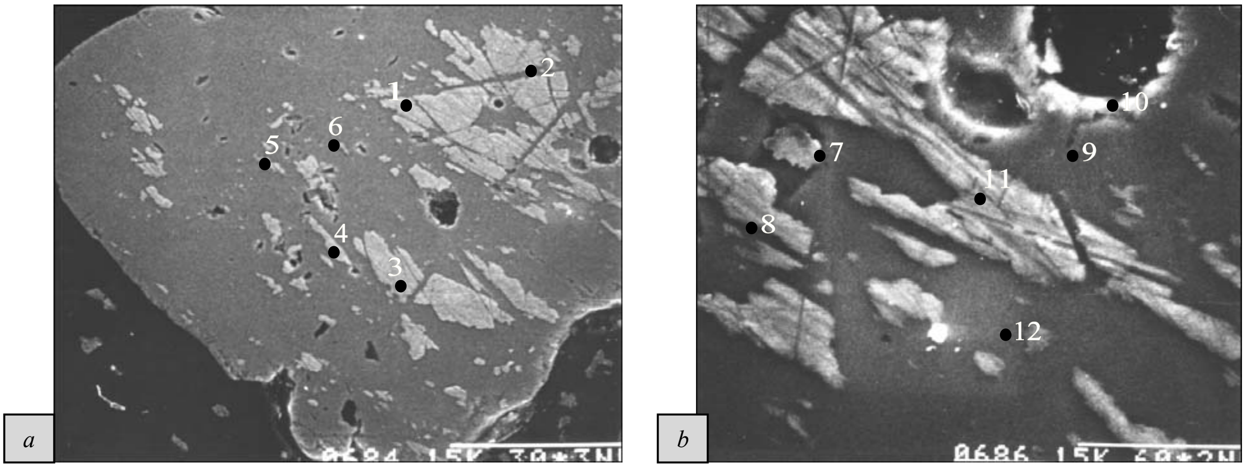


Fig. 3. Electron microprobe photographs of pyrites (dark) and Au-Pd phases (light grey), from the Bučim porhyry copper deposit, with analysis points.
a) primary photograph, b) detail

Table 2

Electron probe microanalyses of pyrites (in %)

Analysis	1	2	3	4	5	6	7	8	9	10	11	12
Au	6,979	0,21	7,627	6,512	0,12	7,54	0,22	0,027	0,1	7,746	6,47	0,033
Fe	39,228	43,636	40,575	39,976	45,458	43,556	43,854	45,438	45,123	39,177	38,932	45,531
S	44,438	53,503	47,352	44,398	53,534	47,342	52,668	51,818	53,265	46,169	45,452	53,926
Cu	0	0	0,01	0,022	0,062	0,012	0	0	0,02	0,034	0	0,024
As	0,157	0	0,019	0,684	0,141	0,02	0,02	0,761	0	0,028	0,042	0,157
Ag	0	0	0,21	0	0	0,73	0,04	0	0,02	0	0	0
Pd	6,33	0,01	1,25	5,65	1,23	0,04	0	2,34	0	6,02	6,784	0,28
Ge	0,31	0,35	–	–	–	0,21				0,25	0,38	
Zn	0,22		–	–	–		0,37			0,26	0,35	
V	0,33	0,25	0,27	0,21	–	0,22	0,41			0,21	0,32	
Ni	0,24	0,47	–		–	0,21	0,54			0,15	0,28	
Se	–	-	0,74	0,52	–	–						
Bi	–	–	0,48	0,65	–	–						
Te	–	–	0,35	0,39	–	–	0,21					
Σ	98,232	98,429	98,883	99,012	100,545	99,88	98,332	100,384	98,528	100,044	99,01	99,951

Palladium concentrations were within the range of 0.040–6.784% Pd. Increased concentrations of gold and palladium caused reductions of Fe and S from their ideal values for pyrite, which should be around 45.55% Fe and 53.45% S. It should be mentioned that increased concentrations of arsenic were found in all analyses where gold and palladium showed increased values (0.019–0.761% As), too.

The studies of chalcopyrite from the Bučim deposit were performed on numerous ore samples, and different types of chalcopyrites were analysed. This was possible because the chalcopyrite is the major ore mineral within the Bučim deposit and the main bearer of copper. Its presence in the Bučim ore is around 1%. Our detailed studies confirmed the microscopy findings of some former authors, but some new phases were also found. Beside the already determined Bi-Se mineralization, the mineral paragenesis py-mgt-chp, which is the b This type of chalcopyrite mainly occurs in veins, veinlets and massive impregnations in association with magnetite and medium-to-high temperature pyrite.

Additional studies are needed to determine the stages of the Au-Pd pair. Within our latest studies particular phases that have resulted from the deformation of the chalcopyrite crystal lattice were determined, but their definite separation was not possible at the moment.earer of increased concentrations of Au and Pd, was confirmed. We would like to stress that the determined concentrations of Au and Pd were related to only one type of chalcopyrite (massive and coarse grained, Figure 4) of the so-called major ore-bearing phase of the Cu-mineralization within the Bučim mine or second generation chalcopyrite.

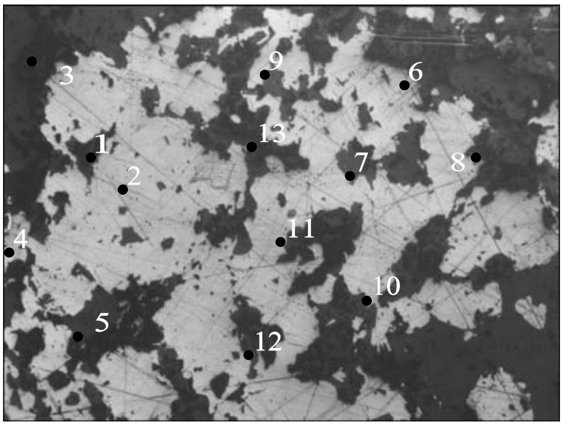


Fig. 4.. Microprobe photograph of chalcopyrite from the Bučim porhyry copper deposit, with analysis points

The results of the microprobe analysis are shown in Table 3, where it can be seen that increased concentrations of Au and Pd were determined in 13 microprobe analyses. Gold concentrations were within the range 0.009–9.095%, while the palladium concentrations were 0.020–8.111%. By analogy with the studied pyrite, increased concentrations of As were determined here, too. However arsenic showed lower values here compared to those in pyrite.

We would also like to point out that significant concentrations of the standard geochemical association of elements for the Bučim chalcopyrite, such as Ni, Co, Pb, Zn, Ag, and so on, were not determined in these studies.

Table 3

Electron probe microanalyses of chalcopyrites (%)

Analysis	1	2	3	4	5	6	7	8	9	10	12	13
Au	6,335	0	6,457	0,286	9,095	7,29	6,923	0,14	0,116	0,23	7,159	0,009
Fe	25,923	29,08	25,128	29,112	25,972	25,728	26,679	29,775	29,707	29,52	25,729	29,346
S	28,737	34,324	29,736	33,595	26,964	28,643	27,884	34,371	35,299	35,577	28,66	34,882
Cu	29,463	33,675	28,678	33,514	26,638	28,912	29,824	34,211	34,153	34,225	27,942	33,692
As	0	0,022	0,048	0	0,045	0,005	0,108	0	0,055	0,074	0,002	0,005
Pd	7,38	0,02	8,11	0,3	7,97	6,81	5,98	1,33	0,42	0,28	7,46	1,43
Ge	0,22	–	–	0,38	0,42	0,35	–	–	–	–	0,29	–
Zn	0,35	–	–	0,44	0,36	0,41	–	–	–	–	0,35	–
V	0,38	0,37	–	0,42	0,44	0,45	0,22	–	–	–	0,42	–
Ni	0,33	–	–	0,35	0,41	0,48	–	–	–	–	0,35	–
Se	–	0,33	0,22	–	–	–	0,49	–	–	–	–	–
Bi	–	0,42	0,31	–	–	–	0,52	–	–	–	–	–
Te	–	0,35	0,25	–	0,22	–	0,42	–	–	–	–	–
Σ	99,118	98,591	98,937	98,397	98,534	99,078	99,048	99,827	99,75	99,906	98,362	99,364

DISCUSSIONS

Determined mineral association in the Bučim deposit, coincide with the similar ones found in several deposits already compared with the Bučim deposit elsewhere Tarkian (1991), Serafimovski (1993), Čifliganec (1993), Petrunov et al. (2001), Volkov et al. (2010) etc. In fact the coincidence is in regards to the major sulphide and sulphosalt minerals and mineral phases as well as in regards to the rare mineral phases with significant participation of gold, silver, tellurium, selenium, bismuth, platinum, palladium etc. The pyrite and chalcopyrite are the most common ore minerals within the deposit and they are constituents of major sulphide parageneses in the Bučim deposit while with the latest mineralogical studies there have been discovered numerous new mineral phases of bismuth, Bi-Se, Cu-Bi-As-S, Au-Ag-Pt-Pd, Au-Pd, etc.

Determined bismuth-selenium mineralization in the Bučim porphyry copper deposit can be considered as typomorph one for gold-bearing type of endogenous mineralizations. Quartz-pyrite-chalcopyrite paragenesis successive order of minerals where bismuth and bismuth-selenium minerals occur as bismuthinite-galenobismutite-krupkaite-friedrichite-emplectite-laitakarite-native bismuth shows that according to the time of their deposition has been engaged substantial amount of copper and iron. Copper is present in bismuthinite in range 0.31÷1.82 %wt Cu, in galenobismutite 0.92 %wt Cu, in krupkaite 0.92÷6.28 %wt Cu, fridrichite 9.50÷10.25 %wt Cu and emplectite 6.55÷14.14 %wt Cu. Iron distribution is more homogenous and ranges from 0.61 to 1.90 %wt Fe. Selenium is not representative for the initial part of the paragenesis, it scarcely occurs in krupkaite (1.12 %wt Se), emplectite (1.85÷2.45 %wt Se) while the most abundant is in the laitakarite (13.5 %wt Se).

Increased concentration of copper and iron in the bismuth-selenium minerals probably are closely related to the intensive corrosion alterations in chalcopyrite. Those alterations can be considered as an example of hydrothermal metamorphism of chalcopyrite. One fraction of selenium could be attributed to the corrosion processes and alterations of chalcopyrite, but during the deposition laitakarite there was probably yield of selenium by the hydrothermal solutions. In the second paragenesis, which also caries certain amounts of bismuth, occur significant concentrations of silver (up to 4.96 %wt Ag), as well as small fraction of selenium (0.26 %wt Se). Determined existence of bismuth-selenium mineralization within the Bučim ore deposit gave us an insight into more detailed geological-genetical model of the deposit, which can be used in the study and exploration of similar deposits-anologues to the Bučim deposit. From the economics point of view it is a necessary to study quantitatively distribution of bismuth, selenium and silver in entire deposit and to make an efforts to foresee possibilities for their valorization.

Characteristic for the Mt-Py-Cp assemblage (earlier and high-temperature) is the geochemical association Fe-Cu-Ni, Co-As-O-S+Au, Ag, and Pd, with magnetite, chalcopyrite, pyrite, and cobaltite, Ni-Co-Fe-sulfides, and native Au (subordinate and rare). Pd is included in the structure of the main, subordinate, and rare minerals.

Later enrichment of the hydrothermal fluids with Cu, Bi, Se, Te, Pb, As, Au, and Ag led to the formation of a Py-Cp assemblages overprinting Mt-Py-Cp aggregates. New minerals were formed, partly as a result of the inclusion of elements "*in situ*": aikinite, bismuthinite, friedrichite, wittichenite, soucekite, emplectite, paderaite, merenskyite, michenerite (Serafimovski et al., 2006), other Pd-Bi-Te phases, tennantite (including. Pd-, Co-, and Ni-bearing), Ni-Co pyrite, Ni-Te phases, Bi-Pb-Ag-S phases, Cu-Fe-Bi-S phases, galena, clausthalite, sphalerite, native gold, and electrum, and (in the uppermost levels) enargite, luzonite, and pearceite (Petrunov et al., 2001).

Au-Pd association has been determined within the pyrite and chalcopyrite of the major ore-bearing phase in the central orebody in the Bučim mine. It should be stressed that this Au-Pd association occupies certain levels (580–540 m) within the Bučim open pit. There, ore-bearing pyrite and chalcopyrite are in association with magnetite and are usually massive and coarse grained.

The relation between concentrations of gold, palladium, and arsenic in pyrite and chalcopyrite from the Bučim deposit showed a high degree of geochemical correlation (Pockov, 1997). This probably points to the wide range of physico-chemical conditions and the interplay between magmatic and hydrothermal processes during the formation of the deposit. Increased concentration of Au and Pd in practice means that there is a substitution of major pyrite constituents by gold and palladium. The fact that gold and palladium form such a mixture in the main mineral phase in pyrite and chalcopyrite equally (temperatures around 250 ºC) and their absence in later phases of the ore-bearing process could indicate stabilization of the crystal lattice of the pyrite in the later evolution of the process.

In chalcopyrite the Au-Pd concentrations are probably related to the mixed mineral phases that we were unable to fully determine, but with the noted presence of Au-Pd in chalcopyrite we have confirmed that there are numerous mineral phases such as Bi-Se minerals (laitakarite, friedrichite, cosalite, etc.), already determined previously by Serafimovski (1993) and Serafimovski et al., (2006).

CONCLUSIONS

Microscope and microprobe studies in the Bučim porphyry copper deposit have determined several mineral groups with representative mineral parageneses where have been determined interesting rare mineral phases of Cu-Bi-Se-Te associations and Au-Pd metals. Two main mineral parageneses, quartz-pyrite-chalcopyrite, have been defined as major bearers of Bi-Se-Te rare mineral phases where predominated bismuthinite, galenobismutite, krupkaite, friedrichite,emplectite, laitakarite and native bismuth and magnetite-pyrite-chalcopyrite as bearer of Au-Pd mineral phases.

The gold content in the studied pyrite is within the range of 0.027–7.746% Au while the palladium content is within the range 0.040–6.784% Pd, and they are related with the special mixture mineral phases characterized by gull gray colour. Increased concentrations of Au-Pd in chalcopyrite (6.335÷9.095% Au and 1.33÷8.11% Pd) are related to the massive medium-to-high temperature chalcopyrite, which constitutes the major ore phase within the Bučim deposit. For more detailed definition of the PGM, additional studies are needed.

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Резиме

РЕТКИ МИНЕРАЛНИ ФАЗИ ПОВРЗАНИ СО ГЛАВНИТЕ СУЛФИДНИ МИНЕРАЛИ ВО ПОРФИРСКОТО БАКАРНО НАОЃАЛИШТЕ БУЧИМ, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: рудни минерали; Au-Pd фази; ретки Bi-Se минерални фази; рудник Бучим

Со најновите детални минералошки испитувања со студиски поларизационен оптички микроскоп и со анализи на електронска сонда во порфирското бакарно наоѓалиште Бучим се констатирани и утврдени неколку карактеристични ретки минерални фази, кои ги сочинуваат металите од златоносно-платинската група и металите од групата Cu-Bi-Se-Te-As. Во бизмутско-селенската група на ретки минерални фази се констатирани бизмутинит, галенобизмутит, крупкаит, фридрихит, емплектит, лајтакарит и самороден бизмут, кои претставуваат нови ретки минерални фази за порфирското наоѓалиште на бакар Бучим, како и минерални фази од групата Au-Pd, во кои многу јасно е утврдено присуство на самородно злато и паладиум со елементи на примесите карактеристични за овие ретки минерални фази. Треба да се потенцира дека и двата типа на ретки минерални фази се констатирани во пиритите и халкопиритите од основните рудни парагенези во наоѓалиштето Бучим. Бизмут-селенските минерални фази се поврзани со основната кварц-пирит-халкопиритска парагенеза, додека минералните фази Au-Pd се поврзани со нешто повисокотемпературните оксидно-сулфидни парагенези од редот на магнетит-пирит-халкопирит (Mt-Py-Cp) и пирит-халкопирит (Py-Cp)