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Cu-Au MINERALS AND TRANSFORMED MINERAL PHASES IN THE OXIDATION ZONE OF THE PLAVICA ORE DEPOSIT, EASTERN MACEDONIA

Todor Serafimovski[1], Goce Zlatkov[2], Goran Tasev[1], Violeta Stefanova[1]

[1]*Faculty of Natural and Technical Sciences, Institute of Geology, "Goce Delčev" University in Štip,*
Blvd. Goce Delčev 89, Štip, Republic of Macedonia
[2]*Genesis Resources Ltd., Lermontova 3/2, 1000 Skopje, Republic of Macedonia*
todor.serafimovski@ugd.edu.mk

Abstract: Within this paper we present the latest mineralogical and chemical studies of particular minerals and mineral phases from oxidation zone and partially from the primary sulphide mineralization within the Cu-Au deposit Plavica. Oxide zone in this ore deposit represents a system of so-called hats of secondary alunitized quartzites intensively oxidized and represented by veinlet and net-like Fe-oxide and Fe-hydroxides. The major feature of this zone is interesting gold concentration. The major part of confirmed gold within alunitized iron quartzites reaches concentrations within the range of 1.80 up to 5.85 g/t Au. The gold is often present as native gold, mostly in Fe-hydroxides and in some places as finely dispersed in pyrite. There its concentration varies from 0.56 g/t up to 0.60 g/t Au. The mineral composition of the oxidation zone is quite extensive (about 31 minerals) of which as principal with prevailing share up to 70% are quartz, alunite, kaolinite and sericite, as secondary minerals accounting up to 11% are pyrite, goethite, chalcocite, hematite, bornite, covellite, malachite and azurite, while as rare mineral phases with share under 5% are chalcopyrite, tetrahedrite, tennantite, enargite, galena, sphalerite and others.

Key words: oxide zone; mineral phase; secondary quartzite; Cu-Au mineralization

INTRODUCTION

The Plavica deposit is well known to the local and regional community. Namely, exploration and exploitation history of the Plavica deposit (in the central parts known as Zlatica) reaches back to Roman times that were undertaking large-scale mining and processing of copper from pyrite-enargite veins as well as limited exploitation of silver and lead. Also, limited mining took place here during and after the so called 'Turkish' era (15th–17th centuries) when gold was extracted for production of coins. In the 20th century, the British company Selection Mines Ltd carried out some exploration in the area and further exploitation of enargite veins took place between 1934 and 1936 (with more than 2800 m of underground exploration workings). Quite an intense programme of exploration and drilling was undertaken by the Zletovo mine and the Geological Survey in the decades following the Second World War (1945–1952; 1961–1962 and 1963–1974). Based on those explorations an extensive programme prepared was by the Geological Survey and RIK "Sileks" and realized in the period 1976–1986 (with respectable 30,325 m of exploration drilling). From the late 1980s, there have been several, further, exploration programmes for Cu and Au by foreign mining companies (e.g. Cominco, Cyprus Amax, Minorco, Goldfields, Rio Tinto, European Minerals) with the emphasis more on Au associated with the peripheral silica bodies. The latest exploration in the Plavica concession area was performed during the period 2011–2014 by the Australian company Genesis Resources International Ltd. All those explorations contributed to creation of intensive professional and scientific database where we would like to point out the workings of Pendžerkovski et al. (1960), Mijalković and Pešić (1966), Janković (1967), Marković (1971), Pantić et al. (1972), Ristić and Klajn (1973), Stojanov (1974, 1980), Bilibajkić and Bilibajkić (1978), Petković and Romić (1977), Ivanov and Denkovski (1978, 1980), Rakić (1978, 1982), Janković et al. (1980), Mudrinić (1982, 1986), Drovenik et al. (1983), Bogoevski and Rakić (1985), Stojanov and Serafimovski (1990), Serafimovski (1990, 1993), Stojanov et al., (1995), Tomson et al. (1998), Serafimovski and Rakić (1998, 1999), Stefanova (2005), Alderton and Serafimovski (2007), Stefanova et al. (2007), Volkov et al. (2010), Serafimovski et al. (2013), Stefanova et al. (2013), Zlatkov et al. (2014) and Ivanovski et al. (2015).

GEOLOGY

In the geological setting of the Plavica deposit participate mainly volcanic and volcano-sedimentary rocks, which exact determination is complex due to intensive presence of hydrothermal alterations. The geological setting of the Plavica deposit as well as its structural-tectonic features are just part of the very complex Kratovo-Zletovo volcanic area where dominate volcanic rocks, intensive hydrothermally altered, brecciated and tectonically moved in different directions (Figure 1).

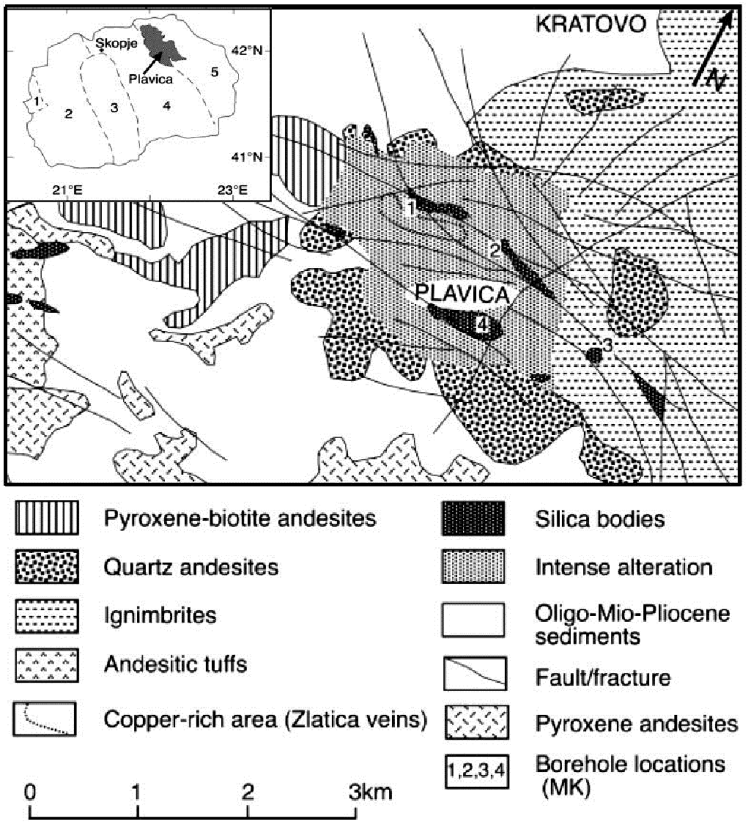

Fig. 1. Simplified geological map of the Plavica area (Alderton and Serafimovski, 2007; modified)

Beside emphasized fault tectonics within the Plavica area dominate ring-like structures and structures of dyke intrusions as a direct product of Tertiary magmatism and its pulsation character. In the geological setting of the Plavica deposit participate mainly volcanic and volcano-sedmentary rocks, which exact determination is complex due to intensive presence of hydrothermal alterations. However, with numerous lithostratigraphic and petrographic studies it was confirmed that in the geological setting of this deposit participate mainly volcanic and volcano-sedimentary rocks, which exact determination is complex due to intensive presence of hydrothermal alterations.

Ignimbrite of dacite-andesite composition are present on NE slopes of the Plavica (Trnjak, Golak, Ramna Niva) and in one wide band envelope southern slopes of the Plavica. They are represented by grey-green to reddish color and composition variable at short distances (andesite-dacite-quartzlatite). Due to their structural setting and inclusion of some older rock some authors named them as ignimbrites. Sometimes propylitized and intensive hydrothermally altered when tectonically crushed these rocks are known for the presence of numerous lead-zinc ore veins. This quite well fits the Plavica deposit into the explanation that although the most high-sulphidation deposits are generated in calc-alkaline andesitic-dacitic arcs characterized by near neutral stress states or mild extension, few major deposits may also occur in compressive arcs characterized by the suppression of volcanic activity (Sillitoe and Hedenquist, 2003), as it is shown in the text that follows, too.

Volcano-sedimentary rocks (stratified tuff) are well spread on the northern margins of the Plavica depositin an elongated belt starting from Šlegovo village and ending to the east, near the Široka Padina locality. Their presence points out that some of the volcanic stages occurred in submarine or sublacustrine conditions. They have well pronounced layering and rapidly changing different kinds of tuffogenous and terrigenous material (tuffogenous sandstone, conglomerate, tuffogenous claystones, sandstones, pieces of different volcanics). These rocks are sometimes hydrothermally altered, mainly along the cracks and fissures.

Propylitized dacite-andesite rocks are the rock counterparts of former composition strongly hydrothermally altered and spread over northern slopes of the Plavica (Rajkovac, Golak, Trnjak) and southern part of the Maričanski Rid.

Hydrothermally altered andesite rocks were determined in western and southwestern margins of the Plavica. They are andesites, which were significantly altered (saved fenocrystals and some colored copmounds), that easily can be classified as biotite-hornblende andesite. Also, at the Plavica as it was mentioned earlier, can be found numerous intensive hydrothermally altered rocks (andesite, dacite, latite, pyroclasts), which sometimes can be extensivelly mineralized by Cu, Ag, Au, Pb, Zn and Mo.

Quartzlatites were determined at several locations (Karac, Dogandžiski Kamen, Plavički Potok). In general, they occur as neck, stock and dyke forms that breakthrough the adjacent dacite-andesite or their tuff counterparts. These rocks are built of cryptocrystalline quartz, K-feldspar with phenocrysts of sanidine, biotite and quartz and characterized by porphyry structure and massive texture. Dykes are common at several places, especially on the northern margin of the Plavica area, where they breakthrough the dacite-andesite and pyroclasts.

The Plavica deposit contains many of the features characteristic of high sulphidation (HS), acid sulphate epithermal mineralization. The common features of this class of deposit, which are also shared by Plavica, include 'vuggy' and massive silica bodies (secondary quartzites) followed by advanced argillic alteration, native gold associated with pyrite and base metal (especially Cu) sulphides and sulphosalts, and a close association with intermediate to acidic volcanic/pyroclastic rocks. At Plavica, the higher gold grades tend to be associated with those silica bodies.

ORE DESCRIPTION

The unique Macedonian high-sulphidation epithermal gold has been determined and studied in the Plavica deposit. At this deposit it was hard to explain the spatial position of the mineralization, its boundaries in regards to adjacent host rocks and size of the ore deposit (Terzić et al., 1986), which have been confirmed by extensive, disseminated mineralization, where distribution of particular ore components and their quantitative ratios are very variable at short distances. The mineralization occurs in four distinct settings: (i) stockwork and disseminated Cu–Au (+Mo, Ag) mineralization occurs in the central and the deepest part of the system (it occupies an area of 6 km^2 and was still reported at depth in the deepest drill hole, 950 m below surface); (ii) veins of quartz, pyrite, sphalerite and enargite (± gold) occur at intermediate levels and appear to be superimposed on the stockwork (at places enargite veins could be followed for distances up to 200 m, thickness from 0.7 to 5 m and a content of Cu ~2% and Au at 1 ppm); (iii) silica bodies occur peripheral to the central zone where both massive and 'vuggy' silica occurs (they contain elevated gold levels, 1 to 10 ppm Au, as well as alunite, jarosite, native sulphur and kaolinite; (iv) around the margins of the caldera, there are small veins with enrichments in Pb and Zn (up to 1% combined Pb+Zn). As such, they bear some similarity to the larger Pb–Zn veins worked in the nearby Zletovo mine, but are much smaller. Recent detailed geological exploration by the Genesis Resources International DOOEL Skopje, mostly in the northeastern part of the Plavica deposit defined one new Cu-Au mineralization type where dominate epithermal gold of high sulphidation with representative elongated lens-like ore bodies (Zlatkov et al., 2014).

Epithermal gold and associated mineral phases have been determined in silicified tuff, secondary quartzite, quartz-pyrite-enargite veins and mainly disseminated within an altered, but mostly silicified volcanic setting. Beside gold within this acidsulphate volcanic environment was determined the presence of contaminated pyrite, zinc-tetrahedrite, enargite, and certainly seligmanite regularly and commonly present copper association led by chalcopyrite, followed by bornite, chalcocite, covellite, as well as slightly higher temperature associations of arsenopyrite and molybdenite. Detailed microscopic studies (Serafimovski and Tasev, 2013) gave some insight into the spatial distribution of gold, copper minerals and associated minerals in form of sulphides and sulphosalts in the Plavica deposit (Zlatkov et al., 2014).

GENERAL FEATURES OF THE OXIDATION ZONE AT THE PLAVICA ORE DEPOSIT

The main feature of the Plavica ore deposit is its zoning in depth. Generally speaking, there are two zones, zone of oxidation that can be followed up to 140 meters at depth and zone of poor primary mineralization, which extends up to 500 m at depth. Extensive exploration drilling followed by mineralogical studies show that can be marked so-called a middle zone of cementation which usually goes between 120 and 220 meters in depth, and in some places along the fissure and fault zones can descend up to 300 m (Figure 2).

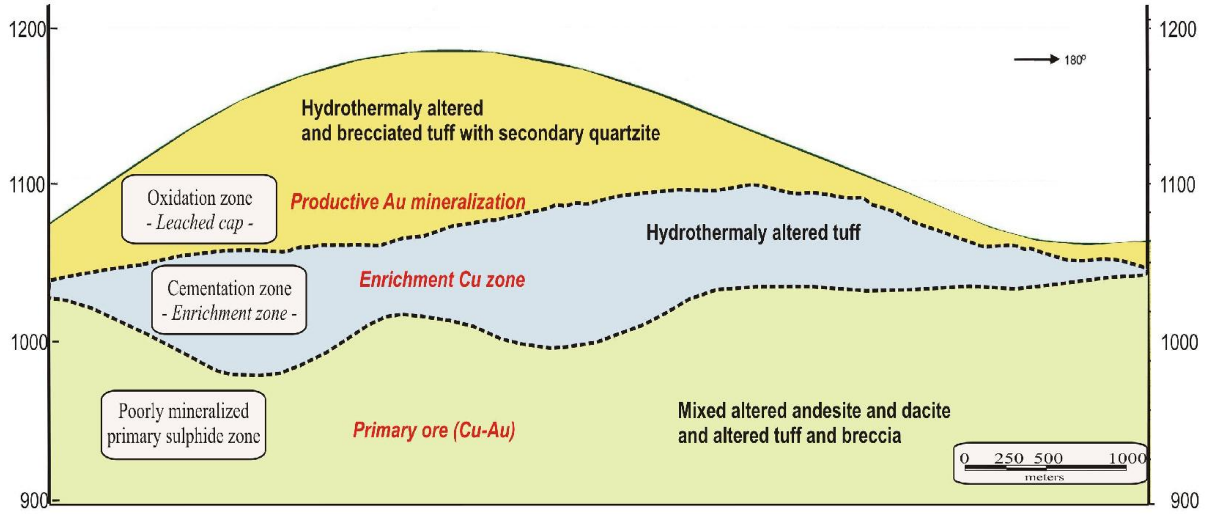

Fig. 2. Schematic illustration of three ore zones in the Plavica Cu-Au polymetalic deposit

In this central area resulted mainly copper sulphosalts and transformed simple copper sulphides. The third zone is zone of poor primary sulphide mineralization represented mainly by chalcopyrite, primary enargite, primary bornite, pyrite, molybdenite, etc., followed by exploration drill holes up to depth of 500 m. However, within these studies we attempted in the zone of oxidation to define secondary (cementation) products (in form of transformed phases due to impact of external agents), too. The main feature of the oxidation zone in the Plavica ore deposit are secondary quartzites, which in many places are alunitized and tectonized with intensive presence of impregnation and developed reticulate veins of Fe-hydroxides (Figure 3).

Silex-secondary quartzites in the central part of the Plavica have a significant distribution. They build the highest parts of the Plavica and stick out of the ground in the form of chops and occur in two elongated zones: northern and southern. Towards the east these silex ore bodies contain significant amounts of alunite that gradually turns into alunite quartzite (Figure 4).

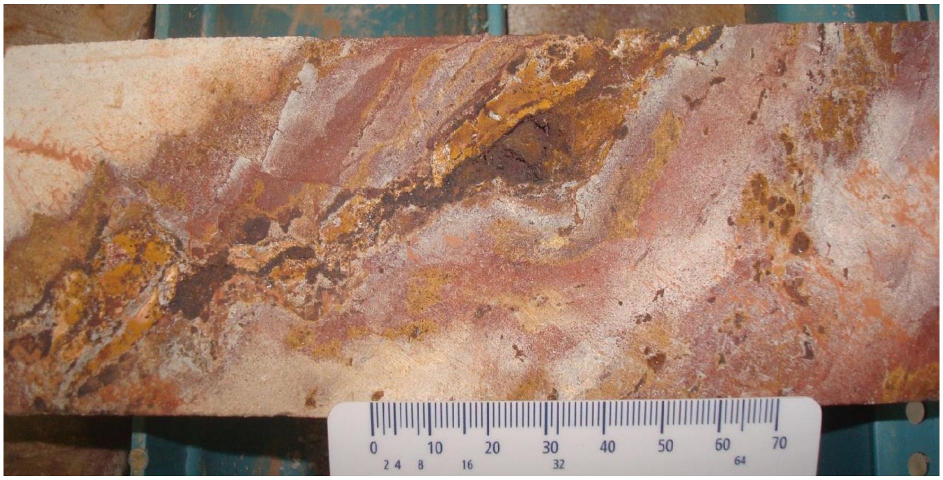

Fig. 3. Intensively altered volcanic rock transformed into quartz-alunite-kaolinite aggregates cross-cut and impregnated by Fe-hydroxides. Illustration of cut drill core from drill hole within the Plavica ore deposit

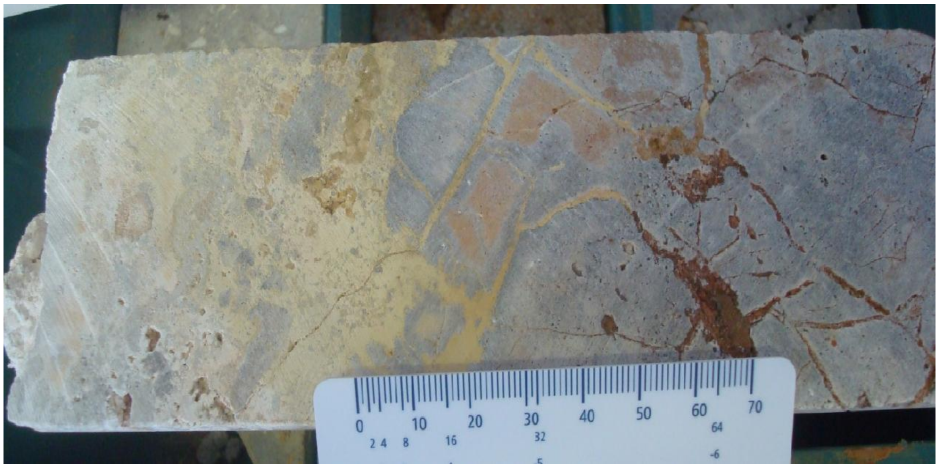

Fig. 4. Seconadry quartzite, intensively alunitized (grey-white mass), cross-cut by Fe-oxide/hydroxide. Illustration of cut drill core from drill hole within the Plavica ore deposit

It is interesting to note that the silex-secondary quartzite except traces of sulphides contained in itself and some quantities of gold (0.1–3.0 g/t Au). Their transitions towards the surrounding rocks are usually not sharp and they gradually transform into the surrounding rocks in form of more or less pronounced silification.

MATERIALS AND METHODS

For the present study three types of raw materials were used: 1) Main samples taken from an exploration drill holes (holes that crossed the zone of oxidation) for technological-metallurgical studies by the hydrometallurgical gold extraction method. The samples were chosen during microscopic screening and proportion of mineral grains ranged from 1 to 4 cm. 2) Ore and petrographic samples were taken from the stored drill core that originated from the immediate vicinity from which the technological-metallurgical samples were taken. These samples were tremendously enriched with iron and locally with Mn-hydroxides volcano-sedimentary rocks, crosscut by the macroscopically visible ore and non-ore mineral aggregates. 3) Veinlets and impregnations of macroscopically visible ore and non-ore minerals occur as relics within oxide mineralizations (main oxide sample).

In addition to those materials were studied certain minerals from primary ore mineralization below the zone of oxidation. From the exploration drill cores were sampled 28 samples from which were prepared 30 polished sections and 16 thin sections. From the main sample were sampled 5 groups of samples with different fractions: over 2 cm, fraction 1.5–1 mm, fraction 1–0.6 mm, fraction 0.6–0.25 mm and fraction <0.25 mm. From the veins and impregnations that exist as relics within the hypergene mineralizations were prepared 30 polished sections.

As far as analyses itself are concerned we would like to stress out that several analytical facilities were used. Both, polished and thin sections for reflected/transmitted light microscopy study were prepared at the laboratory of the Faculty of Natural and Technical Sciences, University "Goce Delčev" in Štip, Republic of Macedonia. Their study under transmitted and reflected light was performed at Carl-ZeissAxiolab-polarizing microscope, with total magnification ranging between 100 and 630 times.

Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analysis on 26 elements was used for 18 mineralized rock samples and different fractions of the main technological-metallurgical sample. Gold content had been determined through the acid extraction in aqua regia (in a optimal molar ratio 1:3 of nitric acid and hydrochloric acid, respectively) and concentrated. Methyl isobutyl ketone later on was analyzed by the ICP-AES.

Microprobe analyses were performed on JEOL-SUPERPROBE 733 characterized by high precision-localization analysis (1–2 μm). Studies were carried out by wavelength dispersion spectroscopy system (WDS) under the following operating conditions: U = 15V, current I = 0.8A; diameter of the electron beam 1 μm. The following standards had been used: synthetic galena – for determining the contents of Pb and S; antimony – for Sb; sphalerite – for Zn; chalcopyrite – for Fe, Cu, and S; synthetic silver – for Ag; arsenopyrite – for As; nickeline (niccolite) – for Ni, and gold nuggets – for Au. Before conducting the aforementioned analysis minerals were studied in COMPO mode, which allowed detection of numerous zonings and inconsistencies in an otherwise homogeneous aggregates in reflected polarized light.

RESULTS AND DISCUSSION

Conducted detailed field activities and laboratory analyses, in particular, ore microscopy and phase mineralogical analysis of samples taken from the oxidation zone clearly confirmed that within these quartz-alunite-kaolinite aggregates there is an association of 31 minerals (Table 1).

Microscopic study showed that in beside the usually transformed and oxide minerals in the zone of oxidation it was determined the presence of a large number of primary minerals such as pyrite, chalcopyrite, tetrahedrite, tennantite, primary bornite, enargite, rarely sphalerite and molybdenite. All those, with lower and higher intensity, were encompassed by the hypergene processes and usually among them were developed secondary minerals and transformed mineral phases such as malachite, azurite, chalcocite, covellite, bornite, goethite, hematite and Mn-hydroxide.

It should be emphasized that in addition to ore-bearing phases with X-ray examinations were encompassed alunite-kaolinite phases, which mainly host the gold-bearing ore, and in the deeper zones and copper ore which in an average ranged from 0.08 to 0.27% Cu. In several places within the quartz-alunite-kaolinite veinlets were confirmed pyrite veinlets corroded by Fe-hydroxides.

The results of the detailed macroscopic-microscopic study of samples from oxidation zone in the Plavica ore deposit generally are synthesized in Table 1, where is made integral grouping of all identified minerals and mineral phases into three groups. The first group includes the major minerals taking overall share of 12–70% of the mineral content in the oxide zone. The second group consists of secondary minerals participating from 5 to 11% of the determined mineral composition of the oxidation zone, and the third group of rare minerals with participation of below 5% of the mineral content in the oxidation zone.

The **main (primary) minerals** are represented by quartz, kaolinite and alunite. They participate in small to micrograined mineral aggregates with one name titles such are quartz-kaolinite-alunite, quartz-alunite, quartz-kaolinite developed along different types of volcano-sedimentary rocks, which had been transformed into secondary quartzites. The dimensions of the separate grains in these aggregates are from 1 mm to 2–3 μm.

Table 1

Mineral composition of rock samples and samples from mine technological specimen from the oxidation zone within the Plavica deposit, Republic of Macedonia

№	Sample №	Laboratory №	Minerals		
			Major (70–12%)	Secondary (11–5%)	Rare (<5%)
1	R_0	RA18939	quartz kaolinite alunite	pyrite	chalcopyrite magnetite
2	R-0	RA18940	quartz kaolinite alunite	pyrite pyrolusite	chalcopyrite magnetite
3	R-10	RA18941	quartz kaolinite alunite	pyrite	chalcopyrite magnetite malachite
4	R-11	RA18942	quartz kaolinite alunite	pyrite bornite	chalcopyrite magnetite enargite malachite
5	R-12	RA18943	quartz kaolinite	alunite pyrite	chalcopyrite malachite
6	R-13	RA18944	quartz kaolinite alunite	pyrite	chalcopyrite Zn-tennantite
7	R-30	RA18945	quartz kaolinite alunite	pyrite chalcocite	chalcopyrite Zn-tennantite
8	R-51	RA18946	pyrite	–	chalcopyrite quartz alunite molybdenite kaolinite siderite
9	R-52	RA18947	kaolinite quartz sericite microcline	chalcopyrite alunite covellite chalcocite	molybdenite
10	R-55	RA18948	quartz kaolinite goethite	pyrite alunite malachite	chalcopyrite enargite
11	R-56	RA18949	quartz kaolinite goethite	pyrite alunite	chalcopyrite bornite
12	R-57	RA18950	quartz alunite	Illite (montmorillonite) pyrite hematite maghemite goethite	dolomite
13	R-58	RA18951	galena sphalerite	–	anorthoclase dolomite anglesite
14	GP- 3	RA18953	quartz kaolnite	bornite chalcocite malachite	sericite pyrite

Note: Mineral diagnostics resulted from macroscopic-microscopic and roentgen structural study of samples from hypergene products, where had been observed vein relics or impregnations of ore and non-ore primary minerals.

The **secondary minerals** are presented by primary (mainly pyrite and Cu-bearing pyrite) as well as by secondary minerals such are goethite, chalcocite, hematite, bornite, covellite, malachite and azurite. Pyrite and Cu- containing pyrite are mainly relics along which develop secondary minerals: chalcocite, hematite, goethite, bornite, malachite and azurite. As a result of intimate intergrowth were formed interesting and complex mineral aggregates: chalcocite-covellite, covellite-malachite, covellite-chalcocite-malachite, azurite-chalcocite, azurite-covellite-chalcocite, goethite-hematite, etc. The dimensions of pyrite and Cu- containing pyrite grains are between 1 mm and a 7–8 µm.

Rare minerals with participation below 5% in the oxide ore are mainly relics of chalcopyrite, tennantite-tetrahedrite and enargite-chalkopyrite-luzonite aggregates. These aggregates are of allotriomorphic structure, zonal wreath-like, veinlet-like and impregnated character. Boundaries between minerals sometimes are unconventional. In places on primary sulphide-sulphosalt aggregates are lying hypergene minerals represented by chalcocite, bornite and covellite, which by the degree of distribution refer to secondary minerals in the zone of oxidation. The dimensions of such polymineral hypergene aggregates range from 0.25 mm to 1–2 µm.

Therefore, from the study of samples from the zone of oxidation is concluded that it is represented by secondary quartzites of alunite-kaolinite and sericite type with relics of sulphide and sulphosalt minerals on which were developed hypergene minerals: malachite, azurite, chalcocite, bornite, covellite, iron hydroxides and oxides.

Quantitative contents of particular minerals determined in the oxidation zone are shown in the Table 2 and Figures 4 and 5, where are shown in a histogram way the percentages of major minerals in this zone and presence of copper in separate mineral phases separately.

Table 2

Percentage of minerals in the oxide zone of the Plavica deposit, Republic of Macedonia

Minerals	Percentage content of minerals in samples													Average content, %	At 100%
	1	2	3	4	5	6	7	8	9	10	11	12	13		
Quartz	61	60	52	53	60	61	56	22	36	36	36	54	32	47.66	47.95
Kaolinite	13	14	17	16	16	15	17	–	23	22	22	16	–	14.53	14.62
Alunite	12	13	12	13	11	12	14	9	8	8	21	8	31	13.23	13.31
Pyrite + (Cu-bearing pyrite)	6	7	10	9	8	8	9	–	9	9	11	4	–	6.92	6.96
Chalcopyrite + (enargite, tennantite-tetrahedrite, bornite, chalcocite, covellite)	3	3	4	4	3	3	3	13	2	2	–	–	–	3.07	3.08
Magnetite	3	2	3	3	–	–	–	–	–	–	–	–	–	0.84	0.84
Malachite	1		1	1	1	–	–	–	–	–	–	–	–	0.30	0.30
Molybdenite	–	–	–	–	–	–	–	2	–	–	–	–	–	0.53	0.53
Siderite	–	–	–	–	–	–	–	3	–	–	–	–	–	0.23	0.23
Sericite	–	–	–	–	–	–	–	–	–	–	–	5	–	0.38	0.38
Goethite	–	–	–	–	–	–	–	–	22	22	–	11	7	4.76	4.78
Hematite	–	–	–	–	–	–	–	–	–	11	11	–	23	3.46	3.48
Maghemite	–	–	–	–	–	–	–	–	–	6	6	–	–	1.23	1.23
Illite	–	–	–	–	–	–	–	–	–	11	11	–	–	1.69	1.70
Dolomite	–	–	–	–	–	–	–	–	–	3	–	–	5	0.61	0.61
TOTAL														99.39	100.00

In regards to the mineralogy and dominant presence in the association in a decreasing manner are quartz, kaolinite, alunite followed by pyrite, while of Cu-bearing minerals occur Cu-bearing pyrite, chalcopyrite, enargite, tennantite, tetrahedrite, chalcocite, covellite, malachite etc. (Figure 5)

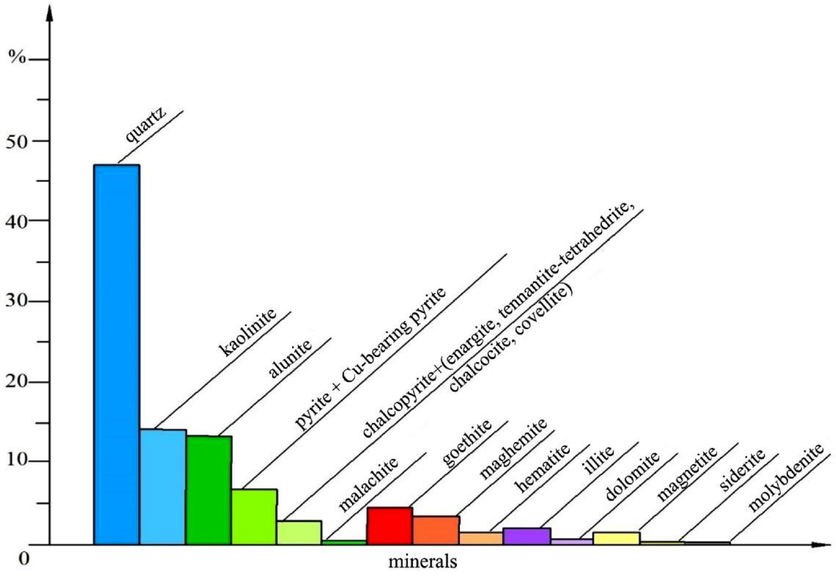

Fig. 5. Mineral composition of the oxide zone, Plavica ore deposit

However, in regards to quantitative presence of separate phases of mineralization, the most common are primary sulphide minerals with approximately 65%, secondary sulphide minerals with 25% and oxide minerals with ~10% (Figure 6).

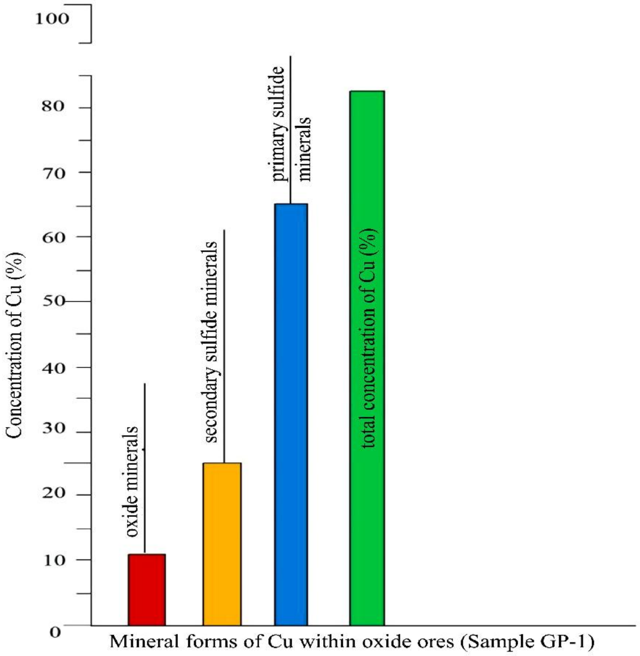

Fig. 6. Mineral forms of Cu in oxide ores, main sample GP-1, Plavica ore deposit

In the Table 3 is shown the mineral composition of oxide ore within the Plavica ore deposit, where the asterisk marks minerals that were determined as relics in the primary sulphide phases.

Table 3

Mineral composition of oxide ore in the Plavica deposit, Republic of Macedonia

Minerals		
Major (70–12%)	Secondary (11–5%)	Rare (<5%)
quartz	pyrite*	chalcopyrite*
kaolinite	goethite	Zn-Sb-tennantite*
alunite	chalcocite	Zn-tennantite *
sericite	hematite	Fe-Zn-tennantite*
	bornite	siderite
	covellite	enargite*
	malachite	Zn-enargite*
	azurite	luzonite*
	Cu-bearing pyrite*	native gold –finegrained and impregnated within Fe-hydroxides
	montmorilonite	dolomite
		molybdenite
		galena*
		sphalerite*
		anglesite
		diaspore?
		maghemite
		magnetite*

Note: 1. Table is prepared according to results obtained for each analyzed sample in Table 1 and results from the microprobe analyses and reflected light microscopic study.
2. With * sign are marked relics of primary minerals

Gold content, its localization in the preferable specific mineral aggregates and shape of the presence were quite different and numerous. The accumulation of gold becomes more preferably among various mineral aggregates from the zone of oxidation. For the determination of gold and its connection to them quantitatively were analyzed following types of samples: main ore sample; portions of the main ore sample and macroscopically different Fe-hydroxide aggregates and relics of primary sulphide mineral aggregates (relics of complex pyrite aggregates made of crystalline pyrite and colomorph pyrite). Also, in this study were used of relic primary sulphide minerals and sulphosalts in reflected light, making it possible to determine separate gold forms in them.

The tables below (Tables 4 and 5) show that the gold in the zone of oxidation is related mainly to the Fe-oxide type of mineral aggregates composed of goethite, hematite and small quantities of quartz. The content of gold in them reaches 6.8 g/t while in aggregates made mainly of quartz and Fe-hydroxides varies from 1.45 to 2.5 g/t. An average content of gold in the main oxide sample was about 2 g/t. Analyzed waste products from the main sample after cyanidation contain about 0.54 g/t Au, which means that during the hydrometalurgical cyanide extraction is not achieved satisfactory gold extraction, which is probably related to the interfering role of alunite, kaolinite and Zn-containing relics of tennantite-tetrahedrite (Figures 7, 8) and Zn-enargite grains as well as along sphalerite grains (Figure 9). Part of the gold appears as fine dispersed among pyrite crystal aggregates. After washing out clay kaolinite-alunite mass of waste products pyrite crystal aggregates were analyzed (Figure 10). It was found that the gold therein ranges from 0.546 to 0.680 g/t. Relic pyrite aggregates with enclosed colomorph grains and aggregates, are characterized by zonal inclusion of copper instead of iron in the pyrite formula. The copper contents there range from 0.20 to 0.78% Cu.

Table 4

Assays for gold by method of inductively coupled plasma of different fractions of sample for laboratory-technological studies and their waste from the Plavica deposit, Republic of Macedonia

Assay №	Sample №	Sampling point	Au. g/t
1. Main ore sample	Ro	Main oxide ore sample	1.54
	R-0		1.38
	R-10		1.89
	R-11		1.50
	R-12		1.52
	R-13		1.41
	R-30		1.38
2	R0 (PA 18939)		1.63
3	R-200		1.87
4	200/2 + 0.8 mm		0.85
5	200/3 (– 0.8 mm)		0.60
6	4	PNDD 0.04/7.70	0.36
7	5	PNDD 0.4/153.70	1.25
8	204		1.54
9	205		0.14
10	206		0.36
11	207		0.40
12	208		0.66
13	209		1.99
14	210		0.12
15	211		>0.05
16	R-54	PNDD 013/58.30 m (pyrite agregate)	0.80
17	R-53-2	PNDD 014/108.60 m (Fe-hydroxide)	4.56
18	PRO-1*	Primary ore flotation waste	0.16

Note: 1) Standard used: ATT BM 03/2011; 2) Conditions of study: T – 21.7 ± 0,1°C; 3) Samples № 10 to 17 had been sampled in 2013; 4) Sample № 18 is sulphide ore flotation waste (flotation had been performed at Nuclear Insitute in Belgrade, Serbia)

Analyzed micrograins of copper sulphosalts coming with oxidized chalcopyrite and relics non-oxidized enargite have proved that are typical Zn-bearing tennantite without Sb (Table 5). Only in one aggregate from an oxidation zone and higher hypsometric part were found Zn-bearing tennantite with significant concentrations of Sb, up to 5.43% Sb. In accordance to that composition, the analyzed copper sulphosalts are located in the middle of the $Cu_{12}As_4S_{13}$-$Cu_{12}Sb_4S_{13}$ mineral group.

Although in advance on the basis of these analyzes, it can be concluded that primary ores within the Plavitsa deposit at depth are characterized by the presence of Zn-tennantite while in the upper part horizons more often occur Sb-bearing Zn-enargite. There as well were recorded increased contents of silver. These facts can be used for preliminary (topo-mineralogical) differentiation of erosion level, which couls help to recover some other surface or shallow gold-sulphide mineralizations of quartz-alunite type in the Kratovo-Zletovo volcanic area.

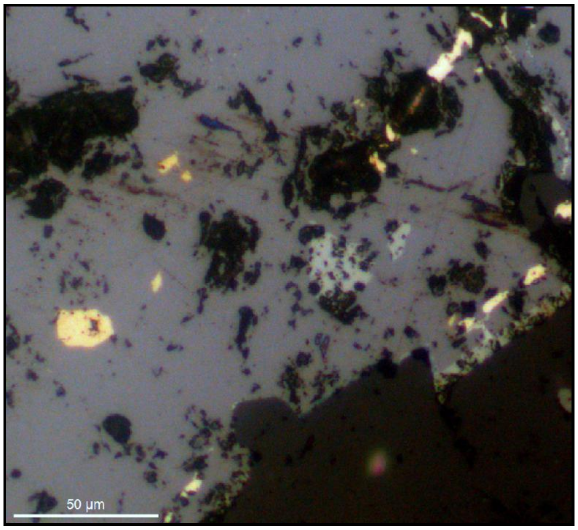

Fig. 7. Tennantite (light grey) developed in sphalerite (grey). There can be seen relict of light yellow mineral phases with gold (left part of figure)

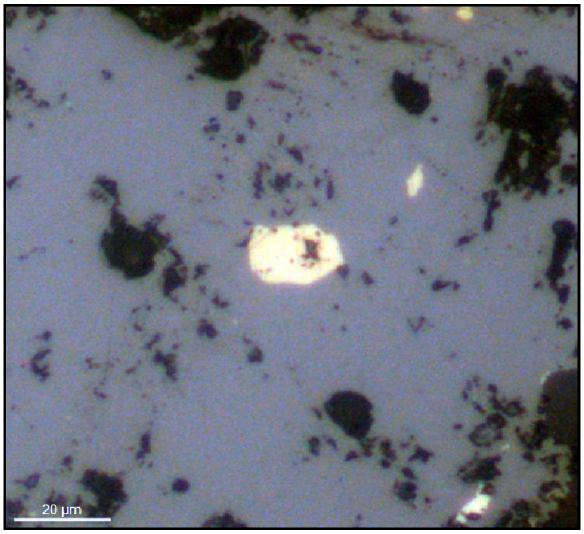

Fig. 8. Detail from Figure 7 within gold mineral phase occur hypergene bornite (purple)

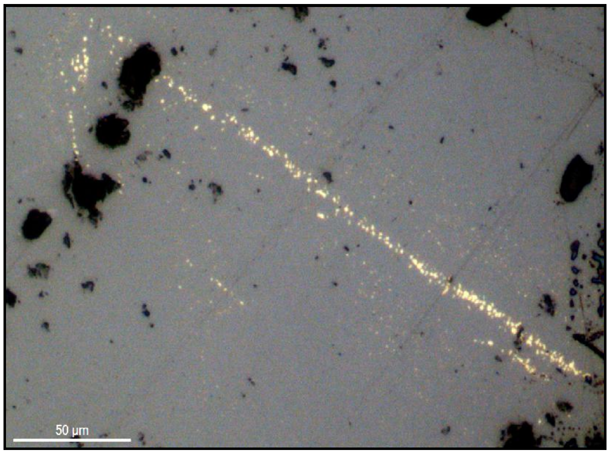

Fig. 9. Un-diagnosed auriferrous mineral phase developed linearly in sphalerite matrix (grey). Dark minerals are quartz relics

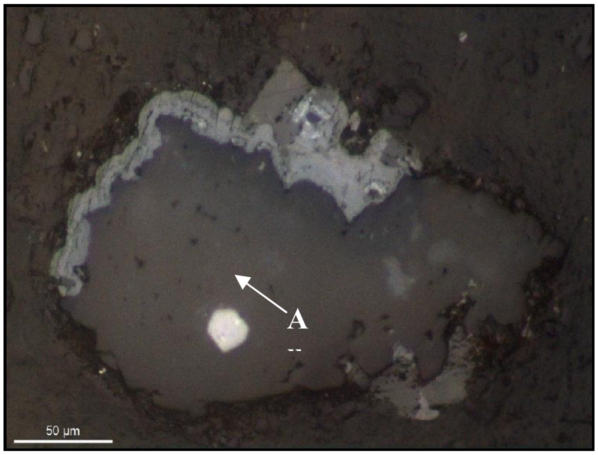

Fig. 10. Corrosion development of hypergene minerals (rim aggregates) on the periphery of quartz in quartz-kaolinite-alunite aggregate. Within automorph quartz grain (yellow-white) occur micron gold-bearing (light yellow)

Gold-bearing capacity of primary sulphide zone and chemistry of some primary sulphide and sulphosalt minerals is defined on the basis of a sulphide sample taken for flotation analysis to produce a copper concentrate. The primary sulphide sample was analyzed for gold and copper and their respective values were 0.31% Cu and 0.27 g/t Au. Study under reflected light of this sample (after removal of the clay fraction) showed that beside pyrite, chalcopyrite, enargite, luzonite, quartz alunite and kaolinite it contains several secondary minerals-chalcocite, malachite, covellite, bornite, brochantite, goethite, hematite, maghemite and hematite. This means that these minerals will go to waste during the flotation regime.

The results of the analysis of this waste have shown that the content of copper and gold is high – respectively 0.193% Cu and 0.160 g/t Au. One part of the copper concentrations are associated with the presence of secondary minerals, while an another part we relate with the phenomena of isomorphism in cationic part of pyrite in place of iron. We made 5 points of microprobe analyses of pyrite, which shows that the copper content in them varied from 0.20 up to 0.78% (this is a fundamentally new moment that should be reckoned with industrial-economic evaluation of the deposit).

Therefore, part of the copper will not be able to separate the so-called copper concentrate flotation of primary ores and probably will go to waste, where pyrite dominates. This arises the need for special consideration and comprehensive study of waste from the flotation of primary ores. It is worth paying attention to the possibility of flotation of Zn-containing tennantite and Zn-containing enargite who come intimately connected with the other primary sulphide minerals and likely will prevent the flotation of the main copper minerals – chalcopyrite and enargite. In Table 9 are given the results of the microprobe analyses of four mineral grains from mineral aggregates, where two of them are typical Zn-containing enargite, and two a pure enargite with real chemical composition close to theoretical. The content of zinc in the Zn-containing enargite is between 6% and 7.56% Zn, representing respectively 0.35 and 0.45 zinc formula unit, which complement the three copper formula units. Such enargite high zinc contents are identified also into samples from the peak of the primary ore zone. This, together with the established Sb-containing tennantite also characteristic of high hypsometric levels of the integral oxide-primary-gold-copper vertical column means that in these levels the content of antimony in mineral phases of the line tennantite-tetrahedrite increases, while in the lower horizons-deposited almost pure arsenic representatives of this series and pure enargite, which formula is close to theoretical.

Table 5

Quantitative analyses of the Au-sulphide sample for laboratory technological studies (2) and waste of these studies (1) – Plavica deposit, Republic of Macedonia

№	Sample	Cu, %	Au, g/t	Concentration of element (mg/kg)											
				Ag	As	Bi	Cd	Co	Mn	Mo	Ni	Pb	Sb	Sn	Zn
1	Waste sample (1)*	0.193	0.16	1.8	160.0		4.8	18.4			9.0	877.2	<10		104.0
2	Ore sample (1)	0.31	0.27	3.4											

* Waste sample was obtained from ore sample flotation waste at Nuclear Insitute in Belgrade, Serbia

Within this study of mineral composition and particular minerals and mineral phases, within three separate zones of the Plavica deposit, were encompassed copper minerals with emphasized representation in the deposit and part of them are carriers of copper ore (enargite, chalcopyrite), while another represent sulphosalt phase (tetrahedrite-tennantite) and poor primary mineralization where beside chalcopyrite an important place occupies pyrite. In the discussion below are shown compositions of these minerals in the Plavica deposit with a proper photodocumentation.

Some of the enargite mineral grains, determined under the polarized optical microscope have been analyzed under the microprobe (Figure 11, points 1–4). Their chemical composition (Table 6) have shown slight discrepancies from the stoichiometric enargite composition (Cu_3AsS_4) in standards. Namely, in points 1 and 2, close vicinity of sphalerite and chalcopyrite, two analyzed enargite grains caused certain impurities in form of Zn and Fe to occur in its composition, substituting part of copper positions. Although the analysis of point 3 was quite close to the standard ones, the point 4 indicated slightly increased presence of antimony.

Microscopic observations in regards to occurrence of tennantite in samples from the Plavica deposit in the best manner were confirmed by electron microprobe analyses (Table 6; Figure 12; points 5 and 6).

As may be seen from the Table 6, tennantite composition is not quite stoichiometrically ideal due to decreased copper, iron and arsenic values at the expense of increased concentration of zinc. Here we would like to give an accent to the fact that the presence of tennantite within this part of the Plavica deposit, beside its importance in regards to mineralogical diversity, stress out that there were two metal stages, an early Cu-rich, Au-poor stage, dominated by enargite-luzonite, and a late Au-rich, Cu-poor stage, associated with intermediate-sulphidation-state sulphides such as tennantite-tetrahedrite and chalcopyrite, and telurides as it was confirmed for genetically similar deposits elsewere (e.g. El Indio, Lepanto; see Arribas, 1995). The transition from quartz-alunite-pyrite alteration to enargite-pyrite and finally to tennantite-tetrahedrite, indicates that the fluid progressively became more reduced and less acid.

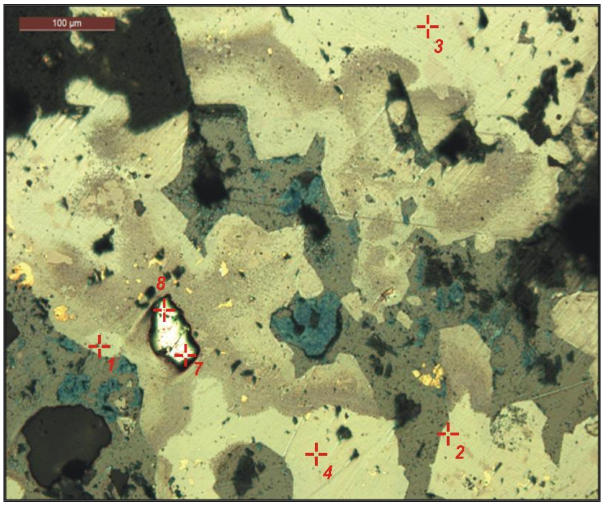

Fig. 11. Complex mineral aggregate of enargite (olive grey matrix) with famatinite (greyish cloud-like impregnations all over enargite), sphalerite (dark grey massive grains), pyrite (single white color grain), chalcopyrite (yellow color disseminations within enargite and sphalerite) and chalcocite-covellite (all sort of blue minerals along the sphalerite grains).
Plane polarized light, Magnif. × 200 II

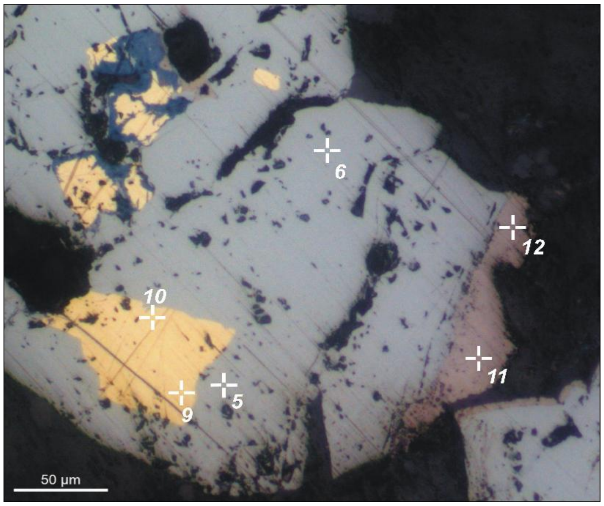

Fig. 12. Complex mineral aggregate of tennantite (grey matrix) with bornite (purple, occupies left margin of the tennantite), chalcopyrite (massive mineral grains, yellow color) and chalcocite-covellite (all sort of blue minerals corroding along the chalcopyrite grain).
Plane polarized light, Magnif. × 200 II

Table 6

Chemical composition of representative minerals from the Plavica deposit (%)

Element	*Chemical analyses (%)*											
	1	2	3	4	5	6	7	8	9	10	11	12
Cu	40.90	40.76	46.54	46.48	39.67	40.58	3.99	0.00	35.01	34.96	61.68	62.01
Fe	1.12	0.97	0.24	0.15	1.55	0.21	43.55	46.72	31.02	30.12	11.21	11.40
Zn	6.00	7.56	0.24	0.00	8.99	9.06	0.00	0.00	0.00	0.00	0.00	0.00
Ag	0.46	0.54	0.09	0.13	0.08	0.87	0.00	0.00	0.00	0.00	0.00	0.00
As	19.55	19.86	17.77	17.21	15.51	20.30	0.00	0.00	0.00	0.00	0.00	0.00
Sb	0.55	0.46	1.08	1.33	5.43	0.88	0.00	0.00	0.00	0.00	0.06	0.00
S	29.60	29.51	34.14	34.60	28.73	29.01	52.52	52.78	34.96	34.29	26.57	25.67
∑	98.18	99.60	100.10	99.90	99.96	100.91	100.06	99.50	100.99	99.37	99.52	99.97

Note: Analysis 1 – (Zn-enargite) $(Cu_{2.57}Fe_{0.08}Zn_{0.35})_{3.00}As_{1.02}S_{3.98}$
Analysis 2 – (Zn-enargite) $(Cu_{2.57}Fe_{0.08}Zn_{0.35})_{3.18}As_{1.06}S_{3.77}$
Analysis 3 – (enargite) $Cu_{2.89}As_{0.91}S_{4.19}$
Analysis 4 – (enargite) $Cu_{2.57}(As_{0.086}Sb_{0.03})S_{4.21}$
Analysis 5 – (tennantite) $(Cu_{9.40}Fe_{0.06}Zn_{2.10})_{11.56}(As_{3.14}Sb_{0.60})_{3.74}S_{13.43}$
Analysis 6 – (tennantite) $(Cu_{9.32}Zn_{2.07})_{11.39}As_{4.29}S_{13.32}$
Analysis 7 – (pyrite) $(Fe_{0.83}Cu_{0.07})_{0.91}S_{1.98}$
Analysis 8 – (pyrite) $Fe_{0.98}S_{1.97}$
Analysis 9 – (chalcopyrite) $Cu_{1.01}Fe_{1.01}S_{2.00}$
Analysis 10 – (chalcopyrite) $Cu_{0.99}Fe_{0.99}S_{2.00}$
Analysis 11 – (bornite) $Cu_{4.69}Fe_{0.97}S_{4.00}$
Analysis 12 – (bornite) $Cu_{4.71}Fe_{0.99}S_{4.00}$

The analysis of the most common mineral within the Plavica deposit, pyrite, in general have shown close to the standard values (Table 6). However, as it can be seen from the results (Table 6), there are slight discrepancies from the almost ideal stoichiometric values of pyrite due to copper impurities in the mineral composition (up to 3.99% Cu). Copper likely entered the structure of pyrite through a coupled substitution (Chouinard et al., 2005).

The major Cu-sulphide, chalcopyrite in regards to its chemical composition (Table 6 and Figure 12, points 9 and 10) have shown pure stoichiometric composition ($CuFeS_2$) without any impurities in form of additional elements (Table 6). Also, as already mentioned it occur as small or coarse grained, quite often encompassed by the processes of replacement of latter sulphosalt phases (covellite, chalcocite, tennantite etc.).

The very same said for the chalcopyrite stands for bornite, too. Microscopic observations in regards to occurrence of bornite in samples from the Plavica deposit in the best manner were confirmed by electron microprobe analyses (Table 6; Figure 12; points 11 and 12). As may be seen from the Table 6, bornite composition is quite stoichiometrically ideal due to absence of any impurities in form of some additional metals beside the copper, iron and sulphur (excluding 0.06% Sb at point 11 in Table 6).

CONCLUSION

Main copper and gold mineralizations in the Plavica ore deposit are related to the strongly altered silicified, alunitized and kaolinitized volcanic rocks. Two mineralized zones were distinguished at depth. The first zone represents typical series of hat-like alunitized secondary quartzites, strongly oxidized and Fe-hydroxides developed within. Thickness of so-called oxide zone is about 140 m. The second mineralized zone is represented by poor Cu-Au ores of sulphide and sulphosalt type. This zone occupies altered volcanic rocks, which are brecciated and cataclized and with exploration followed up to depth of 500 m.

Alunitized secondary quartzites, as the most representative rocks in the oxide zone, are characterized by average gold contents of 2 g/t Au. However, main gold concentrations from 1.8 up to 5.85 g/t Au are localized in settings with increased Fe-hydroxide presence. Copper contents at places reaches up to 0.76% Cu, but however in average is more narrower range of 0.2 to 0.25% Cu and it is related to the cementation zone where chalcocite, covellite and at places bornite and enargite dominate, as well as in zones of primary sulphide mineralizations with dominant chalcopyrite followed by primary enargite and bornite.

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Резиме

Cu-Au МИНЕРАЛИ И ТРАНСФОРМИРАНИ МИНЕРАЛНИ ФАЗИ ВО ЗОНАТА НА ОКСИДАЦИЈА ВО РУДНОТО НАОЃАЛИШТЕ ПЛАВИЦА, ИСТОЧНА МАКЕДОНИЈА

Тодор Серафимовски[1], Гоце Златков[2], Горан Тасев[1], Виолета Стефанова[1]

[1]Факултет за природни и технички науки, Институт за геологија, Универзитет "Гоце Делчев" во Штип,
Бул. Гоце Делчев 89, 2000 Штип, Република Македонија
[2]Генезис Ресурси Лтд., Лермонтова 3/2, 1000 Скопје, Република Македонија
todor.serafimovski@ugd.edu.mk

Клучни зборови: оксидациона зона; минерални фази; секундарни кварцити; Cu-Au минерализација

Во рамките на трудот се презентирани најновите минералошки и хемиски испитувања на поединечните минерали и минерални фази од зоната на оксидација и делумно примарното сулфидно орудување во наоѓалиштето на Cu-Au Плавица. Оксидационата зона во ова наоѓалиште претставува систем од таканаречените шапки од секундарни алунитизирани кварцити интензивно оксидирани и претставени со жиличести и мрежесто развиени оксиди и хидроксиди на железо. Основната карактеристика на оваа зона се интересните содржини на злато. Најголемиот дел од утврденото злато во алунитизираните железни кварцити е со содржина од 1,80 до 5,85 g/t Au. Златото честопати оди и како самородно злато, најчесто по железните хидроксиди, а наместа и како фино дисперзирано во пиритите. Таму неговата содржина варира од 0,56 g/t до 0,60 g/t Au. Минералниот состав на оксидационата зона е доста обемен (околу 31 минерал) и како главни со доминатно учество до 70% се кварцот, алунитот, каолинитот и серицитот, второстепени минерали со учество до 11% се пирит, гетит, халкозин, хематит, борнит, ковелин, малахит, азурит и како ретки минерални фази со учество под 5% се јавуваат халкопирит, тетраедрит, тенантит, енаргит, галенит, сфалерит и др.