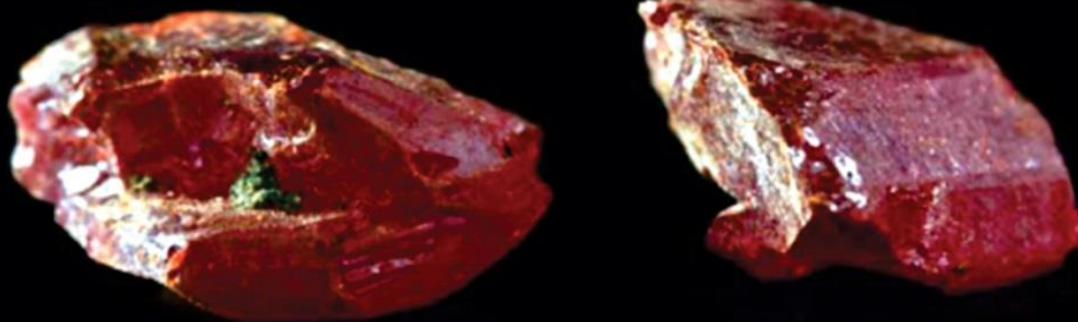


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## COMPOSITION OF SOME MAJOR MINERAL PHASES FROM THE PLAVICA EPITHERMAL GOLD DEPOSIT, EASTERN MACEDONIA

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**Abstract:** High-sulphidation epithermal gold has been determined and studied in the Plavica deposit, which is an integral part of the Kratovo-Zletovo volcanic area. 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 acid-sulphate 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. Most of these accessory sulphide mineral phases within this study were observed under state of the art polarized optical microscope, and the electron microprobe, which results are presented in detail in this paper. For illustration we want to emphasize that in pyrite were found increased concentrations of copper and zinc and less silver, then enargite with increased zinc concentrations (0.24–7.56 Zn), antimony (0.46–1.33% Sb) and silver (0.09–0.54% Ag), tennantite with increased iron (0.21–1.55% Fe), zinc (6.24–9.06% Zn) and silver (0.08–0.87% Ag), while within the molybdenite elevated concentrations were detected for sulfur and iron.

**Key words:** gold; Plavica; mineral phases; composition; high-sulphidation

### 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 (15<sup>th</sup>–17<sup>th</sup> centuries) when gold was extracted for production of coins. In the 20<sup>th</sup> 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 pro-

fessional 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) and Stefanova et al. (2013).

## GEOLOGY

We have to emphasize that 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. 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-sedimentary 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 ignimbrite, stratified volcanic tuff and breccia, dacite-andesite and their pyroclasts as well as quartzlatites that the most often occur as breakthroughs.

**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 Plavica deposit into the explanation that although the most high-sulfidation 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, also.

Volcano-sedimentary rocks (stratified tuff) are well spread on the northern margins of the

Plavica in an elongated belt starting from Slegovo 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 compounds), 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 extensively 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.

Silex-secondary quartzite 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 siliceous ore bodies contain significant amounts of alunite that gradually turns into alunite quartzite. It is interesting to note that the Siliceous-secondary quartzite except traces of sulphides contained in itself and some quantities of gold (0.1–3.0 g/t Au). Their transition towards the

surrounding rocks are usually not sharp and they gradually transform into the surrounding rocks in form of more or less pronounced silification.

At the highest parts of the Plavica at several locations there are increase quantities of diluvial sediments (Beglički Livadi and Dolno Kadiski) in streams of northern slopes and remains of the ancient river terraces.

## METHODOLOGY

The morphology and composition of gold and associated minerals were studied on a JEOL SEM JSM-6010PLUS InTouchScope at the Faculty of Geology and Geography, Sofia University, Bulgaria. The JEOL SEM JSM-6010PLUS InTouchScope had the following features: resolution in High Vacuum mode of 4 nm (20 kV), 8 nm (3 kV), 15 nm (1 kV) and Low Vacuum mode of 5 nm (20 kV) BSE, accelerating voltage of 500 V to 20 kV, magnification ranged from  $\times 5$  to  $\times 300,000$  it had LV detector with multisegment BSED (as a stan-

dard) and optionally equipped with LV-SED, while LV pressures were from 10 to 100 Pa. The LGS type stage was equipped with Eucentric goniometer ( $X = 80$  mm,  $Y = 40$  mm,  $Z = 5$  mm – 48 mm)  $R = 360^\circ$  (endless) possible tilt  $-10 \pm 90^\circ$  (by computer-controlled 2 or 3-axis motor drive). The standard EDS system (silicon drift detector technology), which included possibilities for spectral mapping, multipoint analysis, automatic drift compensation. The JEOL was equipped with 3D Three Dimensional Image Software MP – 45030 TDI, also.

## MINERALIZATION

### *Morphology of ore bodies*

Since the preparation of the first elaborate for calculation of ore reserves in the Plavica-Zlatica deposit (Terzić et al., 1986) has been determined that beside extensive exploration workings it is hard to explain the spatial position of the mineralization, its boundaries in regards to adjacent host rocks and size of the ore deposit. This fact have been confirmed by extensive, disseminated mineralization, where distribution of particular ore components and their quantitative ratios are very variable at short distances.

However, potential of that widely altered and mineralized area is indisputable and defining the various morphological types mineralization will likely to go in phases, as it was confirmed by recent research on the northeastern parts of the Plavica deposit there have been found gold epithermal mineralization of high sulfidation related to sinter-secondary quartzite, oxidized breccias and stratified tuffs.

In general, the ore mineralization within the Plavica deposit, is deposited in empty spaces in fault-crack systems, veins, veinlets and metasomatically has been impregnated in adjacent hydrothermally altered volcanic rocks. Mineralization of impregnated type is the most common near the cracking systems.

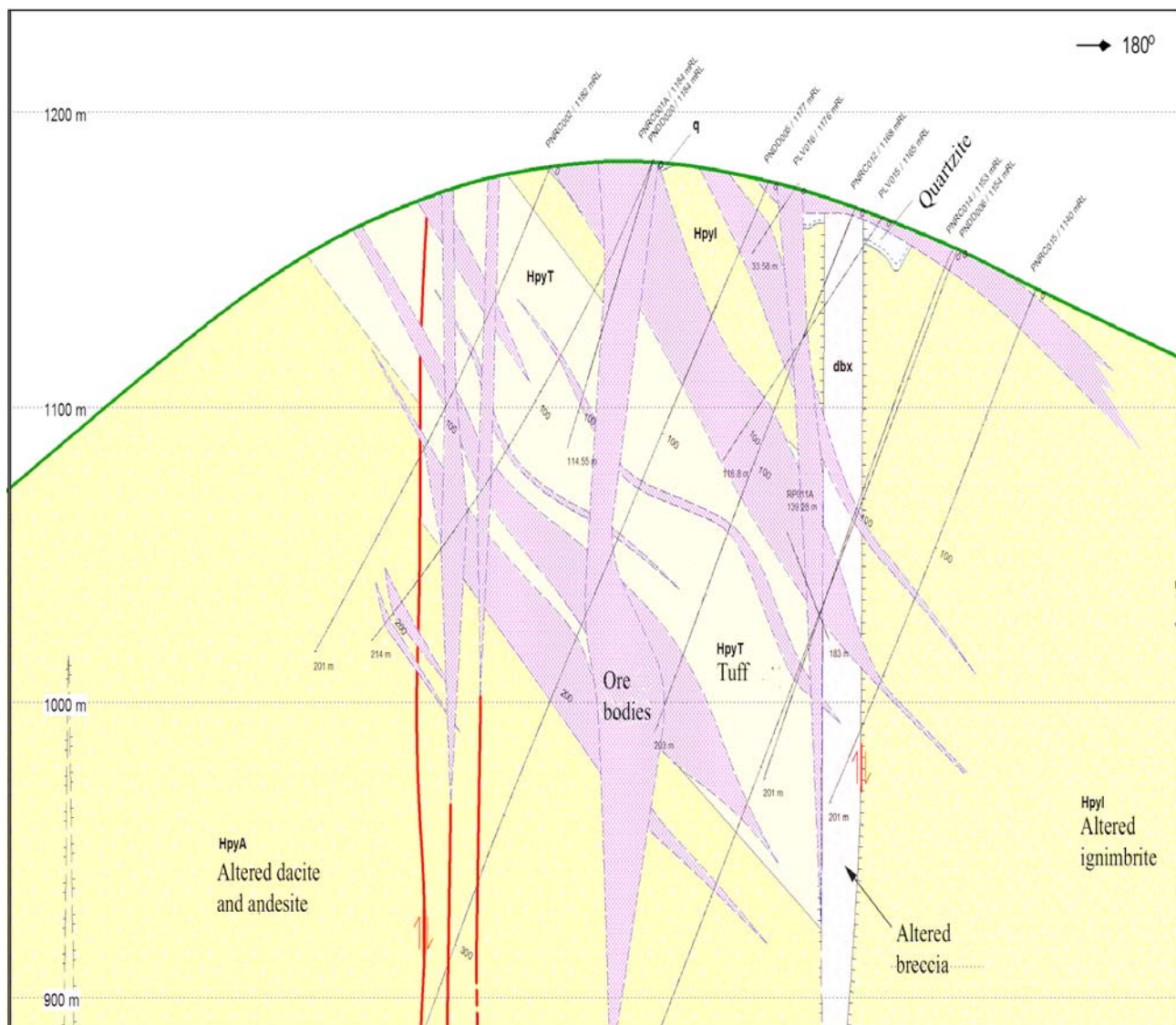
Mapping has revealed the presence of concentric, arcuate fractures around the Plavica deposit, suggesting the presence of a small caldera ~1,5 km across. The presence of a caldera is also strongly supported by the circular form of the outcrop patterns and geomorphology (Figure 1). In addition, there are abundant fractures with a NW–SE, ENE–WSW and E–W strike, and some indication of a radial distribution. It is these fractures in the central parts that host the metallic mineralization.

The mineralization occurs in four distinct settings: (i) stockwork and disseminated Cu–Au (+Mo, Ag) mineralization occurs in the central and deepest part of the system. It is present over an area of 6 km<sup>2</sup> and was still reported at depth in the deepest drill hole (950 m below surface); (ii) veins of quartz, pyrite, sphalerite and enargite ( $\pm$  gold) occur at intermediate levels and appear to be superimposed on the stockwork. Old workings in the Zlatica area followed these enargite veins for distances up to 200 m and show that they had a thickness from 0.7 to 5 m and a content of Cu around 2% and Au at 1 ppm. They seem to occur where the NW–SE structures intersect E–W veins, mostly in the northern part of the deposit (Figure 1) (iii) silica bodies occur peripheral to the central zone. These bodies consist of quartz plus some opal and



are sub-vertical in orientation. Both massive and 'vuggy' silica occurs, the former being widespread in the Crn Vrv region where it is quarried for industrial purposes. These bodies have a maximum development at depths of 100 m but extend to greater depths where they taper out (usually at 400 m). They contain elevated gold levels (sometimes from 1 to 10 ppm) as well as alunite, jarosite, native sulphur and kaolinite. The silica bodies appear to be related to E–W fractures (Figure 1) and crosscut both the stockwork and the enargite veins. In some places, the silica bodies are themselves cut by breccias containing angular silica clasts (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 simi-

larity to the larger Pb–Zn veins worked in the nearby Zletovo mine, but are much smaller. There are also some U-rich veins, although their exact relationship with the Plavica system is unclear. We would like to point out that the detailed exploration performed by the Genesis Resources International DOOEL Skopje, which study was concentrated mostly in the northeastern part of the Plavica deposit (mineralized area known as Plavica-Zlatica) and hill top where dominate secondary quartzites. Those extensive exploration activities defined one new Cu-Au mineralization type where dominate epithermal gold of high sulfidation with representative elongated lens-like ore bodies, which follows the structural controlling forms (Figure 1).



**Fig. 1.** Geological cross section through the Plavica deposit, eastern Macedonia with a display of morphological form of particular gold ore bodies (Serafimovski et al., 2014)

From the geological cross-section (Figure 1) can be seen the very specific form of occurrence of the ore mineralization in comparison to up to date known types of vein and impregnation mineralization.

#### *Mineralogy and alteration*

The mineralogy of the Plavica deposit is complex and several paragenetic stages have been suggested (Ivanov and Denkovski, 1978). The latest data about the mineralogical composition of the Plavica deposit can be found in detailed electron microprobe study of Serafimovski (1993), where the mineral presence and their association has been brought to an higher level of knowledge. Also, later findings of Serafimovski and Rakić (1998, 1999), Alderton and Serafimovski (2007), Stefanova et al. (2013) and Serafimovski and Tasev (2013), contributed to a better understanding of the mineral composition of the Plavica mineral deposit.

With up to date studies has been confirmed that within the PLavica-Zlatica deposit can be found the following ore minerals: pyrite, pyrrhotite, chalcopyrite, magnetite, rutile, scheelite, hematite, molybdenite, galena, sphalerite, bornite, enargite, native gold, melnikovite, tetrahedrite, tennantite, chalcocite, digenite, covellite, proustite, native copper, malachite, azurite, and some other. The latest study have confirmed presence of seligmannite, luzonite, famatinite, petzite, bogdanovite, bezsmertnovite, sylvanite, pearceite, bilibinskite etc. (Serafimovski and Tasev, 2013). Of the non-metallic minerals the most common were quartz, calcite, siderite, oligonite, chalcedony etc.

The common presence of copper minerals, especially the high-sulfidation state sulfosalts enargite-luzonite (White et al., 1995), as well as relatively high-sulfidation state minerals tennantite-tetrahedrite (Barton and Skinner, 1979), was the factors leading us to classify deposit as high-sulfidation type. Also, only scarce sphalerite and arsenopyrite confirmed our conclusion about the type of the deposit.

High-sulfidation mineralization in the Plavica deposit is characterized by the presence of high-sulfidation-state sulfide assemblages dominated by pyrite, sulfosalts (enargite ± luzonite), digenite, bornite and lesser covellite, chalcocite, chalcopyrite, tenantite-tetrahedrite and molybdenite. Traces of colusite (Cu-Sn-V-As-Fe sulfide), sphalerite and galena have also been reported (Serafimovski,

2014) quite similar to genetically same deposits worldwide (Madera, 2000). The most common copper sulfides display a very distinctive replacement sequence from bornite → digenite → chalcocite → exsolution covellite.

Pyrite is by far the most abundant 'ore' mineral present but chalcopyrite, sphalerite, tennantite-tetrahedrite and enargite are also abundant. Gold occurs as small grains dispersed in sulphides (pyrite, chalcopyrite, enargite, galena). Zoning and replacement textures are common, pointing to numerous, discrete, mineralizing events. Petrographical and textural studies suggest the following main stages of mineralization:

- (i) pyrrhotine, pyrite, chalcopyrite;
- (ii) magnetite, hematite, rutile, scheelite;
- (iii) molybdenite, chalcopyrite, pyrite, sphalerite, native gold, tetrahedrite, enargite, bornite;
- (iv) enargite, bornite, chalcocite, chalcopyrite, pyrite, galena, sphalerite, tetrahedrite, tennantite, luzonite, selligmanite, proustite, pearceite
- (v) calcite, barite, siderite (including the Mn-variety, 'oligonite'), hematite (after magnetite – 'martite').

#### *Features of gold in the Plavica deposit*

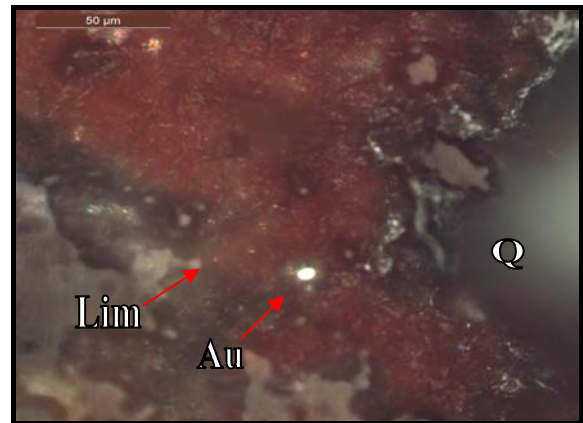
In regards to the mineralization specifics in this part of the studied Plavica deposit of special curiosity is a gold-bearing mineralization that occurs in a variety of morphological forms and spatial presence of native gold and Au-Ag-tellurides. Sometimes native gold can be found along quartz veins of peripheral parts where present are Fe-hydroxides, too. In oxidized parties with dominant Fe-oxide and hydroxide parageneses besides frontal silification often appear later quartz-limonite veins within oxidized breccias, and for transformed Fe-hydroxide aggregates in a such manner (magnetite-hematite-martite-limonite) are related interesting flake-like gold aggregates (Figure 2).

In the another case there are individual grains and elongated aggregates where gold indicates double regular form and resembles a lot to a polyhedron gold. Also, gold occur as flake-like to worm-like aggregates within the limonite-goethite matrix and as a disseminated native gold within regular quartz crystal. Quite often, within the brecciated and silificied rocks, mostly limonitized, can be observed later quartz cavities filled with gold and electrum (Figure 3). These are known as red breccias that macroscopically are fractured and limonitized where in those limonitized parts occur native gold of micron size.





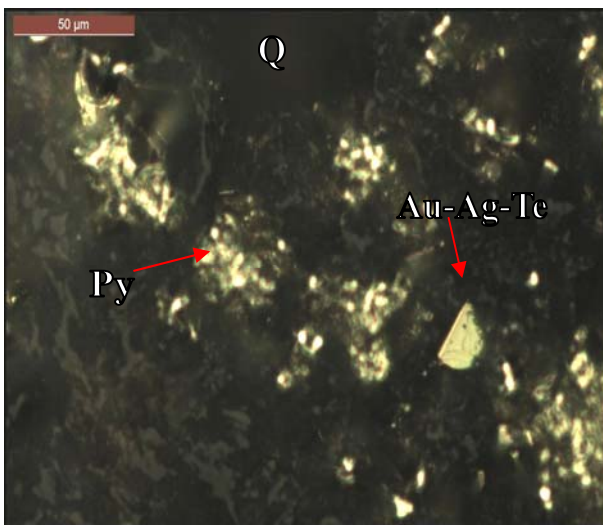
**Fig. 2.** Microphotograph of single horseshoe-like native gold grain within quartz cavity, enclosed within quartz-Fe hydroxide vein (Plane polarized light. Magnif.  $\times 400$  II).



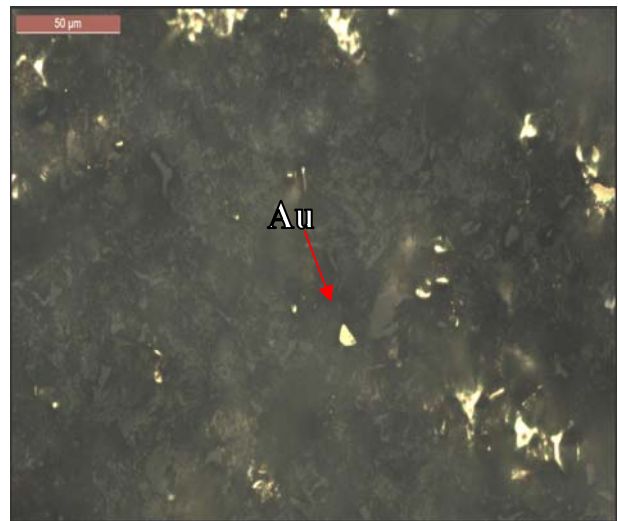
**Fig. 3.** Microphotograph of individual lens-like electrum grain within silica-limonite matrix at the contact with quartz cavity (Plane polarized light. Magnif.  $\times 400$  II).

In some intensely silicified parts where relic pyrites occur were determined telluride of gold and silver (Figure 4), which themselves contain elevated concentrations of arsenic, that causes their polyhedron appearance. In similar areas, but this time directly in aggressively silicified parts was

determined presences of individual grains of native gold in the half-moon like form (Figure 5). Also, in such silicified parties sometimes appear typical gold-bearing forms with representative yellow color, which are usually followed by scattered individual micron size grains.



**Fig. 4.** Microphotograph of multiphase Au-Ag-telluride with certain impurities of arsenic in quartz-pyrite vein (Plane polarized light. Magnif.  $\times 400$  II).



**Fig. 5.** Microphotograph of half-moon like single native gold grain within silicified matrix (Plane polarized light. Magnif.  $\times 400$  II).

A special curiosity in regards to gold were determined late idiomorphic quartz crystals that enclosed usually several gold grains (Figures 6, 7), where gold is diverse in size and form (droplet-like, irregular worm-like up to gold druses).

Very representative micromorphological forms of elongated native gold aggregates can be seen on the rims of the quartz-limonite caverns, where sometimes gold is accompanied by sylvanite. Also,

individual grains of native gold occur in quartz veins or quartz caverns or their marginal sections (Figures 8, 9). Here it is worthwhile to mention that there can be seen micron size grains of native gold occurring in typical teardrop shapes representative for higher levels of the epithermal ore-bearing system.

At some particular locations gold occur in large and beautiful aggregates (Figure 9), which

are outside the veinlets, but within silicified parts. We would like to want to emphasize that the gold in these parts is varied in shape and size, but the most representative are allotriomorphic aggregates and especially feathery-like form aggregates. At some places in relic grains of idiomorphic pyrite idiomorphic is found some native gold in it. Few times we noticed presence of native gold in repre-

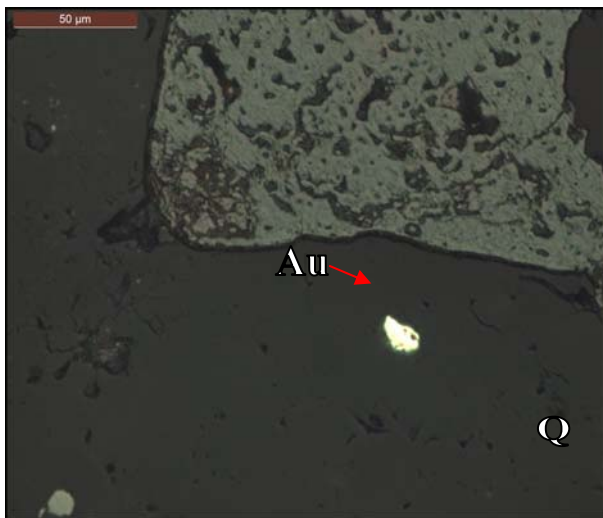


**Fig. 6.** Microphotograph of well developed native gold druse and individual gold grain in later quartz crystal (Plane polarized light. Magnif.  $\times 630$  II)

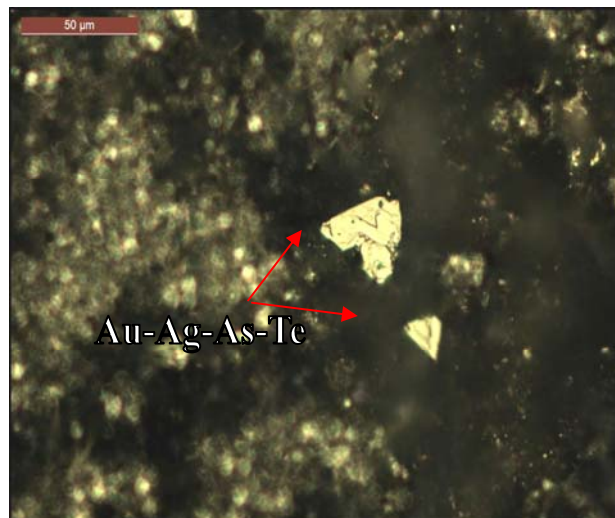
sentative two-phase and multifaceted idiomorphic aggregates and forms. This kind of native gold is characteristic of certain polymetallic stages with high presence of arsenic generated low temperature epithermal zones related to predominantly intensive silicification of volcanic rock or characteristic secondary quartzite.



**Fig. 7.** Microphotograph of small grains of native gold within crystalline quartz in brecciated silica-limonite matrix (Plane polarized light, Magnif.  $\times 630$  II).



**Fig. 8.** Microphotograph of individual grain of native gold with representative droplet-like form, within quartz vein (Plane polarized light, Magnif.  $\times 400$  II)



**Fig. 9.** Microphotograph of allotriomorphic aggregates of native gold at the margin of quartz cavern (Plane polarized light. Magnif.  $\times 630$  II)

### **Composition of some major mineral phases**

Also, we made efforts to confirm analytically some of the minerals present within the ore mineral association in the Plavica deposit. Our preliminary results have confirmed enargite, molybdenite and pyrite compositions under the electron microprobe at the Faculty of Geology and Geography, Sofia University, Bulgaria.

### **Enargite**

Some of the enargite mineral grains, determined under the polarized optical microscope LEICA DMP 4500 equipped with digital still camera and complementary software LEICA LAS (Figure 10), have been analyzed under the microprobe (Figure 10b, points 1–4; Figure 12b, point 1)

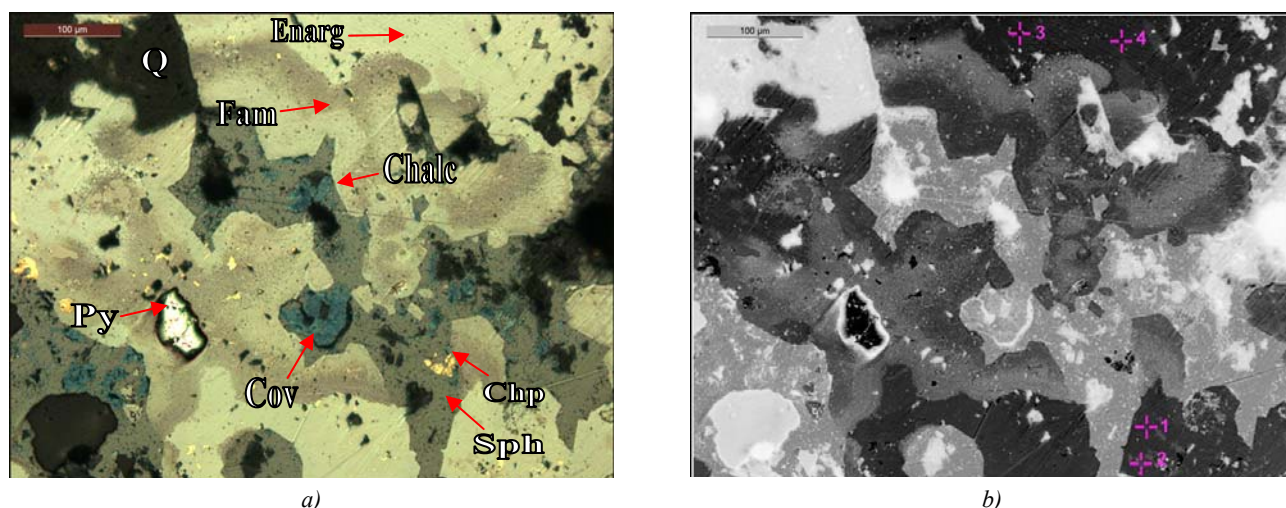


Fig. 10

a) Microphotograph of complex, massive externally and internally corroded quartz-pyrite-enargite-farnesite aggregate, which encloses chalcocopyrite and sphalerite as well as latter chalcocite, covellite and other sulphosalts (Plane polarized light. Magnif.  $\times 200$  II);  
 b) SEM microphotograph of Zn-enargite (points 1 and 2) and enargite (points 3 and 4) mineral grains (Backscattered electrons (BSE), Magnif.  $\times 1600$ )

The chemical composition of enargite, as it is shown in Table 1, have shown slight discrepancies from the stoichiometric enargite composition ( $\text{Cu}_3\text{AsS}_4$ ) in standards.

Namely, in points 1 and 2, close vicinity of sphalerite and chalcopyrite, to 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.

Table 1

Chemical composition of Zn-enargite (points 1 and 2) and enargite (points 3, 4 and 5) from the Plavica deposit

Element	Chemical analysis (%)				
	1	2	3	4	5
Cu	40.90	40.76	46.54	46.48	48.69
Fe	1.12	0.97	0.24	0.15	1.37
Zn	6.00	7.56	0.24	–	–
Ag	0.46	0.54	0.09	0.13	–
As	19.55	19.86	17.77	17.21	16.81
Sb	0.55	0.46	1.08	1.33	–
S	29.60	29.51	34.14	34.60	33.09
$\Sigma$	98.18	99.60	100.10	99.90	99.96

Note: Analysis 1 –  $(\text{Cu}_{2.57}\text{Fe}_{0.08}\text{Zn}_{0.35})_{3.00}\text{As}_{1.02}\text{S}_{3.98}$   
 Analysis 2 –  $(\text{Cu}_{2.57}\text{Fe}_{0.08}\text{Zn}_{0.35})_{3.18}\text{As}_{1.06}\text{S}_{3.77}$   
 Analysis 3 –  $\text{Cu}_{2.89}\text{As}_{0.91}\text{S}_{4.19}$   
 Analysis 4 –  $\text{Cu}_{2.57}(\text{As}_{0.086}\text{Sb}_{0.03})\text{S}_{4.21}$   
 Analysis 5 (MRD-002) –  $(\text{Cu}_{2.94}\text{Fe}_{0.11})_{3.00}\text{As}_{0.83}\text{S}_{4.15}$

### Tennantite

Although relatively scarce, tennantite was determined in several samples during the optical microscope study (Figure 11a) and electron microprobe analyzer (Figure 11b). 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 2).

Table 2

Chemical composition of tennantite from the Plavica deposit

Element	Chemical analysis (%)			
	1	2	3	4
Cu	41.04	39.67	40.58	40.76
Fe	0.86	1.55	0.21	0.54
Zn	7.56	8.99	9.06	6.24
Ag	0.47	0.08	0.87	0.47
As	19.72	15.51	20.30	19.96
Sb	0.55	5.43	0.88	0.39
S	29.76	28.73	29.01	29.62
$\Sigma$	99.96	99.96	100.91	97.98

Note: Analysis 1 –  $(\text{Cu}_{9.47}\text{Fe}_{0.22}\text{Zn}_{1.70}\text{As}_{0.06})_{11.45}(\text{As}_{3.86}\text{Sb}_{0.06})_{3.92}\text{S}_{13.63}$   
 Analysis 2 –  $(\text{Cu}_{9.40}\text{Fe}_{0.06}\text{Zn}_{2.10})_{11.56}(\text{As}_{3.14}\text{Sb}_{0.60})_{3.74}\text{S}_{13.43}$   
 Analysis 3 –  $(\text{Cu}_{9.32}\text{Zn}_{2.07})_{11.39}\text{As}_{4.29}\text{S}_{13.32}$   
 Analysis 4 –  $(\text{Cu}_{9.63}\text{Zn}_{1.48})_{11.11}\text{As}_{3.99}\text{S}_{13.90}$





**Fig. 11.**

**a)** Microphotograph of colloformally corroded tennantite within quartz-limonite matrix. (*Plane polarized light, Magnif. x 200 II*);  
**b)** SEM microphotograph of tennantite from the Plavica deposit (points 1, 2, 3, 4). (*Backscattered electrons (BSE), Magnif. x 1900*)

As may be seen from the Table 2, 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-sulfidation-state sulfides such as tennantite-tetrahedrite and chalcopyrite, and telurides as it was confirmed for genetically similar deposits elsewhere (e.g., El Indio, Lepanto; see Arribas, 1995). The transition from quartz-alunitepyrite alteration to enargite-pyrite and finally to tennantite-tetrahedrite, indicates that the fluid progressively became more reduced and less acid.

#### *Pyrite*

Also, our study included the most common ore mineral within the Plavica deposit, pyrite (Figure 12).

The analysis of the most common within the Plavica deposit, pyrite, in general have shown close to the standard values (Table 3).

However, as it can be seen from the results above, there are slight discrepancies from the almost ideal stoichiometric values of pyrite due to narrow range of copper impurities in the mineral composition (0.24 – 3.99% Cu) as well as zinc impurity that reaches up to 1.69% Zn. Copper likely

entered the structure of pyrite through a coupled substitution, as well as zinc, too (Chouinard et al., 2005).

#### *Molybdenite*

Although hard to find, luckily we managed to find molybdenite in few of the studied samples from the Plavica deposit (Figure 13a,b,c; Table 4).

Analyzed composition of this molybdenite shows slight discrepancy from the stoichiometric values (Fron del and Wickman, 1970) due to small increase of sulfur and iron and decrease of molybdenum (Table 4).

The presence of molybdenite points out that this sample came from the high-temperature zones within the Plavica mineralized system, which roots can be traced down to the certain intrusion as mentioned for similar genetic type deposits elsewhere (Arribas, 1995).

#### *Ag-sulfides*

Silver-bearing sulfides are extremely rare in the Plavica deposit, which is quite common for deposits of the same genetic type elsewhere (Holley, 2012). Although nearly 24 bright BSE spots were examined in a total of 8 samples through an EMP analyses, only one slightly less than 1 µm grain of Ag-bearing sulfide was detected (Figure 14).

During EMP analysis, Fe, Ag, and S were detected in this particular grain (Table 5), with an approximate ratio of 1Ag : 7Fe : 8S.

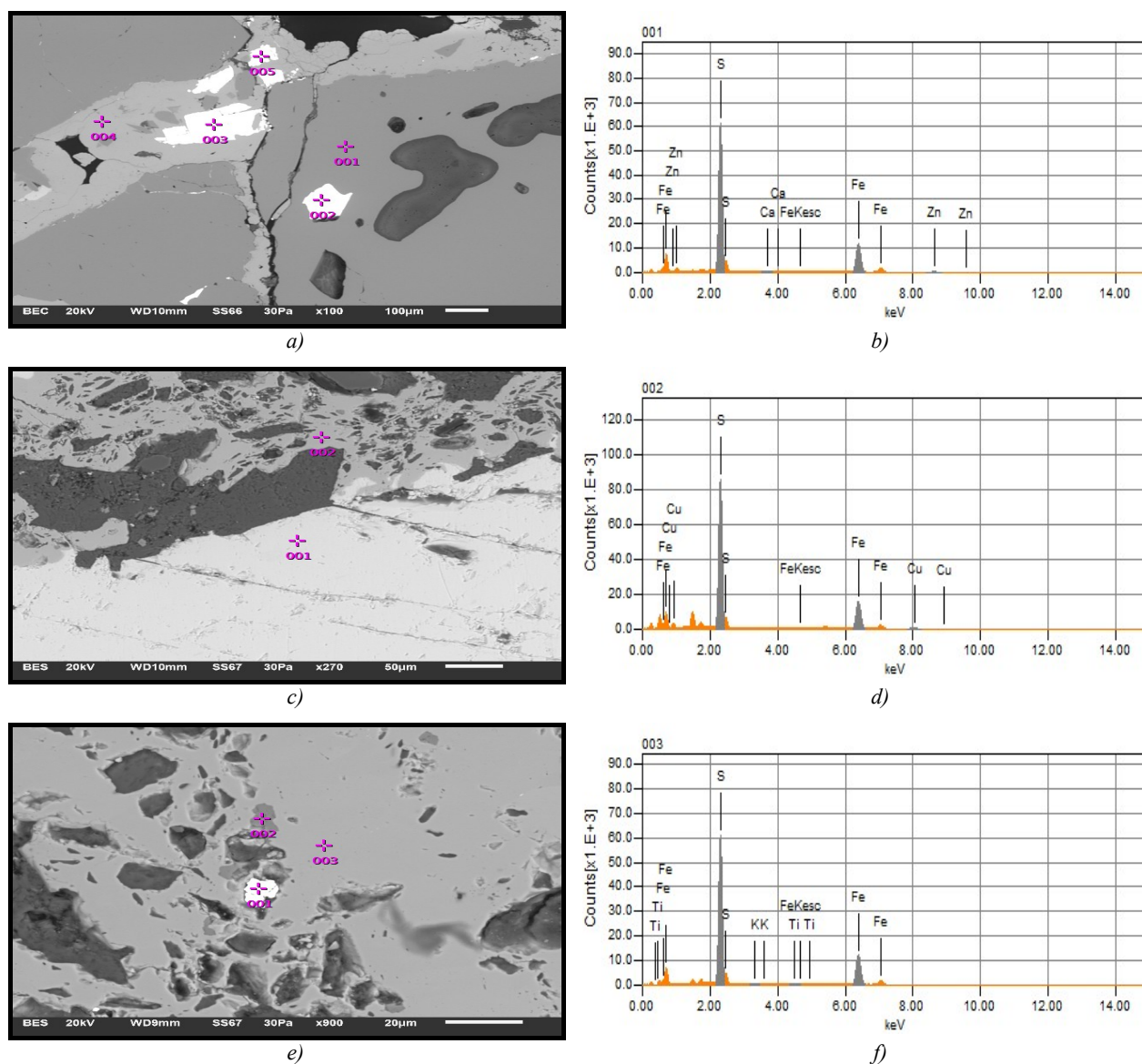


Fig. 12

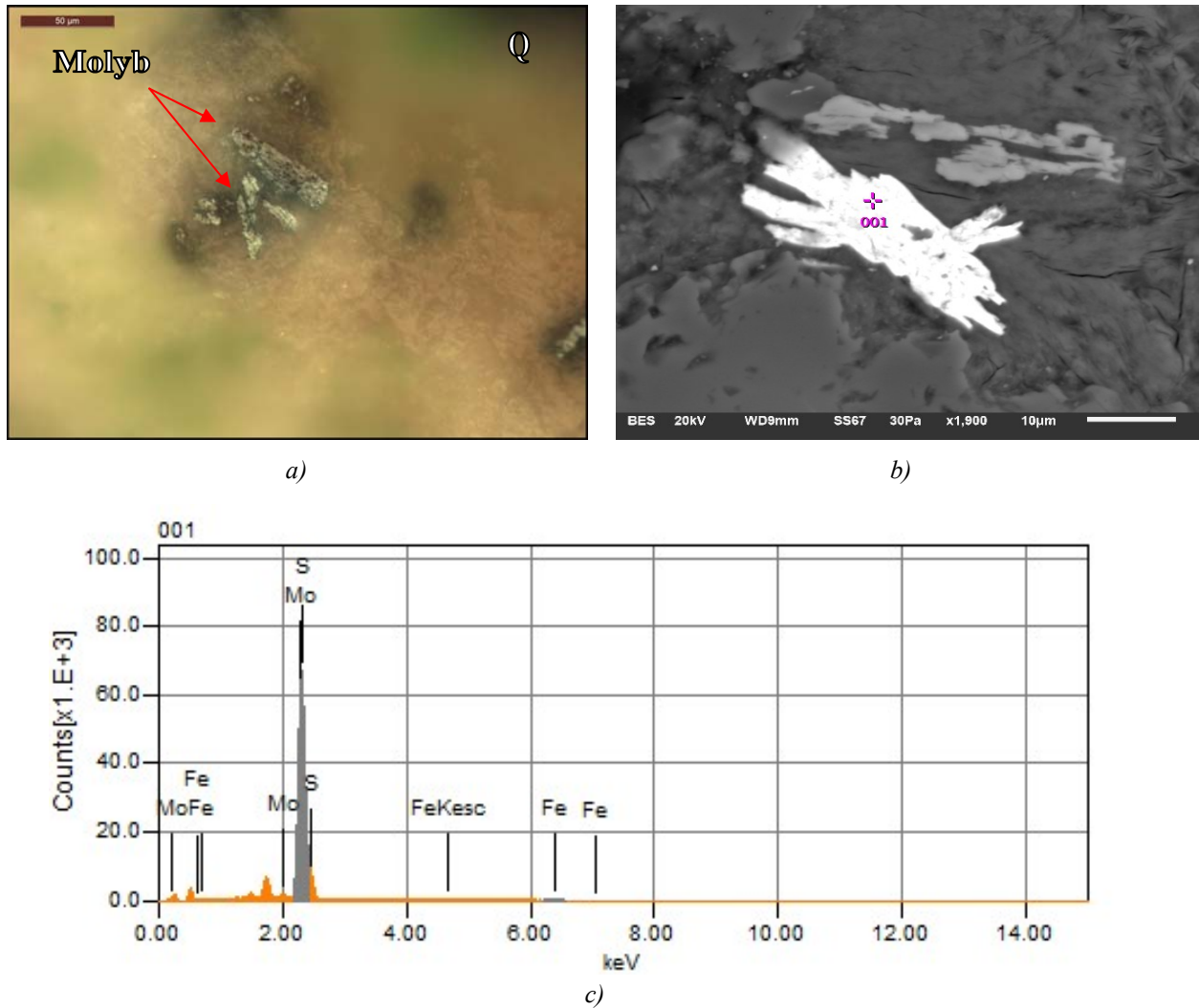
- a) SEM microphotograph of pyrite from the Plavica deposit (point 001; analysis 8) (Backscattered electrons (BSE), Magnif.  $\times 100$ );  
 b) EDS spectrum of the pyrite from the Plavica deposit (point 1; analysis 8);  
 c) SEM microphotograph of pyrite from the Plavica deposit (point 002; analysis 9) (Backscattered electrons (BSE), Magnif.  $\times 100$ );  
 d) EDS spectrum of the pyrite from the Plavica deposit (point 002; analysis 9);  
 e) SEM microphotograph of pyrite from the Plavica deposit (point 003; analysis 10) (Backscattered electrons (BSE), Magnif.  $\times 100$ );  
 f). EDS spectrum of the pyrite from the Plavica deposit (point 003; analysis 10);

Table 3

## Chemical composition of pyrite from the Plavica deposit

Element	Chemical analysis (%)									
	1	2	3	4	5	6	7	8	9	10
Fe	47.93	43.83	42.76	44.04	44.06	44,22	43,20	45.62	43.55	46.72
Cu	0.24	0.30	0.43	0.42	0.42	0,44	0,78	0.00	3.99	0.00
S	51.79	55.54	56.76	55.50	55.46	55,30	55,60	52.78	52.52	52.78
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.69	0.00	0.00
$\Sigma$	99.96	99.67	99.95	100.00	89.94	99,96	99,58	100.09	100.06	99.5

**Note:** Analysis 1 –  $\text{Fe}_{1.03}\text{S}_{1.97}$ ; Analysis 2 –  $\text{Fe}_{0.78}\text{S}_{1.73}$ ; Analysis 3 –  $(\text{Fe}_{0.90}\text{Cu}_{0.01})_{0.91}\text{S}_{2.09}$ ; Analysis 4 –  $(\text{Fe}_{0.93}\text{Cu}_{0.01})_{0.94}\text{S}_{2.06}$   
 Analysis 5 –  $(\text{Fe}_{0.94}\text{Cu}_{0.01})_{0.95}\text{S}_{2.05}$ ; Analysis 6 –  $(\text{Fe}_{0.94}\text{Cu}_{0.01})_{0.95}\text{S}_{2.01}$ ; Analysis 7 –  $(\text{Fe}_{0.93}\text{Cu}_{0.01})_{0.92}\text{S}_{2.07}$ ;  
 Analysis 8 –  $(\text{Fe}_{0.89}\text{Zn}_{0.01})_{0.92}\text{S}_{1.98}$ ; Analysis 9 –  $(\text{Fe}_{0.83}\text{Cu}_{0.07})_{0.91}\text{S}_{1.98}$ ; Analysis 10 –  $\text{Fe}_{0.98}\text{S}_{1.97}$



**Fig. 13**

- a) Microphotograph of rod-like aggregates of molybdenite in quartz matrix (Plane polarized light, Magnif.×400 II)
- b) SEM microphotograph of rod-like aggregates of molybdenite and position of analysis (Backscattered electrons (BSE), Magnif.×1900;
- c) EDS spectrum of the molybdenite from the Plavica deposit

**Table 4**

*Chemical composition of the molybdenite (points 1) from the Plavica deposit*

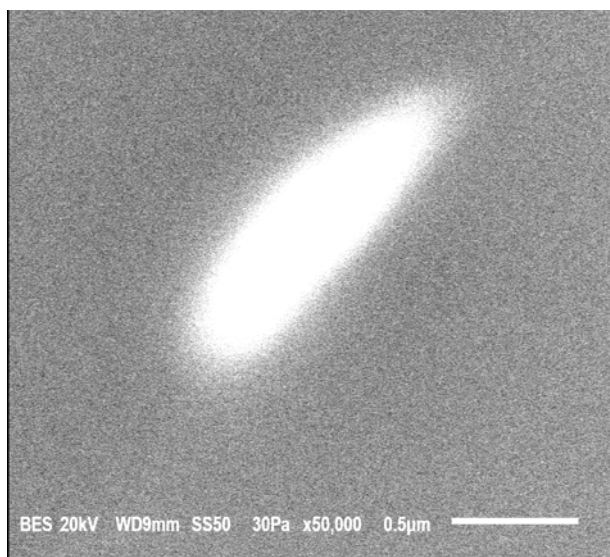
PL-3599.1	Mass %	Atom %	Sigma	Net	K-ratio	Line
S	42.52	68.72	0.07	2077177	1.253796	K
Fe	0.62	0.58	0.02	9106	0.016237	K
Mo	56.86	30.71	0.21	1419269	1.339991	L
Total	100.00	100.00				

**Table 5**

*Chemical composition of the Ag-sulfide from the Plavica deposit*

MRD-002.3	Mass %	Atom %	Sigma	Net	K-ratio	Line
S	50.83	65.59	0.15	165947	0.100167	K
Fe	43.51	32.24	0.22	48621	0.086695	K
Ag	5.66	2.17	0.15	8076	0.007754	L
Total	100.00	100.00				





**Fig. 14.** SEM microphotograph of space fog-like aggregates of Ag-bearing mineral grain (Backscattered electrons (BSE), Magnif.  $\times 50000$ )

Although the precise stoichiometry for the Ag sulfide grain cannot be determined based on this analysis, but mineral of appropriate composition could be Ag-bearing pyrite. However, this fact is of high scientific importance since it suggests that the high sulphidation epithermal Au + Ag mineralization is deposited from oxidizing, hot acidic fluids in which S occurs as  $\text{SO}_2$  and so displays characteristic ore mineralogy and zoned hydrothermal alteration. The particular process of formation, the most probably, places a physical separation between the source intrusion and epithermal mineralization (Corbett and Leach, 1998; Serafimovski et al., 2014). The ore fluid commonly breaks into an initial fast travelling volatile-rich phase and later slower liquid-rich phase. The first one vent from cooling intrusions and rise rapidly, within a structure without reaction with host rocks or ground waters, depressurization resulted in exsolution of  $\text{SO}_2$  which then became oxidized to progressively form a more acidic fluid as it rises to higher crustal levels, typically within permeable reactive volcanics or breccias, and so provide characteristic zoned mineral assemblages dominated by: residual vuggy silica, alunite, pyrophyllite-diaspore, dickite, kaolin to marginal illite. The later liquid-rich phase commonly deposits Au-Ag mineralization with enargite, including the low temperature polymorph luzonite, and pyrite along with gangue of alunite, barite and local sulphur. In most instances the later mineralization brecciated the core vuggy silica.

### *Alteration mineralogy*

Alteration of the volcanic rocks is intense in the centre of the deposit and in the vicinity of the silica bodies. Four alteration types are dominant, quite similar as it was shown for deposits elsewhere (Meyer and Hemley, 1967):

(i) sericitic alteration, with sericite and quartz, plus minor titanite, tourmaline, barite and adularia;

(ii) advanced argillic alteration, characterized by kaolinite, alunite, zunyite, pyrophyllite, diaspore and corundum;

(iii) silicification is widespread, particularly as massive replacement bodies;

(iv) propylitic alteration.

Most of the volcanic rocks surrounding the Plavica deposit have been affected and now contain varying amounts of chlorite, epidote, sericite, calcite, rutile and magnetite. The alteration is mostly pervasive in nature and not clearly vein-related. However, a crude zonation of these alteration types appears to be present: the central and deeper parts exhibit sericitization while the advanced argillic alteration occurs in the surrounding areas (including the silica bodies). Mineralization appears to be more closely related to the argillic and silicic alteration assemblages. Aforementioned alteration types and their zonation (especially association alunite-kaolinite-pyrophyllite-diaspore) quite well fit in models proposed for high-sulphidation epithermal type around the World (Hemley et al., 1969, 1980; Reyes, 1990). Also, although pyrophyllite may form at a temperature  $<160^\circ\text{C}$  if the silica concentration were high, its coexistence with dickite, illite or diaspore could easily suggest paleotemperatures of  $>200^\circ\text{C}$  (White and Hedenquist, 1995).

This retrograde alteration sequence formed during the waning stage of the high-sulphidation hydrothermal system, and is interpreted to represent high temperature oxidation by gradual ground water encroachment during thermal waning of the hydrothermal system as it was mentioned for genetically similar deposits elsewhere (Rohrlach et al., 1999). The distribution and characterization of high-sulphidation mineralization within the various subtypes of advanced argillic alteration without any doubts requires more detailed and subtle study.

Supergene processes in the upper part of the deposit have led to the formation of malachite, azurite, smithsonite, anglesite, cerussite, hydrated Fe- and Mn-oxides, chalcocite, digenite, native copper and covellite.

## CONCLUSION

This study of ore minerals study enriched the knowledge of the mineral association within the Plavica deposit, especially in the epithermal part of high sulphidation where special contribution was given in definition of morphological features of epithermal gold. The latest findings during the electron microprobe analysis gave the compositions of several representative mineral phases, regular associates of epithermal gold with their specifics. Enargite have shown increased values of zinc (0.24–7.56 Zn), antimony (0.46–1.33% Sb), silver

(0.09–0.54% Ag) and iron (0.15–1.37% Fe). Tennantite has been characterized by certain impurities of iron (0.21–1.55% Fe), zinc (6.24–9.06% Zn) and silver (0.08–0.87% Ag). Discrepancies from the ideal composition have shown pyrite, too, due to increased presence of copper (0.24–3.99% Cu), zinc (up to 1.69% Zn) and rarely silver (up to 5.66% Ag). Although at lower intensity, the molybdenum stoichiometry was disrupted to by very slightly increased sulfur and iron, resulting in decrease of molybdenum.

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## Резиме

## СОСТАВ НА НЕКОИ ГЛАВНИ МИНЕРАЛНИ ФАЗИ ОД ЕПИТЕРМАЛНОТО НАОГАЛИШТЕ ПЛАВИЦА, ИСТОЧНА МАКЕДОНИЈА

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todor.serafimovskit@ugd.edu.mk**Клучни зборови:** злато; Пластица; минерални фази; состав; висока сулфидизација

Епитермалното злато од висока сулфидизација е констатирано и проучувано во наоѓалиштето Пластица кое е дел од кратовско-злетовската вулканска област. Епитермалното злато и придружните минерални фази се констатирани во силифицираните туфови, секундарните кварцити, кварц-пирит-енергитските жици и главно расеани во алтерисаната, но претежно силифицирана вулканска основа. Покрај златото, во рамките на оваа кисело-сулфатна вулканска средина е утврдено присуство на контаминирани пирити, цинкотетраедрити, енергити, селигманити и секако редовно присутната бакарна асоцијација предводена од халкопирит, следена од борнит, халкозин, ковелин, како и нешто повисокотемпературните придружници арсено-пи-

рит и молибденит. Најголем дел од овие придружни сулфидни минерални фази во рамките на овие проучувања се третирано и со студиски оптички микроскоп, но и со електронска микросонда, а резултатите се детално презентирани во рамките на овој труд. За илустрација сакаме да потенцираме дека во пиритите е утврдено зголемено присуство на бакар и цинк и поретко на сребро, во енергитот се зголемени концентрациите на цинк (0.24–7.56 Zn), антимон (0.46–1.33% Sb) и сребро (0.09–0.54% Ag), тенантитот е со зголемени концентрации на железо (0.21–1.55% Fe), цинк (6.24–9.06% Zn) и сребро (0.08–0.87% Ag), додека кај молибденитот само нешто покачени концентрации се одредени за сулфурот и железото.