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The Plavica epithermal polymetallic system: mineralogical and geochemical data

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Keywords: polymetallic mineralization, volcanic structures, mineral and geochemical associations

ABSTRACT: The latest results from the mineralogical and geochemical investigations and studies of the Plavica polymetallic mineral deposit, Eastern Macedonia, are presented. These results improve our knowledge about the development of typical mineral parageneses and geochemical associations of the basic ore metals and elements. The most common minerals are pyrite and chalcopyrite, followed by enargite, chalcocite, bornite, tetrahedrite, and some rare minerals such as luzonite, seligmannite, pirseite, etc. The geochemical studies of ore minerals and soils established a wide association of rare, scattered elements and rare earth elements, with increased contents of La (6-21 ppm), Ce (4-28 ppm), Pr (1-3 ppm), Eu (11 ppm), Tm (3 ppm), which are clear evidence that the formation of ore fluids was in the deeper parts of the Earth's crust. The analyses performed during the investigation of the borehole samples (from stocwork-disseminated mineralizations) shows the average contents of 0.2-0.3 %Cu, 0.25 g/t Au, 5-10 g/t Ag, etc. Gold contents in the secondary quartzites are within range of 0.1-10 g/t Au.

1 INTRODUCTION

Regional and detailed geological investigations of the Plavica-Zlatica area (Kratovo-Zletovo volcanic complex, Eastern Macedonia) have been conducted on Cu-Au, stockwork-disseminated, mineralization in intense hydrothermally altered Tertiary volcanic rocks of the Plavica volcanic structure. This structure is one of the most striking volcanic forms in the large Kratovo-Zletovo volcanic area. It is a tectonically deformed and faulted old volcanic caldera 20 km^2 in diameter. The volcanic rocks, which comprise the volcanic structure, are of Tertiary age (32 to 16 Ma) and include dacites, andesites and their tuffs. A striking feature of the Plavica volcanic structure is its hydrothermally altered and mineralized central part. Silicification zones (called "secondary quartzites" from the Russian literature) are the principle host of epithermal gold.

Beside copper, which is the main ore metal, high concentrations of Au, Ag, Mo, Pb, Zn, Sb, etc., are present. This association of elements indicates a polymetallic character of the Plavica hydrothermal mineral deposit, typical of high-sulfidation epithermal ore bodies elsewhere.

The Plavica volcanic structure and the polymetallic mineralization in the Plavica deposit have been the subject of investigation by previous authors (e.g., Ivanov & Denkovski 1978; Stojanov 1980; Rakic 1982; Serafimovski & Mudrinic 1991; Serafimovski 1990, 1993; Serafimovski & Boev 1996; Serafimovski et al. 1997; Stojanov & Denkovski 1997; Serafimovski & Rakic 1998, 1999). Mineral exploration in the Plavica volcanic and mineralized area continues.

2 GEOLOGICAL FEATURES

The Plavica polymetallic copper deposit is located in a complex volcanic caldera, built of different kinds of Tertiary volcanic rocks. Numerous petrology studies indicate that the volcanic rocks are built of ignimbrites, stratified volcanic tuffs and breccias, dacite-andesites and their pyroclastics, and quartz latites (Fig. 1). The occurrence of secondary quartzite (residual silica after acidic leaching) in the western part is an important feature of the Plavica ore structure. The age of these volcanic rocks has been determined (K/Ar method) as Oligocene-Miocene or more precisely 32-16 Ma. Adjacent volcanic rocks are intensively altered over an area of 6-8 km^2. This is the most intensively deformed part in the area of consideration. The volcanic rocks in the central part of the Kratovo-Zletovo volcanic area were affected by regional propylitization with common occurrences of hydrothermally altered rocks, particularly in parts of earlier volcanic centers (Plavica, Crn Vrv,

Borovik, etc.) the most pronounced being sericitization, kaolinitization, silicification, alunitization and pyritization, and, to a lesser extent, other kinds of hydrothermal alteration. Fracture zones of regional and local character are present in the central part of the area. Zones of intensive fracturing, extending E-W and NW-SE, are the most common. Nevertheless, the basic feature of the structural composition, particularly in the area of Plavica, is the presence of a large number of fractures distributed radially relative to the central part (Fig. 1).

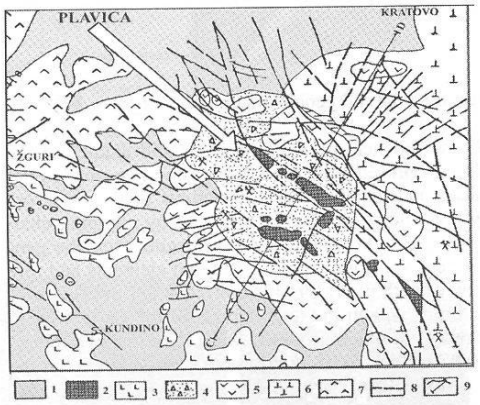

Fig 1. Geological scheme of the Plavica volcanic structure (Serafimovski 1993). 1. Mio-Pliocene volcanogene-sedimentary rocks (andesite tuffs, partially stratified, tuffaceous sandstones and breccias); 2. Silex-secondary quartzites; 3. Labrador-augutic andesites (andesite-basalts); 4. Hydrothermaly altered, pyritized and mineralized rocks (andesites, dacites, latites and piroclastites); 5. Dacito-andesites; 6. Ignimbrites with dacitic composition; 7. Augito-biotitic hornblende andesites; 8. Faults (partially mineralized); 9. Exploration drill holes.

Large masses of strongly silicified rocks which, because of their resistance to erosion form characteristic "riffs", occur inside the old calderas, along fractures of W-E strike in the central parts of the Plavica and Crn Vrv. At Plavica they occur over an area of around 0.2 km^2, and at Crn Vrv over an area >0.4 km^2 (Fig. 1). They have a sub-vertical extent and become smaller in size at depth. Deep drilling indicates that their "roots" go extend to over 400 m in depth, where they gradually pinch out.

Polymetallic mineralization, located in the central parts of the Plavica volcanic structure, was controlled spatially, genetically and parageneticaly by the structures of the volcanic center, fault structures, and Tertiary subvolcanic intrusions of dacite-andesitic composition. The ore mineralization, was formed largely along the trench-fault systems as veins and veinlets. Ore is also disseminated in adjacent hydrothermally altered volcanic rocks by metasomatic processes. The disseminated mineralization most commonly is located around the trench systems (Fig. 2).

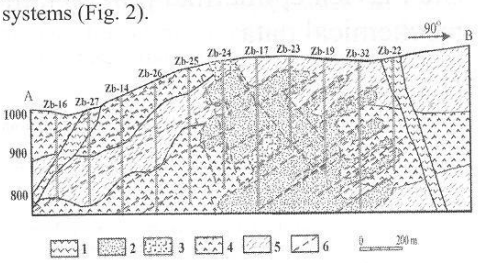

Fig. 2. Geological cross-section through the Plavica deposit (Serafimovski 1993). 1. Fresh quartz latite; 2. Cu mineralization; 3. Hydrothermally altered (dacite) quartz latite; 4. Hydrothermally altered dacite-andesite; 5. Hydrothermally altered volcanic tuffs and agglomerates; 6. Faults

The morphology of ore bodies in the Plavica ore deposit is different. The mineralization formed as ore veins and stockwork-disseminated ore bodies. The scale and contours of the ore bodies are not defined in detail yet. According to recent exploration (mostly by drilling), stockwork-disseminated mineralization has been determined over an area of 0.2 km^2. at depth ore mineralization was found to 300 m, but even to 600-1000 m (drillhole Zb-5). The average content of the copper is 0.2% Cu. The content of the copper is higher in the enargite ore veins or quartz-pyrite-enargite ore veins, which are located in the area of Zlatica, but those ore bodies are small. During exploration activities (by adits) individual enargite veins were followed up to 200 m along strike, with an average thickness of 0.7-5 meters and average copper content of 1.93% Cu.

In the area of the Plavica deposit Pb-Zn ore veins also occur. These veins are located in the marginal parts of the Plavica volcanic structure. In places Pb-Zn ore veins occur in the central part of the volcanic structure, but they are usually small and contain <1 wt% Pb and Zn.

In the Plavica epithermal system the gold mineralization related to secondary quartzite zones is of interest. In addition to intense silicification haematization, alunitization, jarozitization, etc., occur. The content of gold varies over the range of 0.1-10 g/t Au, but the most common values are 1 g/t Au. The gold is disseminated in the secondary quartzites, which are in form of lenses and can be followed at depth to 150 m.

3 MINERALOGICAL AND GEOCHEMICAL DATA

The Plavica ore deposit contain the following minerals: pyrite, pyrrhotite, chalcopyrite, magnetite, rutile, scheelite, haematite, molybdenite, sphalerite, galena, bornite, enargite, luzonite, native gold, melnikovite,

tetrahedrite, tennantite, chalcocite, prustite, digenite (as primary sulfides) and covellite, native copper, malachite, azurite, etc (as the secondary sulfides). Non ore minerals are represented by quartz, calcite, chalcedony, siderite, Mn-calcite, barite, etc.

The most common mineral is pyrite, which is present even in the pre-ore stage and accompanies all hydrothermal stages. The most important mineral of the stockwork and stockwork-disseminated mineralizations is chalcopyrite, which is the second most common mineral. Most of it formed during the main sulfide phase. The rest of the sulphides and sulphosalts have a variable and irregular presence.

Ten ore samples had their mineral and chemical composition analyzed by electron microprobe (Tab. 1). Also, the presence of Ni, Au, Ag, and Sb in pyrites, Au, Ag, and Sb in enargites, Au, Ag, Se, and Sb in chalcopyrites, and Ag, Sb, and Zn in seligmannites was determined. During those analyses were determined until then unknown minerals in the Plavica deposit (seligmannite, luzonite and pirseite, Tab. 1).

Table 1. Quantitative X-ray spectral microanalyses of the most important ore minerals from Plavica (wt%)

Sample	1	2	3	4	5	6	7	8	9	10
Cu	34.4	34.3	34.8	-	0.4	48.9	48.3	14.6	44.4	42.5
Fe	31.2	30.6	30.2	46.0	45.9	-	-	-	0.8	1.1
Ag	-	-	0.1	-	-	-	0.2	0.2	-	-
Au	-	0.2	-	-	-	-	0.2	-	-	-
As	-	-	-	-	-	18.9	19.2	17.1	19.0	10.9
Sb	-	0.1	-	-	-	0.4	-	0.2	2.2	12.9
Zn	-	-	-	-	-	-	-	0.3	5.4	6.6
Pb	-	-	-	-	-	-	-	-	-	-
Ni	-	-	-	0.4	0.5	-	-	-	-	-
Se	-	-	0.2	-	-	-	-	-	-	-
S	34.8	34.7	34.5	53.6	53.2	31.8	32.3	21.5	28.2	26.0
Σ	100.4	99.9	99.7	100.0	100.0	100.0	100.0	100.1	100.0	100.0

Note: 1, 2, 3-chalopyrite; 4, 5-pyrite; 6, 7-enargite; 8-seligmanite (lamellae with enargite); 9-tennantite and 10-two–phase tennatite-tetrahedrite aggregate. All analyses were done in X-ray spectral microprobe laboratory at the Commitee of Geology-Sofia, Bulgaria (Analyst: S. Mankov). The lowest level of detection was 0.1 wt%

The minerals have standard compositions, very close to the theoretical values (Tab. 1). We identified siligmannite for the first time in the mineral association of the Plavica mineral deposit.

The study of distribution of the main ore metals and elemental composition indicate the polymetallic character of the Plavica ore deposit. The content of main ore metals in the deposit is 0.2-0.3% Cu, < 1% Pb and Zn, 0.25 g/t Au, 5-10 g/t Ag and in decreasing order, Mo, Sn, W, Bi, Ni and Co. Disseminated elements are represented by Cd, In, Ge, Te and Se, while rare earth elements represented by Nd, Eu, Tb, Dy, Tm, were determined in chalcocite (Tab. 2).

Table 2. Mass spectrometer analyses of main ore minerals from the Plavica mineral deposit (%)

Elem.	Chalcopyrite	Enargite	Chalcocite	Pyrite
Fe	29.5999	13.2600	7.0000	42.7200
Li	0.0018	0.1167	0.0001	0.0008
Be	0.0009	0.0098	0.0001	0.0005
B	0.0180	-	-	-
F	-	-	-	-
P	-	-	-	-
Cl	0.0054	0.0265	0.0043	0.0166
Mn	-	-	0.0026	0.0223
V	0.0004	0.0020	0.0001	0.0006
Cr	0.0008	0.0030	0.0001	0.0006
Co	0.0015	0.0141	0.0006	0.0552
Ni	0.0128	0.0679	0.0040	0.0148
Zn	-	-	-	0.0242
Pb	0.0719	0.0697	-	-
Cd	0.0030	-	-	0.0024
Ga	0.0001	0.0002	0.0001	0.0001
Ge	-	0.0002	0.0001	0.0001
Se	0.0003	0.0018	0.0003	0.0016
Te	0.0011	0.0447	0.0009	0.0014
Br	0.0001	0.0001	0.0001	0.0000
Rb	0.0002	0.0017	0.0004	0.0004
Sr	0.0111	0.0289	0.0072	0.0275
Ba	0.0519	0.0351	0.0606	0.0089
Cs	0.0001	-	-	0.0001
Y	0.0017	0.0062	0.0025	0.0036
Zr	0.0021	0.0179	0.0012	0.0109
Cu	0.1000	0.1000	0.0000	0.1000
Mo	0.0001	0.0009	0.0003	0.0002
W	-	-	-	0.0001
Sn	0.0035	0.0553	0.0020	0.0018
Bi	0.0008	0.0103	0.0003	0.0011
Sb	0.0185	-	-	0.0116
As	-	1.0000	-	0.1000
Ti	0.0001	0.0005	0.0002	0.0001
Hg	-	-	0.0106	-
La	-	0.0022	0.0007	0.0004
Ce	-	0.0028	0.0015	0.0004
Pr	-	-	0.0003	0.0001
Nb	-	0.0017	-	0.0002
Nd	-	-	0.0011	0.0002
Eu	-	-	0.0011	-
Tb	-	-	0.0001	-
Dy	-	-	0.0009	-
Tm	-	-	0.0004	-

Based on geochemical exploration performed during last two years (mostly of the soils above the secondary quartzites) and results obtained, the following interpretation is possible. From the geochemical data the gold is not related to some of the elements present in Plavica's geochemical association. The method applied was regression analysis using a linear model y=a+B*x and exponential model: y=exp(a+b*x). Calculations established negative correlation values and low values, which leads to the conclusion that there is no correlation. The highest correlation occurs between the Sr and U, 0.96 or 96% (Figure 3). Other pairs with some correlation

are: Bi-Rb, Nb-Zr, Rb-Th, Rb-Zn, Sn-Sb, Rb-V, Sr-Y, Sr-Zr, U-Y and V-W.

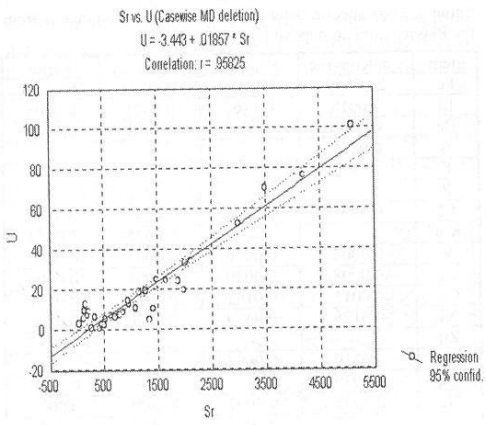

Fig. 3. Correlation between Sr and U from soil samples over the Plavica deposit

Analyses of the secondary quartzites found a good correlation for Au-Sb and Au-Cu pairs, with correlation values of 0.5573 and 0.5779, respectively (Serafimovski and Rakic, 1998).

4 CONLUSION

According to our research and that on similar deposits it can be concluded that the Plavica epithermal deposit consists of three styles of ore mineralization. One is the hydrothermal copper mineralization in the stockwork-disseminated ore body. This ore mineralization may be related to porphyry Cu-Au mineralization (Stojanov 1980). The average content of the copper is 0.2% Cu.

The second type of mineralization in the Plavica deposit are the enargite ore veins or quartz-pyrite-enargite ore veins, which are located in the area of Zlatica, although these ore bodies are small. Some enargite veins have average copper content of 1.93 wt%. In the marginal parts of the Plavica volcanic structure, in addition to the enargite veins there are also Pb-Zn ore veins. Neveretheless, they are small and contain <1 wt% Pb and Zn.

The third type of mineralization in the Plavica deposit is epithermal gold ore related to zones of secondary quartzites. This mineralization contains gold in the range of 0.1-10 g/t Au, with the most common values about 1 g/t Au. The gold is disseminated in the secondary quartzites, which form lenses and can extend to 150 meters depth.

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