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# PROCEEDINGS

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## THE CEROVO-CEMENTACIJA 2 PORPHYRY Cu DEPOSIT, EASTERN SERBIA – ORE MINERALOGY AND PARAGENETIC ANALYSIS

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### Abstract

*The Cerovo-Cementacija 2 porphyry Cu deposit, hosted by hydrothermally altered hornblende andesite, located into the Bor Metallogenic Zone, eastern Serbia, has been investigated. In this porphyry Cu deposit, the following mineral parageneses have been established: i) pyrite-chalcopyrite with Mo; ii) quartz-pyrite with Au; iii) digenite-chalcocite-covellite with Au; iv) chalcidony by sulfatization and sulphation; v) malachite-azurite-limonite. Chalcopyrite is the major Cu mineral and it is the most abundant compared to other established Cu-sulfide minerals. By the ascending and descending hydrothermal processes along the Zone-1 (cementation zone), chalcopyrite was commonly transformed into secondary Cu sulfide minerals (digenite, chalcocite, anilite, covellite, etc.), while those appearances is less represented to the Zone-2 (transitional zone).*

**Keywords:** *porphyry Cu deposit, ore mineralogy, paragenetic analysis, Cerovo-Cementacija 2, Serbia*

### 1. INTRODUCTION

The Cerovo-Cementacija 2 (CC-2) porphyry Cu deposit is spatially located in the Bor Metallogenic Zone (BMZ), eastern Serbia, which belongs to the Carpathian-Balkan Metallogenic Province [1]. It is part of the Mali Krivelj orefield and is localized in the Kraku Bugaresku reef. This orezone is characterized by occurrence of active porphyry-types copper deposits ("Cerovo" and "Mali Krivelj"), than porphyry-type copper deposits with noticeable zones of secondary sulfide enrichment ("Cementacija-Kraku Bugaresku" and "CC-2"), than vein-type copper deposits ("Kraku Bugaresku" and "Kraku Bugaresku-Sever"), as well as the occurrences of copper mineralization at various sites [2].

The CC-2 porphyry Cu deposit was hosted by hydrothermally altered hornblende andesite. On the surface of the terrain above the deposit limonitization is widespread, which with depth goes into the zone of intensive kaolinization, than chloritization, pyrophyllitization, epidotization and zeolitization. Deeper, the most pronounced changes are sulfidization and silification. In addition to hydrothermally altered andesites, andesitic pyroclastic, quartz diorite porphyry, hornblende-biotite andesites, and volcanic breccias also occur to a lesser extent [2].

Mineralogical tastings have been accomplished during 2018. in the orezones of the CC-2 porphyry Cu deposit. The polished sections taken from BT-6 and BT-7 technology-exploratory boreholes (composites) for ore microscopy study were used. The samples was shared into three composites: a) Zone-1 (cementation Cu mineralization); b) Zone-2 (transitional Cu mineralization); and c) Zone-3 (primary Cu mineralization). The aim of this study has been to determine the ore and rock-forming minerals, chemistry of the sulfide minerals, as well as to analyze data of the composition of its mineral parageneses and associations within the CC-2 porphyry Cu deposit.

## 2. ORE MINERALOGY

According to the ore microscopic examination and electron probe micro analyses (EPMA), the CC-2 porphyry Cu deposit consists of following minerals (Zone-1, -2 and -3): **sulfides** (*pyrite, pyrrhotite, chalcopyrite, bornite, digenite, chalcocite, covellite, anilite, molybdenite, galena, galena-(Se), sphalerite*); **sulfosalt** (*famatinite*); **native elements** (*gold, electrum, sulfur*); **oxides** (*rutile, anatase, magnetite, hematite, cassiterite*); **hydroxides** (*Cu-limonite, getit-limonite*); and **gangue minerals** (*quartz, silicates, carbonates, chalcedony, malachite, azurite, apatite, leucoxene, monazite-(Ce), yttrialite, zircon, bassanite, gypsum*). The main minerals of Cu are chalcopyrite and the group of chalcocite, whose abundance varies.

*Chalcopyrite* is the major Cu mineral and it is the most abundant compared to other established Cu-sulfide minerals. It occurs in part with pyrite aggregates, and in part is associated to the quartz-silicate matrix (Fig. 1). By the ascending and descending hydrothermal processes along the Zone-1 (cementation zone), chalcopyrite was commonly transformed to secondary sulfide minerals of Cu (*digenite, chalcocite, anilite, covellite, etc.*), while that appearance is less represented to the Zone-2 (transitional zone) (Fig. 2). These processes commonly occur along the edges of chalcopyrite surfaces, when the chalcocite group of minerals forms a "wreath" or "rings", while in the central parts a lagging relict of chalcopyrite in the shape of "rags" or "islands" (Fig. 2). In Zone-3, these events are not observed except for the local occurrences of bornite and chalcocite. EPMA gave the stoichiometric chemical composition of chalcopyrite, without the presence of other metals (<0.02 wt%).

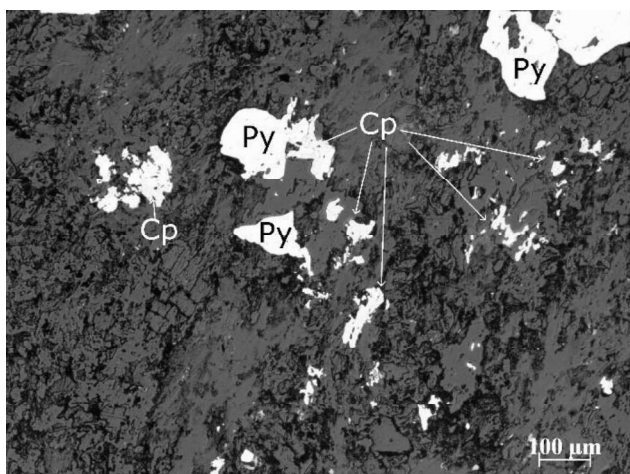


Figure 1.

Cross sections of chalcopyrite aggregates (Cp) in quartz-silicate matrix and as cement pyrite grains (Py). Reflected light, air, IN (Zone-3)

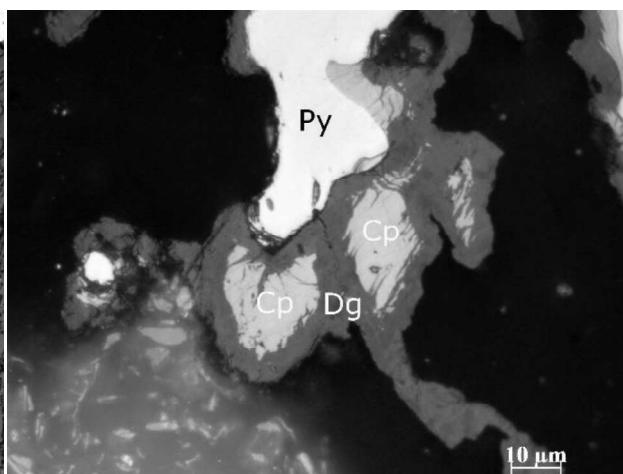


Figure 2.

Digenite (Dg) replaces chalcopyrite (Cp) and cements pyrite (Py). Reflected light, oil, IN (Zone-1)

The *chalcocite group* is completely widespread, dominated by digenite over chalcocite, and spatially associated to Zone-1 and -2 (Fig. 2). They occur commonly along the edges of chalcopyrite surfaces, and are less cement of cataclazed pyrite grains in paragenesis with covellite and anilite. A rare occurrence in digenite of emulsion native gold has been observed. Chalcocite is fewer represented and is spatially associated with all three Zones. It belongs to the cementing secondary sulfide minerals, and does not form larger free surfaces.

*Covellite* is poorly represented and is spatially associated with all three Zones. It commonly associated with the chalcocite group and pyrite, when their rims and cracks cemented and suppressed it.

*Bornite* occurs in trace in form of inclusions in recrystallized pyrite. It is spatially associated with Zone-3.

*Famatinite* appears in trace and is spatially associated with Zone-2 and -3. EPMA gave following empirical formula:  $(\text{Cu}_{2.52}\text{Zn}_{0.45}\text{Fe}_{0.04})_{\Sigma=3.01}(\text{Sb}_{0.61}\text{As}_{0.40})_{\Sigma=1.01}\text{S}_{3.98}$ . It should be emphasized that famatinite contains isomorphous Zn and less Fe, while part Sb is replaced by As.

*Pyrite* is the most represented sulfide mineral and for the most part isomorphically developed as a lonely grains or form larger skeletal aggregates. It appears in several generations. Coarse aggregates of pyrite commonly are cataclazed and reabsorbed by the younger chalcopyrite, which is mainly suppressed and cemented it. The pyrite from the cementation zone is commonly surrounded by digenite, covellite, chalcocite and bornite, while recrystallized pyrite contains copper-sulfides, pyrrhotite, rutile, bassanite and meta-crystals of quartz. In addition to pyrite, droplet of relicts pyrrhotite in recrystallized pyrite are observed in Zone-3, which is characterized by completely different optical properties compared to the hexagonal or monoclinic variety. It has no birefractance or anisotropy and is harder than pyrrhotite (?). According to EPMA, the composition corresponds to the empirical formula  $\text{Fe}_{0.95}\text{S}_{1.05}$  with a slightly increased S content (three analyzes).

*Molybdenite* is a rare mineral. For the time being, it has been determined in flotation products (rough Cu concentrate) from the Zones-2 and -3, with Mo contents of 0.05 wt% and 0.08 wt%, respectively. It was not observed in Zone-1. It appears in the form of short-flat flakes [3].

*Galena* is a rare mineral. Only found in the flotation products (rough Cu concentrate) from the Zones-1 and -2, with Pb contents of 0.20 wt% and 0.05 wt%, respectively [3]. In Zone-3, Se-bearing galena (Fig. 3) associated with chalcopyrite in the form of inclusions in pyrite (2-5  $\mu\text{m}$ ), has following empirical formula:  $\text{Pb}_{0.99}(\text{S}_{0.81}\text{Se}_{0.20})_{\Sigma=1.01}$ .

*Sphalerite* is a rare mineral. Only found in the flotation products (rough Cu concentrate) from Zones-1 and -2 in Zn content of 0.21 wt% and 0.11 wt%, respectively [3].

*Native gold* in all three Zones has been identified as a very rare. It commonly occurs in the shape of droplets, or emulsion grains in quartz-silicate matrix, and sulfide minerals, but in a lesser extent. The size of droplet emulsion grains does not exceed 2  $\mu\text{m}$ . Native gold has not been quantitative analyzed, but only qualitative confirmed (EDS analysis) [3].

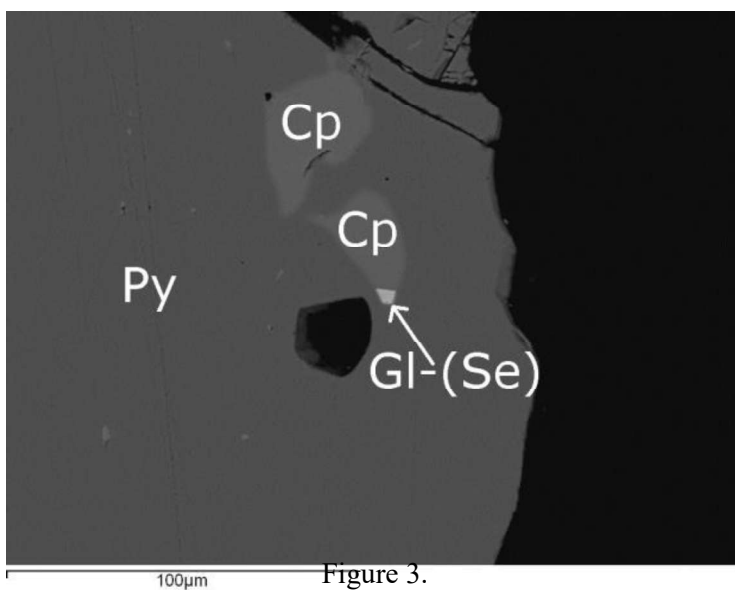


Figure 3. Se-bearing galena [Gl-(Se)] on the edge of chalcopyrite (Cp) as inclusion in pyrite (Py). Electronic microphotography, BEI (Zone-3)

### 3. PARAGENETIC RELATIONS

These studies defined the CC-2 porphyry Cu deposit as pyrite-chalcopyrite mineralization, with a noticeable and locally emphasized process of secondary enrichment of Cu mineralization. In some parts of the locality, the presence of a "surface oxidation subzone" was barely noticeable (the predominant minerals are Cu-oxycarbonates with  $\text{H}_2\text{O}$  – malachite and azurite, Fe-oxide – hematite, and Cu- and Fe-oxyhydroxides – Cu-limonite and limonite-getite).

Based on the ore microscopic examinations, the paragenetic relationship was established at the existing different stages of mineralization. The older type of mineralization (primary mineralization) belongs to the medium-temperature hydrothermal stage. Later, in the conditions of ascendant, descendent, and alteration hydrothermal processes, when the deposit was exposed to physical and chemical changes together with the hosted rocks, leads to intensive transformations of primary sulfide minerals (secondary mineralization). During these events, two subzones were formed: a zone of total cementation and a zone of partial cementation (mixed). The transition between these zones is not sharp. There is definitely no subzone of whole oxidation, which is strongly pronounced in the spatially close to Cerovo-Cementacija 1 porphyry Cu deposit. In the secondary mineralization, three subzones have been formed in this deposit: the zone of complete oxidation, the zone of partial oxidation and the zone of cementation [4].

Minerals belonging to the older parageneses of mineralization are: *pyrite I*, *pyrrhotite*, *chalcopyrite*, *bornite I*, *famatinite*, *sphalerite*, *galena*, *molybdenite*, *native gold I*, *magnetite*, *rutile*, *cassiterite*, *quartz* and *carbonates*. These minerals are the product of the middle-temperature hydrothermal stage, which were deposited in the wider area of the BMZ [1]. In the primary type of mineralization, chalcopyrite is a major copper mineral. It occurs as irregular aggregates associated with cataclazed pyrite, also, in the form of smaller “nests”, which formed tiny surfaces along the silicates (chlorite, biotite). There was no noticeable exsolution of the droplet emulsion grains in the native gold. It rarely contains veinlets of famatinite, which were commonly resorbed by recrystallized pyrite. Molybdenite, sphalerite and galena are extremely rare. Sphalerite belongs to the variety of poor iron content (cleophane).

Younger paragenetic mineralization responds to transformation processes (metasomatism of primary sulfides by descending and ascending solutions, as well as weaker shallow surface oxidation), which above primary part of ores, form two substages of mineralization: sulfide enrichment zone (alteration + cementation) and transitional mixed zone (cementation + primary). The first substage includes minerals – *bornite II*, the chalcocite group (*digenite*, *chalcocite I*, *anilite*), *covellite*, *pyrite II*, *native gold II* and *electrum*; the second substage includes minerals – the chalcocite group (*chalcocite II*), *hematite*, *leucosene*, *malachite*, *azurite*, *limonite-goethite* and *chalcedony*.

The sulfide minerals of Fe and Cu have the following contents within the CC-2 porphyry copper deposit: Zone-1 (sulfide mass 5.3 wt%, of which pyrite 88%, and Cu minerals 12%); Zone-2 (sulfide mass 3.3 wt%, of which pyrite 81%, and Cu minerals 19%); and Zone-3 (sulfide mass 7.3 wt%, of which pyrite 95%, and Cu minerals 5%).

## ACKNOWLEDGEMENTS

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