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Алена Здравковић, Александар Пачевски, Предраг Дабић, Периша Живковић



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## HALKANTIT KAO SEKUNDARNI MINERAL BAKRA U LEŽIŠTU ČOKA MARIN, SRBIJA

Alena Zdravković<sup>1</sup>, Aleksandar Pačevski<sup>1</sup>, Predrag Dabić<sup>1</sup>, Periša Živković<sup>2</sup>

<sup>1</sup>Univerzitet u Beogradu - Rudarsko-geološki fakultet, Đušina 7, Beograd, Srbija,

<sup>2</sup>Nikole Tesle 11, Majdanpek, Srbija, E-mail: alena.zdravkovic@rgf.bg.ac.rs

### Ključne reči: halkantit, Čoka Marin, ruda bakra, sekundarni mineral

Halkantit - bakar (II) sulfat pentahidrat je najzastupljeniji član istoimene grupe minerala opšte formule  $M^{2+}SO_4 \cdot 5H_2O$  ( $M = Cu, Mg, Fe, Mn$ ). U prirodi se najčešće pojavljuje kao sekundarni mineral u oksidacionim zonama Cu ležišta u vidu zrnastih ili masivnih agregata koji često obrazuju forme nalik stalaktitima, dok je pojavljivanje pločastih kristalnih agregata ređe. Potpuno razvijene kristalne pljosni halkantit može obrazovati prilikom kontrolisane kristalizacije u laboratorijskim uslovima, dok je u prirodi ta pojava izrazito retka. Sintetički napravljeni kristali halkantita su intenzivno plave idiohromatske boje, dok prirodni mogu biti i plavozelenih nijansi koja potiče od varijacija u sadržaju Fe primesa. Sintetički halkantit, tzv. „plavi kamen” ima široku upotrebu kao fungicid, baktericid i algicid u voćarstvu i povrtarstvu, a krupni, lepo razvijeni sintetički kristali predstavljaju atrakciju među ljubiteljima minerala i deo su mnogih mineraloških kolekcija.

Polimetalično Cu-Au-Ag-Pb-Zn ležište Čoka Marin u kojem je dominantno učešće pirita i sulfida bakra, čine tri rudna tela manjih dimenzija i rezervi, a nalazi se u istočnoj Srbiji oko 15 km južno od Majdanpeka. Pripada ležištima masivnih sulfida bakra dobro poznate Borske metalogenetske zone. U rudnom telu Čoka Marin-1 otvorena su dva potkopa na kotama 534 i 553 m.n.v. Ovo rudno telo ispresecano je sistemima raseda i pukotina, a prostire se do visine od 575 m. Deset godina nakon otvaranja potkopa „Sveti Sava” 2003. godine (kota 553), na pojedinim delovima zidova i tavanica glavnog hodnika obrazovane su kore sekundarnih minerala u vidu kristalnih agregata plavozelene boje, površine oko 1 m<sup>2</sup> i debljine 2-5 cm. Uzorci kristalnih agregata su detaljno pregledani binokularnom lupom i pritom su po boji i morfologiji izdvojene različite faze koje su analizirane primenom skenirajuće elektronske mikroskopije sa energetska - disperzivnom spektrometrijom (SEM-EDS) i metodom rendgenske difrakcije na prahu (eng. *XRPD*). Binokularnim pregledom uzoraka utvrđeno je dominantno prisustvo plavozelenih kristalnih agregata između kojih je parcijalno prisutna glinovita masa smeđe boje, dok su retko prisutni fibrozni agregati bež boje sa sedefastim sjajem. Kristalni agregati su prozračni, staklaste sjajnosti, nepravilno razvijenih pločastih formi veličine do 0,5 cm i debljine do 0,1 cm, lako se lome i imaju nepravilan prelom. Semikvantitativnom SEM-EDS analizom utvrđeno je da su ovi agregati izgrađeni od sulfata bakra sa sadržajem gvožđa do oko 0,6 tež.%, dok fibrozni agregati predstavljaju sulfat kalcijuma. Kako ova metoda nije sasvim odgovarajuća za determinaciju minerala sa različitim sadržajem vode, potpuna identifikacija pomenutih sulfata izvršena je rendgenskom analizom prašenog materijala i pritom je ustanovljeno prisustvo halkantita -  $CuSO_4 \cdot 5H_2O$  (pločasti plavozeleni agregati) i gipsa -  $CaSO_4 \cdot 2H_2O$  (sporadični fibrozni agregati). Druge soli bakra sa manjim ili većim sadržajem vode koje bi se mogle očekivati u asocijaciji sa halkantitom kao i drugi sulfati iz halkantitske grupe, nisu detektovani u ispitivanim uzorcima.

Otvaranje rudarskih radova, a potom višegodišnje mirovanje istih u potkopu „Sveti Sava” inicirali su različite fizičko-hemijske procese koji su doveli do precipitacije kristalnih agregata halkantita kao recentnog sekundarnog minerala. Izloženost rude kiseoniku i cirkulacija atmosfere vode predisponirana sistemom pukotina u rudnom telu, doveli su do oksidacionog rastvaranja primarnih sulfida i stvaranja kisele rudničke drenaže obogaćene bakrom. U otvorenim prostorima rudnika evaporacijom rastvora i njihovim prezasićenjem vremenom je došlo do precipitacije veće količine hidratisanog sulfata bakra. Halkantit, kao lako rastvoran sulfat predstavlja privremeni kolektor bakra koji sprečava mobilnost ovog potencijalno toksičnog elementa iz rudničkih voda u životnu sredinu, sve dok ne dođe do promena uslova sredine (temperatura, vlaga, pH). S druge strane, obrazovanje dobro razvijenih kristalnih agregata halkantita može biti veoma atraktivno za posetioce i podstaći razmatranja mogućnosti iskorišćenja neaktivnih i napuštenih rudnika u pravcu geoturizma.

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## CHALCANTHITE AS A SECONDARY COPPER MINERAL IN THE ČOKA MARIN DEPOSIT, SERBIA

Alena Zdravković<sup>1</sup>, Aleksandar Pačevski<sup>1</sup>, Predrag Dabić<sup>1</sup>, Periša Živković<sup>2</sup>

<sup>1</sup>University of Belgrade - Faculty of Mining and Geology, Đušina 7, Belgrade, Serbia,

<sup>2</sup>Nikole Tesle 11, Majdanpek, Serbia, E-mail: alena.zdravkovic@rgf.bg.ac.rs

**Key words:** chalcantinite, Čoka Marin, copper ore, secondary mineral

Chalcantinite - copper (II) sulfate pentahydrate is the most common member of the eponymous group of minerals of the general formula  $M^{2+}SO_4 \cdot 5H_2O$  ( $M = Cu, Mg, Fe, Mn$ ). In nature, it most often appears as a secondary mineral in the oxidation zones of Cu deposits in the form of granular or massive aggregates that often form stalactitic forms, while the occurrence of platy crystalline aggregates is less frequent. Well-developed crystal faces of chalcantinite can be formed during controlled crystallization in laboratory conditions, while in nature this phenomenon is extremely rare. Synthetic chalcantinite crystals are intensely blue idiochromatic in color, while natural ones can also be blue-green shades that originate from variations in the content of Fe impurities. Synthetic chalcantinite, so-called "Blue stone" is widely used as a fungicide, bactericide and algacide in fruit and vegetables growing, and large, well-developed synthetic crystals are an attraction among mineral lovers and are part of many mineral collections.

The polymetallic Cu-Au-Ag-Pb-Zn deposit of Čoka Marin, in which the dominant minerals are pyrite and copper sulfides, consists of three ore bodies of smaller dimensions and reserves, and is located in eastern Serbia about 15 km south of Majdanpek. It belongs to the deposits of massive copper sulfides of the well-known Bor metallogenic zone. In the ore body Čoka Marin-1 two adits were opened at elevations 534 and 553 m above sea level. This ore body is intersected by systems of faults and cracks, and extends to a height of 575 m. Ten years after the opening of the "Sveti Sava" adit in 2003 (elevation 553), crusts of secondary minerals in the form of blue-green crystalline aggregates, measuring about 1 m<sup>2</sup> and 2-5 cm thick, were formed on certain parts of the walls and ceilings of the main hallway. Samples of crystalline aggregates were examined in detail with a stereo microscope, and different phases were separated by color and morphology, which were analyzed using Scanning electron microscopy with Energy-dispersive spectrometry (SEM-EDS) and X-ray powder diffraction (XRPD). Stereo microscope examination of the samples revealed the dominant presence of blue-green crystalline aggregates, rarely presence of beige fibrous aggregates and partially presence of a brown clay mass. Crystal aggregates are translucent with vitreous luster and irregularly developed platy forms up to 0.5 cm in size and up to 0.1 cm thick which are brittle and have an uneven fracture. Semiquantitative SEM-EDS analysis showed that the platy aggregates were composed of copper sulfate with an iron content of up to 0.6 wt%, while fibrous aggregates are composed of calcium sulfate. As this method is not quite suitable for the determination of minerals with different water content, complete identification of these sulfates was performed by X-ray diffraction analysis of powdered material which proved the presence of chalcantinite -  $CuSO_4 \cdot 5H_2O$  (platy blue-green aggregates) and gypsum -  $CaSO_4 \cdot 2H_2O$  (sporadic fibrous aggregates). Other copper salts with a lower or higher water content that could be expected in association with chalcantinite, as well as other sulfates from the chalcantinite group, were not detected in the analyzed samples. The opening of mining works, and then their long-term inactivity in the "Sveti Sava" adit, initiated various physical and chemical processes that led to the precipitation of crystalline aggregates of chalcantinite as a secondary mineral. Ore exposure to oxygen and circulation of atmospheric water through the predisposed system of cracks in the ore body led to oxidative dissolution of primary sulfides and the creation of acidic mine drainage enriched with copper. In the open spaces of the mine, a larger amount of hydrated copper sulfate was precipitated by evaporation and supersaturation of the solution over time. As easily soluble sulfate - chalcantinite is a temporary copper collector that prevents the mobility of this potentially toxic element from mine water into the environment, until there are changes in environmental conditions (temperature, humidity, pH). On the other hand, the formation of well-developed chalcantinite aggregates can be very attractive to visit and encourage consideration of the possibility of using inactive and abandoned mines for the purpose of geotourism. This paper has been financed by the „Contract on realisation and financing of scientific research of SRI in 2022“, Nr. 451-03-68/2022-14/ 200126