First occurrence of the mineral osakaite $\text{Zn}_4(\text{OH})_6(\text{SO}_4)_2\cdot5\text{H}_2\text{O}$ for Bulgaria

Първа находка на минерала осакаит $\text{Zn}_4(\text{OH})_6(\text{SO}_4)_2\cdot5\text{H}_2\text{O}$ за България

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Abstract. Osakaite, a new mineral for Bulgaria, was discovered in stalactites from the Gyudyurska mine, South Petrovitsa deposit, South Rhodope. The chemical composition determines isomorphous inclusion of $\text{Cu}^{2+}$ and composition $\text{Zn}_3\text{Cu}(\text{OH})_6(\text{SO}_4)_2\cdot5\text{H}_2\text{O}$. The mineral is a product of the interaction of mine waters passing through Zn and Cu-sulfide ores. During prolonged storage in atmospheric conditions, part of the osakaite crystals were dehydrated to the formation of the minerals namuwite $\text{Zn}_3\text{Cu}(\text{OH})_6(\text{SO}_4)_2\cdot4\text{H}_2\text{O}$ and lahnsteinite $\text{Zn}_3\text{Cu}(\text{OH})_6(\text{SO}_4)_2\cdot3\text{H}_2\text{O}$.

Keywords: stalactite, osakaite, namuwite, lahnsteinite.

Introduction

The hydrothermal Pb-Zn deposits are situated in the central parts of the Rhodope Massif in Bulgaria, named as Central Rhodopes (Madan) Dome (Ivanov et al., 2000). The core of the Dome referred to as Arda unit (Ivanov et al. 2000) is constituted by high-grade ortho- and parametamorphites, affected by an intensive migmatization and anatexis (Cherneva, Georgieva, 2005).

The hydrothermal Pb-Zn deposits in the Central Rhodopes are hosted in the Rhodopean metamorphic complex represented by various migmatized gneisses, amphibolites, mica schists, some marble layers, and rare pre-ore rhyolitic dykes, intruded in metamorphic rocks. Two structural-morphological types – veins, attached to fault structures and hydrothermal metasomatic bodies with lenticular or irregular morphology among the marbles, represent the ore deposits.

The ore bodies in the Madan ore field consist of ore veins, complex stockwork zones and metasomatic skarn-ore bodies. Studies on the main ore minerals: galena, sphalerite, pyrite and chalcopyrite and less common ones such as arsenopyrite, tetrahedrite, tennantite, pyrrhotite, silver and bismuth sulfosalts have been carried out by many authors, and the results have been published in dozens of works. A summary of the results of these studies can be found in Kolkovski and Manev (1988) and Vasileva et al. (2009).

However, data on secondary minerals, which are product of mine waters, is scarce or absent. The recent work presents an occurrence of secondary exogenous mineral formations from the Gyudyurska mine.

Materials

The samples for the present study were collected by Petko Petrov and Svetla Stariradeva from the Gyudyurska mine, South Petrovitsa deposit in July 2019. The exact sampling location is level 675 about 1 km into the main gallery where mine waters percolate. The samples are light blue stalactites with a light blue-green sticky crust. Up to 1 cm wide stalactites are formed on a various substrate. Material for the present study was taken from samples deposited in the main collection (sample 24400) and the scientific auxiliary collection – sample 8324 nsf of the Earth and Man National Museum.
**Methods for characterization**

Macrophotos of the material were taken with Olympus camera at daylight illumination. Microphotos were taken with Leica M60 Stereomicroscope Trinocular. The mineral phase identification was carried out by X-ray powder diffraction. XRD patterns were recorded with D8 Advance, Bueker diffractometer, using Co Kα radiation on vertical Θ/Θ goniometer, and a step size of 0.02 (2Θ). Diffracplus EVA software using ICDD PDF-2 crystallographic database was applied for the structural data and semi-quantitative phase analysis. Scanning Electron Microscope (SEM) fitted with Energy Dispersive Spectrometer (EDS) performed the SEM investigations and chemical analysis of some samples. Apparatus JEOL – model JSM-6010PLUS/LA, 20 kV accelerating voltage and spot size 65 nm were used.

**Results and discussion**

Several different types of samples have been examined from the stalactites: samples of single disintegrated small and larger crystals; crystals from the core of the stalactites and crystals from the stalactites surface.

The sizes of the stalactite entities are in the range: length from 1–2 to 8 cm (Fig. 1a) and cross-section from 0.5 × 0.5 cm to 1 × 3 cm. A preserved typical for the stalactites central hole characterizes the small entities, while in larger specimens the stalactite tube is filled up and a drapery forms on the stalactites surface.

The stalactites are composed of a pale light blue to white, transparent fine-grained material with a pearly sheen. The size of the individual flakes is up to 1–2 mm, and most are saddle shaped. The individual crystals show a trigonal or pseudohexagonal shape (Fig. 1c, d). EDS chemical results indicate the presence of Zn, Cu, S and O (Fig. 1e) in the analyzed material.

The powder diffraction analysis of a sample of small and larger crystals from disintegrated parts of the stalactites reveals that the mineral consists of three zinc hydroxy-sulfate-hydrate minerals – osakaite (PDF No 78-0246), namuwite (PDF No 35-0528) and lahnsteinite (according to Rastsvetaeva et al., 2012) (Fig. 1f). The structures of the three minerals are built of identical octahedral-tetrahedral hydroxide layers with cationic vacancies (octahedron:vacancy = 3:1). In the octahedra, zinc is coordinated by (OH)-groups and oxygen atoms from SO₄ group, and the composition of the tetrahedra is Zn(OH)₂H₂O. Zinc tetrahedra Zn(OH)₂(H₂O) and sulfate groups in this case decorate the layer on both sides and thus it can be described as a “double decorated layer” (Hawthorne, Schindler, 2000). The layers are interconnected by water molecules located in the interlayer space. All three minerals are characterized by the same type of hydroxide layer and differ only in number of interlayer water molecules (Fig. 1g). The chemical composition of the three minerals can be represented by the general formula Znₙ(OH)ₓSO₄·nH₂O, where n = 5, 4 and 3. The highest hydrated mineral is osakaite (n = 5), namuwite is with n = 4, and the least hydrated representative of the group is the mineral lahnsteinite (n = 3). The different amount of interlayer water molecules leads to small differences in the parameters, despite the change of symmetry (osakaite P1; namuwite P3; lahnsteinite P1). The value of d spacing of the first basal reflection 00l in the structures of the minerals osakaite, namuwite and lahnsteinite are in direct correlation with the water content (Fig. 1f, g).

For the mineral osakaite nine natural finds have been reported, while for lahnsteinite only one has been reported, which is the holotype for the mineral (Ohnishi et al., 2007; Rastsvetaeva et al., 2012). The uneven distribution of the mineral occurrences is probably due to their dehydration-hydration properties. All three minerals are characterized by mutual transition during dehydration-rehydration reactions (Bear et al., 1986, 1987; Stanimirova et al., 2017), as no visible change in morphology is observed.
To determine the likely primary mineral in the stalactites studied, two types of samples were examined: 1) a sample taken from inside the stalactites, which is assumed to have been least exposed to external influences, and 2) a sample taken (scraped) from the surface, i.e., the probability that it is exposed to dehydration is the greatest.

The XRD shows that the composition of the two samples is respectively osakaite for the inner part of the stalactite and namuwite for the outer part (Fig. 1h). This result suggests that in the conditions and manner of formation, the highest hydrate mineral osakaite is formed as the primary mineral, while the formation of namuwite is most likely a consequence of exposure of the stalactites in drier conditions. This is also confirmed by the registration of a mixed osakaite-namuwite composition of sample from the near-surface zone of the stalactite (Fig. 1h). In addition, the above-mentioned presence of lahnsteinite in the sample of small-disintegrated crystals indicates advanced dehydration caused by a long-term exposure at room conditions.

Conclusions

A new mineral for Bulgaria osakaite \((\text{Zn,Cu)}\text{(OH)}\text{SO}_4\cdot5\text{H}_2\text{O})\) was discovered in stalactites from the Gyudyurska mine in South Petrovitsa Pb-Zn deposit. The identified mineral occurrence is the 10th in the world. In addition to osakaite, the stalactites also contain namuwite and lahnsteinite. We assume that osakaite is the only mineral formed in natural conditions, while the other two resulted of its dehydration at room conditions.

References


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