

Beaverite from the Chala gold-base metal ore deposit: A new mineral for Bulgaria

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Abstract. Beaverite has been observed in the Chala epithermal gold-base metal deposit, Spahievo ore field, Eastern Rhodopes, Bulgaria. The deposit is hosted in Oligocene latites, latitoandesites and coarsy phenocrysts latites. The ore mineralization is connected with adularia-sericite (low-sulfidation) wall-rock type alteration. An important feature of the deposit is the widespread mineralization of secondary phosphate, phosphosulfate and sulfate minerals (wavellite, turquoise, variscite, faustite, cacoxenite, jarosite, anglesite, brochantite, osarizawaite, svanbergite, plumbogummite, hinsdalite, etc.). Beaverite has been found on the surface, in an old exploratory trench with outcropped quartz veins, as well as in the oxidizing zone of the Chala underground mine. On the surface the mineral associates mainly with osarizawaite, while in the mine it could be found together with primary sulfides (galena, chalcopyrite, sphalerite, pyrite) and with secondary minerals (brochantite, osarizawaite, jarosite, anglesite, plumbogummite, hinsdalite, montmorillonite, etc.). The mineral forms fine-grained earthy masses, which as seen under SEM consist of tiny trigonal-rhombohedral crystals. The colour is yellow-brownish to yellow-green and even greenish. The chemical composition of the beaverite has no significant deviations from that reported in the literature. The same is true for the X-ray data. Beaverite origin is of supergene, a product of oxidation of the primary sulphides.

Key words: beaverite, osarizawaite, oxidizing zone, adularia-sericite type epithermal deposit

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Резюме. Биверитът е открит в златно-полиметалното епитермално находище Чала, Спахиевско рудно поле, Източни Родопи, България. Находището е вместило в олигоценски латити, латитоандезити и едропорфирни латити. Вместващите скали са хидротермално-метасоматично изменени. Рудната минерализация е свързана с адулар-серицитов (нискосулфиден) тип изменение. Важна особеност на находището е широката проява на вторични фосфатни, фосфатосулфатни и сулфатни минерали (вавелит, тюркоаз, варисцит, фаустит, какоксенит, ярозит, англезит, брошантит, осаризаваит, сванбергит, плумбогумит, хинсдалит и др.). Биверитът е намерен на повърхността, в стари проучвателни канали с разкрити кварцови жили и също в дълбочина в окислителната зона. На повърхността минералът асоциира главно с осаризаваит, докато в дълбочина той се среща с първични сулфиди (галенит, халкопирит, сфалерит, пирит) и вторични минерали (брошантит, осаризаваит, ярозит, англезит, плумбогумит, хинсдалит, и др.). Биверитът образува землести маси, които се състоят от микроскопични тригонално-ромбоедрични кристали. Цветът е жълтокафяв до жълтозелен и много рядко зеленикав. Рентгеноструктурните данни и химичният състав ясно определят минерала като биверит. Биверитът е със супергенен произход. Той е свързан с окислението на първичните сулфиди.

Ключови думи: биверит, осаризаваит, окислителна зона, адулар-серицитов тип епитермално находище

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Introduction

Beaverite, $\text{PbCu(Fe,Al)}_2(\text{SO}_4)_2(\text{OH})_6$, was firstly described by Butler and Schaller (1911) from the Beaver county (Utah, USA). The osarizawaite, $\text{PbCu(Al,Fe)}_2(\text{SO}_4)_2(\text{OH})_6$, differs from beaverite only by the Al content. Both minerals have been described in a limited number of deposits. Beaverite was found in USA (Butler, Schaller, 1911; Breidenstein et al., 1992), Kazakh Republic (Vitovskaya, 1960), Congo (Van Tassel, 1958), Uzbekistan (Kassimov, 1958), Russia (Kartsenko, 1993), Japan (Ito, 1969; Taguchi et al., 1972), Chili (Paar et al., 1980), Canada (Jambor, Dutrizac, 1983) and other localities with different geological conditions.

Both minerals have been found in the oxidizing zones together with other supergene minerals - mainly of Pb and Cu. Taguchi (1961) regarded osarizawaite as an aluminum analogue of beaverite. Kostov (1993) included both minerals to the anglesite-linarite group of the Zn-Cu-Pb(U) association of the sulfate class. According to Dana's New Mineralogy (Gaines et al., 1997) both minerals belonged to the group of alunite: osarizawaite - in the alunite subgroup and beaverite - in the jarosite subgroup. Strunz (1970) placed beaverite also into the alunite group (natroalunite-jarosite-beaverite). Kashkai (1970) described a group of alunite and its structural analogues where both minerals are the end members of one isomorphous series. Due to the difference in the ionic radii of Al^{3+} (0.51\AA) and Fe^{3+} (0.64\AA). Despite of this he admitted the possibility of isomorphism between Al^{3+} and Fe^{3+} if both Cu^{2+} and Zn^{2+} present.

Materials and methods

The studied specimens were collected in 1996 by one of the authors (Petko Petrov) in the oxidizing zone of the Chala deposit. The samples were collected from the exploratory tunnel 1, level 520, chimney 1. Additional samples were collected from vein outcroppings. Representative sample of studied materials is deposited in the collections of the Geological

Institute (M.I.2001.6.1).

It is not possible to separate enough pure substance for wet chemical analyses. The methods used for investigations of the samples are:

- Powder Debye-Scherrer X-ray analysis, Fe/Mn, visual estimation of the intensities; analyst M. Semchova, Geological Institute);
- X-ray diffractometry (DRON 1, Cu/Ni, 2θ 2–100°, 35 mA/24 KV, analyst G. Bechev, MGU);
- Electron microprobe analysis (JSM-35 CF with TRACOR NORTHERN - TN 2000; accelerating voltage 20 kV; analyst C. Stanchev, LGI - EOOD);
- Scanning electron microscopy (SEM JEOL JSM-T 3000; analyst E. Mandova, Geological Institute).

Geological setting

Chala is a low temperature hydrothermal-metasomatic deposit related to the epithermal gold-polymetallic deposits of adularia-sericite (low sulfidation) type (Kunov, 1999). It is situated in the Spahievo ore field, at the Eastern periphery of the Borovitsa caldera, which is a part of the Borovitsa volcanic area (Harkovska et al., 1989). The latites, latite-andesites, trachytes and monzonites in Spahievo ore field are of Priabon-Oligocene age and are affected by hydrothermal-metasomatic alteration of different intensity (Radonova, 1973; Kunov, 1991, 1999, and others). Propylites, quartz-sericite metasomatites, argillites, secondary quartzites (with sericite, kaolinite, alunite, diaspore and other minerals) and adularia-sericite metasomatites are well expressed. The fault structures played an important role in the ore formation process (Maneva, 1989). The characteristic feature of the deposit is the presence of secondary phosphate and sulfate mineralization of turquoise, cacoxenite, augelite, svanbergite, pyromorphite, corcrite, plumbogummite, hinsdalite, osarizawaite and others (Kunov et al., 1986; Kunov, 1995, 1996, 1999).

Description of beaverite

Kunov (1995), describing osarizawaite from the Chala deposit, have published analyses of an osarizawaite-beaverite mixture and supposed the presence of a pure beaverite phase.

Beaverite was found together with galena, sphalerite, chalcopyrite, pyrite, osarizawaite, anglesite, brochantite, jarosite, quartz, cerussite, montmorillonite and hinsdalite. It is yellowish-brown, and rarely yellow-green to green, especially when mixed with osarizawaite. It forms non homogenous yellow-greenish to brown fine grained earthy aggregates together with osarizawaite, jarosite and limonite.

Using SEM (Fig. 1) one can see that the earthy aggregates consist of fine trigonal crystals. Two habit types of beaverite crystals were observed:

- steep-rhombohedral, bounded by faces of the rhombohedron $\{30\bar{3}1\}$, rarely together with small pinacoidal faces;
- steep-complex, bounded by crystal faces (Fig. 2) of the hexagonal prism $\{10\bar{1}0\}$, and the two rhombohedra $\{30\bar{3}1\}$ and $\{04\bar{4}1\}$.

The first rhombohedron is better developed and only its faces form the top of the crystal. In some cases small pinacoidal faces can be seen on SEM photographs.

The SEM investigations of osarizawaite crystals show the same combination of forms,

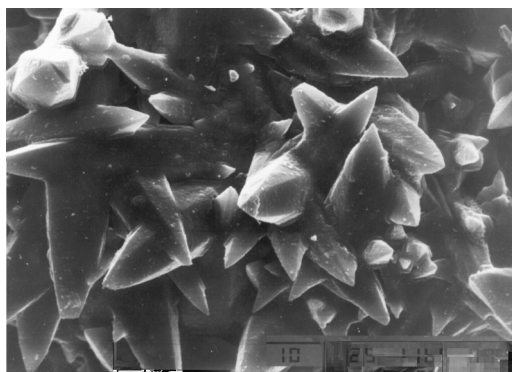


Fig. 1. SEM photomicrograph of beaverite crystals
Фиг. 1. SEM микрофотография на биверитови кристали

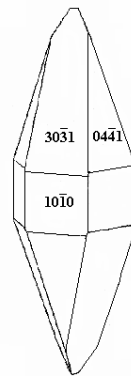


Fig. 2. Morphology of the steep-rhombohedral beaverite crystal

Фиг. 2. Морфология на остроромбедричен кристал на биверит

though they are with a barrel shape habit. In the literature usually for beaverite is reported $R\bar{3}m$ symmetry (Dana et al., 1953; Strunz, 1970; Kostov, 1993). The crystals, observed on SEM images seems to have a center of symmetry, which means that their symmetry can be $R\bar{3}m$. This is the symmetry proved also in the latest structural paper on beaverite (Breindenstein et al., 1992) and chosen by the authors to present the beaverite crystal, shown on the Fig. 2.

The X-ray diffraction pattern obtained from small amount of relatively pure material allowed to identify the mineral as beaverite, well corresponding to the published data (JCPDS, 1974). A very thin film on a flat surface was prepared using a few milligrams of beaverite and was examined with an X-ray diffractometer. The peaks are not sharp. That is why the cell parameters were not calculated. The wide peaks suggest some non-homogeneity of the crystals. The principal X-ray characteristics for I/dA are: $10/5.83$; $8/3.07$; $4/3.34$ and 2.85 .

Pure beaverite was proved in the investigated samples though as a minor phase, as compared to the osarizawaite in the mixture of both minerals (Table 1). Beaverite from Chala has less Fe_2O_3 and PbO compared with

the theoretical composition. The other peculiarity is the varying water content. In all of the analyses reported for beaverite, including the type locality, the beaverites are close to the theoretical composition, but some Al is present. Taguchi et al. (1972) described beaverite rich in Al.

The investigations of samples from the outcropped quartz-sulfide veins proved the presence of osarizawaite-beaverite mixture as well as relatively pure phases of both minerals.

It is still not proved that the sample with chemical composition, intermediate between beaverite and osarizawaite consists of a single phase intermediate between beaverite and osarizawaite or is a mixture of the two minerals.

It is not an exception the two minerals to grow together. Paar et al. (1980) established for osarizawaite and beaverite from Herminia mine, Sierra Gorda, Chile that osarizawaite is the major phase and forms the core of the crystals. The beaverite is the minor phase and forms their rims. Similar zoned crystals were established for beaverite and plumbojarosite by Jambor and Dutrizac (1983).

Conclusions

The mineral associations and geological situation suggest the supergene origin of beaverite. Kasimov (1958) accepted that beaverite from the Sarta-Boutkan gold deposit in Central Asia is also of supergene origin, formed as a result of substitution of cerussite in the oxidizing zone. He did not find beaverite directly deposited on primary sulfides. Quite similar is the origin of beaverite in Akchagil deposit in Central Kazakhstan (Vitovskaya, 1960). The data for beaverite from the Chala deposit allow us to accept its of supergene origin, as well. Galena, chalcopyrite and pyrite, which are widespread in the deposit, are the main source components for beaverite. Another peculiarity of the deposit, the almost absolute lack of primary carbonate mineral leads to formation of osarizawaite, beaverite and brochantite instead of more common malachite and azurite. Presence of beaverite and

osarizawaite could be used to find the outcrops of base metal veins.

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Table 1. *Chemical composition of minerals from the Chala deposit, wt %*
Таблица 1. *Химичен състав на минерали от находище Чала, тегл. %*

	1	2	3	4	5	6	7	8
Al ₂ O ₃	-	2.56	3.05	2.40	4.03	11.25	16.71	16.48
Fe ₂ O ₃	23.60	19.01	18.43	17.99	19.13	8.08	0.63	-
SO ₃	23.66	24.72	25.03	25.34	23.60	24.37	25.47	25.87
PbO	32.99	31.12	32.93	31.91	32.50	33.75	35.60	36.07
CuO	11.76	13.31	12.74	12.49	10.74	12.40	12.57	12.85
H ₂ O	7.99	9.28*	7.82*	9.87*	10.00	10.15*	9.02*	8.73
O=10								
Al	-	0.34	0.40	0.33	0.52	1.4	2.00	2.00
Fe	2.00	1.61	1.55	1.59	1.58	0.64	0.05	-
Pb	2.00	0.94	0.99	1.01	0.96	0.96	0.97	1.00
Cu	1.00	1.13	1.08	1.11	0.89	0.99	0.96	1.00

1 - beaverite, theoretical composition; 2, 3, 4 - beaverites from Chala; 5 - beaverite, Beaver County, Uta, USA, (JCPDS, 17-476); 6 - osarizawaite-beaverite mixed phase, Chala (Kunov, 1995); 7 - osarizawaite, Chala (Kunov, 1995); 8 - osarizawaite, theoretical composition. H₂O* determined by difference to 100%; the crystallochemical formulae are calculated using the method of oxygen charges (Boulah, 1964)

1 - биверит, теоретичен състав; 2, 3, 4 - биверити от Чала; 5 - биверит, Бивер, Юта, САЩ (JCPDS, 17-476); 6 - смесена фаза осаризаваит-биверит, Чала (Kunov, 1995); 7 - осаризаваит, Чала (Kunov, 1995); 8 - осаризаваит, теоретичен състав. H₂O* - разлика до 100%; кристалохимичните формули са изчислени по метода на кислородните заряди (Boulah, 1964)