

Chemistry and morphology of the alunite from the advanced argillic alterations in the Chelopech high-sulphidation epithermal deposit, Bulgaria

Химизъм и морфология на алуניתа от интензивно аргилизитовите изменения на високосулфидизираното епитермално находище Челопеч, България

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Introduction

Alunite and aluminium phosphate-sulphate minerals (APS) are part of the alunite supergroup, that contains more than 40 mineral species with the general formula $DG_3(TO_4)_2(OH, H_2O, F)_6$, where D is a large cation (K, Na, NH_4 , H_3O , Ag, Pb, Hg, Ca, Ba, Sr, Rb, Tl, Bi, REE) G site is occupied by Al, Fe, Cu, Zn, Sn, V, Cr, Ga, Mg, and T site is dominated by P, S and As (Jambor, 1999; Dill, 2001; Bayliss et al., 2010). Alunite has a trigonal symmetry with a space group $R\bar{3}m$. Alunite and APS minerals form during hypogene as well as supergene processes. These minerals are typical as occurrence in the advanced argillic alteration (AAA) zones from the high-sulphidation epithermal deposits. In these conditions complex solid solutions (s.s.) can form. The aim of this study is to describe the morphology and geochemistry of the alunite from the AAA zones in Chelopech high-sulphidation epithermal deposit, Bulgaria, which will yield additional information about the formation of the deposit.

The Chelopech deposit is located within the northern part of the Panagyurishte ore region that belongs to the Banat–Srednogie metallogenic belt. It is hosted by an Upper Cretaceous volcanic and volcano-sedimentary complex. The volcanic rock assemblage is composed of dacite-andesitic lavas, breccias with volcanic elements and various tuffs. Part of these rocks has been intensively altered to an advanced argillic style and hosts the economic Cu-Au orebodies of the deposit.

Description of alunite

Alunite from the Chelopech deposit is widespread in the AAA zones. Using two deep drillings, the mineral

is documented at depths up to 2000 m. In the area of Sharlodere (altitude 750 m) where altered rocks crop out on the recent surface, alunite associate with APS, quartz, dickite, kaolinite, pyrite, enargite and anatase. In the underground mine levels, from altitude 450 m to 250 m, the alteration assemblage is composed of quartz, dickite, kaolinite, nacrite, pyrite, APS and anatase. At deeper levels APS, diaspore, pyrophyllite, and zunyite occur together with alunite.

Alunite is usually present as tabular 5–250 μ m crystals. The dominant form of the crystals is a combination of basal pinacoid {0001} and rhombohedral faces (Fig. 1). Alunite is chemically heterogenous. A distinct zoning was established with the BSEI images. The zoning is due to variations, mainly in the K/Na con-

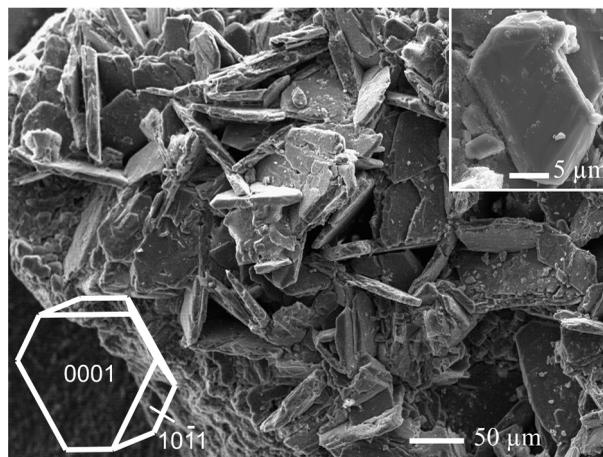


Fig. 1. SEM image of tabular alunite crystals showing combination of basal pinacoid {0001} and rhombohedral faces

tent. Generally, the chemical composition of alunite is mixed with K predominance, but sometimes approach natroalunite compositions, without reaching the end phases. K₂O content reach up to 9.75 wt.%, or up to 0.85 atoms per formulae unit (*apfu*), whereas Na₂O content reach up to 5.05 wt.%, or up to 0.69 *apfu*. Small quantities of Ba (up to 0.125 *apfu*), Ca (0.289 *apfu*), Sr (0.094 *apfu*), Ce (0.031 *apfu*), La (0.016 *apfu*), Nd (0.01 *apfu*), as well as PO₄³⁻ (0.473 *apfu*) were detected. The increased content of PO₄³⁻ is connected with the increase of Ca, Ba, Sr and Ce. These cases probably represent solid solutions between alunite and APS. In some analyses, small amount of F (up to 0.246 *apfu*) was detected also.

APS minerals often occur as zonal grains with an irregular shape in the central part of the alunite crystals (Georgieva et al., 2002).

(H, O, S) isotopic signatures of alunite from the Chelopech deposit show characteristics of magmatic-hydrothermal systems. Sulphur data indicate essentially a magmatic origin for S. O and H data suggest that hydrothermal fluids result from a mixing between magmatic fluids and an external component, which is identified as seawater-derived fluids or meteoric water in the vicinity of a sea. The alunite-pyrite S isotope fractionations imply formation temperatures of 213±7 °C for the mineral assemblages of the AAA in the deposit (Lerouge et al., 2006).

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Discussion

Alunite from the Chelopech deposit is present as tabular crystals. At the upper parts of the deposit, alunite occurs together with APS existing as cores in it crystals. The chemical zoning, essentially due to K-Na substitution and the common presence of APS s.s. in the cores of the alunite crystals suggests frequent changes and variety of the fluid composition during their formation. The spatial relationship between alunite and APS s.s. suggest that complete s.s. between them is not possible, probably due to a textural differences, as presumed by Hikov et al. (2010). Alunite is formed from magmatic dominated fluids. After Deyell and Dipple (2005) a large K/Na variation in fluid is required to precipitate both K- and Na-rich alunite at high temperature. At lower temperature, much less variation in fluid composition can yield compositions near those of the end-members. The mixed K-Na composition of alunite in Chelopech deposit, without reaching end members, suggests moderate temperature of formation and variation of K/Na, as conditions of formation. Alunite forms by low pH (0.8–5.3) sulphate fluids with high oxygen potential. According to Ripp et al. (1998), APS minerals form in conditions of high activity of PO₄³⁻ ions, high oxygen potential and a large pH interval (pH 3–8). Joint presence of these two minerals suggests formation of the AAA zone in the Chelopech deposit in pH interval of 3–5.