



Geochemistry of alunite group minerals in hydrothermally altered rocks from the Asarel porphyry copper deposit, Central Srednogie

Геохимия на алунитовата група минерали в хидротермално променените скали от меднопорфирното находище Асарел, Централно Средногорие

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Introduction

Alunite and aluminium phosphate-sulphate (APS) minerals are object of increasing interest in the last 30 years. They are part of the alunite supergroup (Jambor, 1999) with general formula $DG_3(TO_4)_2(OH,H_2O)_6$, where D are large cations (K, Na, Ag, Ca, Sr, Ba, Pb, Bi, La, Ce, Nd) with coordination number larger or equal to 9. G site is occupied by cations in octahedral coordination (Al, Fe, Cu, Zn), and T site – by S, P, As in tetrahedral coordination. In Bulgaria they are widespread in the zones of advanced argillic alteration. First data for alunite in Asarel gave Radonova and Stefanov (1974) and Ignatovski and Tzvetanov (1981). Svanbergite and woodhouseite are described by Velinov et al. (1991). We present new data of chemical and stable isotope composition of alunite and APS minerals, which throw additional light of the origin of deposit.

The Asarel porphyry copper deposit is located in Panagyurishte ore region, part of the Late Cretaceous Apuseni-Banat-Timok-Srednogie (ABTS) magmatic and metallogenic belt. The Asarel magmatic center represents a volcano-plutonic edifice emplaced in Paleozoic metamorphic and plutonic basement. The following volcanic rocks are distinguished: andesites to latites; basaltic andesites; andesites to dacites. The volcanics are intruded by comagmatic porphyritic bodies of quartz diorite, quartz monzonite to granodiorite porphyrites and granite porphyry (Nedialkov et al., 2007). Propilitic, propilite-argillic, argillic, argillic-sericitic, sericitic and advanced argillic alteration types are established (Popov et al., 1996). Advanced argillic alteration is divided in two subtypes: pyrophyllite (acid-chloride) and alunite (acid-sulphate) Kanazirski (1996). Alteration zoning is expressed by successive replacement of advanced argillic alteration,

sericitization, argillization and propilitization from the center to the periphery and from the top to the bottom of the deposit.

Characteristic of the alunite group minerals

Alunite is the main mineral in the acid-sulphate type advanced argillic rocks. Ignatovski and Tzvetanov (1981) separate alunitic body with complex structure including small bodies of pyrophyllite, dickite and diaspore. The distribution of alunite is irregular from 10 to 60%. It is fine- to coarse-grained, with tabular crystals. Always associate with quartz, APS minerals, rutile and pyrite, often with diaspore, dickite, kaolinite, pyrophyllite, zunyite and barite. APS minerals usually occur as cores in the central part of alunite crystals and have pseudocubic or irregular forms. Zonality marking the transition alunite-APS minerals is often observed as well as partial dissolution of previous deposited alunite or APS minerals followed by later precipitation of the same or similar phases. APS minerals also occur outside the alunitic zone in the pyrophyllite type advanced argillic alteration in association with quartz, pyrophyllite, dickite, kaolinite, diaspore, zunyite, pyrite ± alunite. APS minerals always occur but in small quantities (1–2%). They form pseudocubic crystals between 5 and 250 μm or xenomorphic aggregates.

Alunites from Asarel are mixed K-Na to natroalunites with Na/K ratio varying from 1:10 to 10:1 without reaching the end phases. Admixtures of Ca, Sr and Ba up to 0.10 atoms per formulae unit (a.p.f.u.) are permanent, while light REE, Fe, F and As are rare. Increasing concentration of 2- and 3-valent cations in D position is accompanying by increasing content of PO_4^{3-} up to 0.12 a.p.f.u. Sometimes Sr, Ca and Ba content raise (together up to 0.45 a.p.f.u.) as well as

PO_4^{3-} up to 0.42 a.p.f.u. These are mixed alunite-APS phases, part of them being single zones from zonal alunite-APS crystals. APS minerals themselves are mainly svanbergite and woodhouseite-svanbergite solid solutions (s.s.), rarely woodhouseite. Ca/Sr ratio vary from 10:1 to 1:19, being mostly between 1:1 and 1:10. Maximal concentration of Sr is 0.78 a.p.f.u. (18.55% SrO). PO_4^{3-} changes from 0.6 to 1.35 (usually < 1) a.p.f.u. Barium admixtures are permanent in low concentrations but there are some cases with high Ba content in mixed Ca-Sr-Ba APS s.s. where Ba reach up to 0.36 a.p.f.u. (11.68% BaO). Concentration of K and especially Na decrease in svanbergite and increase in mixed Ca-Sr APS s.s. Light REE content (La, Ce, Nd) is usually low up to 0.03 a.p.f.u. but sometimes increase (for example: La – 0.08 and Ce – 0.19 a.p.f.u.). These are PO_4^{3-} rich phases which are florencite-svanbergite s.s.

Stable (S, O, H) isotope composition of alunite from Asarel shows characteristics of magmatic-hydrothermal systems (Lerouge et al., 2006). The isotope temperature from pyrite-alunite pair (292 ± 11 °C) confirm the suggested temperature for the mineral assemblage of alunite, svanbergite, diaspore, zunyite and pyrophyllite. Magmatic fluids dominate but dilution with surficial waters up to 50% is important.

Discussion

Alunite and APS minerals have wide distribution in the advanced argillic alteration zone of the Asarel porphyry copper deposit. Usually they occur together like APS cores in alunite crystals. Their relationships indicate that APS minerals can be formed before (or without) alunite or together with alunite (zonal alunite-APS crystals) or after alunite, sometimes after

partial dissolution of alunite. This indicates frequent changes of the fluid composition during their formation and predetermines the broad variety of chemical and textural differences. Alunite forms by low pH (0.8–5.3) sulphate fluids with high oxygen potential. High activity of PO_4^{3-} and broad interval of pH (3–8) is important for the APS minerals. Their formation is connected to the destruction of apatite in magmatic rocks (Stoffregen, Alpers, 1987). Apatite is dissolved by low pH acid fluids causing advanced argillic alteration. Hikov (2004) proved that Sr is concentrated in advanced argillic zones where it is fixed in APS (svanbergite and svanbergite-woodhouseite s.s.). PO_4^{3-} , Ca and Sr play a major limiting role for the amount of APS minerals because they are redistributed during the hydrothermal alteration. Alunite and APS minerals are formed from magmatic dominated fluids between 200 and 300 °C.

Alunites from Asarel are mostly natroalunites as alunites from other deposits in the Srednogorie zone. **APS minerals show good miscibility between woodhouseite and svanbergite.** Svanbergite dominate in Asarel which is probably due to the higher concentration of Sr in advanced argillic alteration rocks (up to 3000 ppm). Our data are insufficient to suppose full miscibility between natroalunite and APS minerals. It can be presumed that although there are some mixed phases, the complete solid solution alunite-svanbergite (alunite-woodhouseite) is not possible. The lack of barium APS phases is probably due to its big ionic radius and the formation of barite which is stable in these conditions. Light REE have inert behaviour during advanced argillic alteration and include in APS minerals. Their concentration in the altered rocks is more than 20 times less than Sr and the formation of florencite would be an exception.

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