

Alunite from the advanced argillic alterations in the Chelopech high-sulphidation epithermal Cu-Au deposit, Bulgaria: Chemistry, morphology and genetic significance

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Abstract. Alunite has been determined in the advanced argillic zone of alteration, as well as along with the Cu-As-S ore mineralization in the Chelopech high-sulphidation epithermal deposit. On the Earth surface, alunite is associated with aluminium phosphate-sulphate (APS) minerals, quartz, dickite, kaolinite, pyrite and anatase. At deeper levels, diaspore, pyrophyllite, APS minerals and zunyite occur together with alunite. The temperature of formation of the advanced argillic alteration assemblages is considered to range from less than 200°C at the recent surface to more than 300°C in the deeper levels of the hydrothermal system. As a part of the ore mineralization, alunite is associated with enargite, pyrite, quartz and barite. The close spatial and temporal relationship between these minerals and the Cu-As-S ore mineralization suggests similar Eh-pH conditions for the ore-forming process.

Key words: alunite genesis, advanced argillic mineral assemblage, high-sulphidation epithermal system, Chelopech Cu-Au deposit

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Силвина Георгиева, Надежда Велинова. Алунит от интензивно аргилизитовите изменения на високосулфидизираното епитермално Cu-Au находище Челопеч, България: химизъм, морфология и генетично значение

Резюме. Алунитът е установен в интензивно аргилизитовия тип изменения, както и заедно с Cu-As-S рудна минерализация във високосулфидизираното епитермално Cu-Au находище Челопеч. На съвременната повърхност алунитът асоциира с алуминиево фосфатно-сулфатни (APS) минерали, кварц, дикит, каолинит, пирит и анатаз. В по-дълбоките нива заедно с алунита се появяват диаспор, пирофилит, APS минерали и зунит. Приема се, че температурата на образуване на интензивно аргилизитовите изменения варира от <200°C в по-високите участъци до >300°C в по-дълбоките нива на хидротермалната система. Като част от рудната минерализация алунитът се среща заедно с енаргит, пирит, кварц и барит. Тясната пространствена и времева връзка между тези минерали и Cu-As-S минерализация показват сходни Eh-pH условия за формиране на рудообразователния процес.

Introduction

Alunite is a 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^{2+} , Hg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Rb^+ , Tl^+ , Bi^{3+} , REE^{3+}) with a coordination number greater or equal to 9. G site is occupied by Al^{3+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , Sn^{2+} , V^{3+} , Cr^{3+} , Ga^{3+} or Mg^{2+} in octahedral coordination, and T -site is dominated by S^{6+} , P^{5+} and As^{5+} in tetrahedral coordination (Jambor 1999; Dill 2001; Bayliss et al. 2010). Alunite has a trigonal symmetry with a space group $R\bar{3}m$. The mineral forms between 15 and 400°C during hypogene as well as supergene processes as an alteration product of Al-bearing minerals in relatively oxidizing, S-rich environments (Stoffregen & Alpers 1992). It occurs in many environments, including volcanic and hot spring systems, metamorphic and sedimentary rocks. Different chemical substitutions are possible in the alunite structure including Fe^{3+} for Al^{3+} (Brophy et al. 1962), PO_4^{3-} or AsO_4^{3-} for SO_4^{2-} , and Na^+ , H_3O^+ , Ca^{2+} , or Sr^{2+} for K^+ (Scott 1987; Stoffregen & Alpers 1987, 1992). Depending on conditions and environment various in composition alunite and APS solid solutions (s.s.) are formed (Dill 2001). The most important substitution in alunite is of Na^+ for K^+ leading formation of natroalunite. The temperature dependence of the K-Na substitution in alunite has been analyzed in various studies of high-sulphidation deposits (Aoki 1991; Stoffregen & Alpers 1992; Aoki et al. 1993; Arribas et al. 1995; Deyell & Dipple 2005). The data suggests that substitution by Na is favoured at high temperature. The mineral is typical for advanced argillic alteration (AAA) zones from the high-sulphidation epithermal deposits, wherein it forms as a result of hypogene magmatic-hydrothermal and steam-heated alterations or supergene processes (Rye et al. 1992). Generally, the host rocks in these deposits are acidic to intermediate pyroclastic, volcanic and subvolcanic varieties.

Alunite in Bulgaria is widespread mainly in the AAA zones related or not with high-sulphidation epithermal and/or porphyry copper deposits. The mineral of hydrothermal-metasomatic origin is described in more than 24 deposits located mainly in Srednogorie metallogenic belt and in Eastern Rhodopes (Kunov 1999).

The presence of alunite in the altered rocks of the Chelopech high-sulphidation epithermal deposit was initially mentioned in the works of Chipchakova (1966) and described by Radonova (1969). Alunite is present in the advanced argillic zone of alteration as well along with the Cu-As-S mineralization (Georgieva et al. 2002, 2011). The aim of this study is to provide additional information about the spatial development, chemical composition and morphology of the mineral. The genetic significance of the alunite and the corresponding assemblages are discussed.

Geological setting

The Chelopech deposit is located within the northern part of the Panagyurishte ore region that belongs to the Banat-Srednogorie metallogenic belt (Popov & Popov 2000). It is hosted by an Upper Cretaceous volcanic and volcano-sedimentary complex, transgressively overlying Precambrian gneisses, shists and amphibolites and Paleozoic phyllites and shists. The genesis of the deposit is related to the Late Cretaceous magmatism (Popov et al. 2000). The Upper Cretaceous rock sequence consists of Turonian sedimentary rocks, Coniacian-Santonian dacite-andesites, sandstones and marls (Chelopech Formation), argillaceous limestones (Mirkovo Formation) and Campanian-Maestrichtian terrigenous flysh (Chugovitsa Formation) (Moev & Antonov 1978; Popov & Kovachev 1996). Based on paleontological dating Stoykov & Pavlishina (2003) determine the age of the sedimentary rocks from the Chelopech Formation as Turonian. The Coniacian-Santonian volcanic rock assemblage (Chelopech Formation) is composed of lavas, breccias with volcanic

elements and various tuffs. Stoykov et al. (2002) defined the igneous rocks dominantly as andesite to trachydacite. Part of this rock assemblage has been intensively altered to an advanced argillic style and hosts the economic Cu-Au ore bodies of the deposit. Sedimentary rocks of the Chelopech-, Mirkovo- and Chugovitsa Formations cover partly the altered volcanic complex and the ore deposit. U-Pb dating on zircons from the host andesites reflecting maximum age of 91.45 ± 0.15 Ma (Moritz et al. 2003) and 91.3 ± 0.3 Ma (Stoykov et al. 2004). The Chelopech deposit includes more than 20 ore bodies, most of them hosted by breccias. Textural relationships indicate multiple breccia events of different origins – phreatomagmatic and magmatic hydrothermal injection breccias (Moritz et al. 2003; Chambefort 2005). The morphology of the ore bodies is variable, with disseminated, massive, banded and vein-type ore. The vertical development of economic ore is known down to a depth of 600 m below the recent surface and is open downward.

The Chelopech deposit is the largest and the only producing high-sulphidation Cu-Au deposit for the time being in the Panagyurishte district, Bulgaria. It ranks among the major high-sulphidation deposits of the world, with a tonnage and a gold grade comparable to important deposits of the Circum-Pacific region such as El Indio (Chile), Lepanto (Philippines) and Pierina (Peru) (Moritz et al. 2004). The past production of the deposit (since 1954) is of 11.5 Mt with 1.0% Cu, 3.0 g/t Au and remaining resources of 31 Mt with 1.39% Cu, 3.5 g/t Au (Strashimirov et al. 2002). The late information about it is given in the Technical report for the Chelopech project, Bulgaria (Chelopech Mining EAD 2011). After it since the mine started the past production is approximately 19.8 Mt of ore with 1.2% Cu, as at January 1 2011, proven reserves are 14.59 Mt at 3.66 g/t Au and 1.37% Cu, with probable reserves of 6.26 Mt at 4.37 g/t Au and 1.04% Cu, for a total of 20.85 Mt at 3.87 g/t Au and 1.27% Cu. According to the same source the ore concentrate from the deposit containing Cu,

Au and Ag is currently shipped for processing to the Tsumeb Smelter in Namibia, which is a subsidiary of Dundee Precious Metals Inc.

Hydrothermal alteration and ore assemblages

Moutafchiev & Chipchakova (1969) described the alteration products in the Chelopech deposit as secondary quartzites, which include alunite, kaolinite and sericite facies to quartz-sericite alteration imposed on earlier propylitic alterations. Popov et al. (2000) distinguished propylitic, propylitic-sericitic, sericitic, sericitic-advanced argillic and advanced argillic (acid-chlorine and acid-sulphate) pre-ore alteration type. Lately, Kanazirski (2011) and Popov et al. (2012) define the alteration sequences as propylitic, propylitic-sericitic, sericitic and advanced argillic (acid-chlorine) types of alteration. The authors disregard the presence of alunite and APS minerals established in advanced argillic and sericitic zone (Georgieva et al. 2002, 2011; Lerouge et al. 2006) and determine the deposit as high-intermediate sulphidation epithermal type with domination of intermediate sulphidation (acid-chlorine) type of hydrothermal system. Numerous investigations of the alteration style and ore forming processes (Petrunov 1994, 1995; Georgieva et al. 2002, 2011; Moritz et al. 2004; Lerouge et al. 2006) characterized Chelopech Cu-Au deposit as typical for epithermal high-sulphidation system, discussed in details by Arribas (1995) and Hedenquist et al. (2000). Three main alteration zones are distinguished laterally in the host rocks. The most intensive alteration, that hosts the ore bodies consist of advanced argillic zone with “vuggy” silica and massive silica areas. The advance argillic alteration assemblage is composed of quartz, dickite, kaolinite, pyrite, anatase, alunite and APS minerals, representing mainly svanbergite-woodhouseite solid solutions series. The AAA zone is spatially followed by the sericitic zone of alteration characterized with sericite, quartz, illite, pyrite, APS minerals, halloysite and anatase

(Georgieva et al. 2002). The external propylitic zone is composed of chlorite, albite, epidote, carbonate (calcite), sericite, rutile, pyrite (Radonova 1969; Georgieva et al. 2002). According to Radonova (1969) andalusite is present in AAA zones with limited distribution in separate rock volumes with a maximum content of 15%. The presence of corundum only in one thin section is reported as well.

Two deep drill-holes (600 and 600a) reveal that the advanced argillic alteration is developed in the volcanic rocks down to a depth of more than 2000 m. A vertical variation of the mineral composition is observed with development of diaspore, pyrophyllite, alunite and zunyite at depth (Georgieva et al. 2002).

Three successive stages of the ore-mineralizing process have been recognized at the Chelopech deposit (Petrunov 1994, 1995): (1) Fe-S, with disseminated and massive pyrite of banded texture (considered to be of hydrothermal sedimentary-diagenetic origin); (2) Cu-As-S, with enargite and tennantite and (3) Pb-Zn-S. Major part of the late polymetallic ore stage is developed below and at the periphery of the economic gold-bearing pyrite-enargite-chalcopyrite ore bodies, that is beyond the AAA zone. The predominant minerals are pyrite, enargite, tennantite, chalcopyrite, bornite and barite. Great number of subordinate and rare minerals is associated with the Cu-As-S main economic ore stage, including sulphides, sulphosalts, tellurides, selenides and native metals. These minerals refer to a large geochemical association: Cu, Fe, S, As, Sb, Te, Bi, Se, Sn, Mo, Ge, Au, Ag, Pb, Zn, Hg, and Ga (Terziev 1968; Petrunov 1994, 1995).

Materials and methods of study

The samples were collected from present-day surface in the area of Sharlo Dere (easternmost part of the Chelopech deposit – elevation 750 m) and the underground galleries of the mine level 405 (300–350 m below the present-day surface). Samples from two 2-km deep drill-holes (600 and 600a at elevations 400 m,

248 m, 193 m, 122 m, -158 m, -400 m and -770 m) were used as well. The samples referred to the advanced argillic and sericitic zones of alteration from the central, western and easternmost part of the deposit.

The mineral assemblages and the paragenetic relationship of alunite with the other minerals were studied by transmitted and reflected light microscopy. X-ray powder diffraction (Siemens 500 diffractometer) and DTA (MOM – Budapest) methods was used for defining the mineral composition of the rocks in the AAA zone (Geological Institute, BAS). The chemical composition was determined using a CAMECA CAMEBAX SX-50 electron microprobe (University of Lausanne, Switzerland and BRGM, Orléans, France). The analyses were made by EDS system with acceleration voltage at 15–20 kV, beam current at 2–6 nA and beam diameter at 1µm. The chemical zoning of alunite crystals and grains was examined with a JEOL scanning electron microscope (SEM) at the University of Geneva, Switzerland. Samples SHD7 and SHD3c were studied for (H, O, S) stable isotopes. Oxygen, hydrogen and complementary sulphur isotope ratio were measured by Delta S Finnigan-Mat gas-source mass spectrometer at the Laboratory of Stable Isotopes and Low Radioactivity, BRGM, Orléans, France.

Results

Alunite from the Chelopech deposit is widespread in the AAA zone. In the area of Sharlo Dere (altitude 750 m) where altered rocks crop out on the recent surface, alunite associate with APS minerals, 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 minerals and anatase (Fig. 1). At deeper levels APS minerals, diaspore, pyrophyllite, and zunyite occur together with

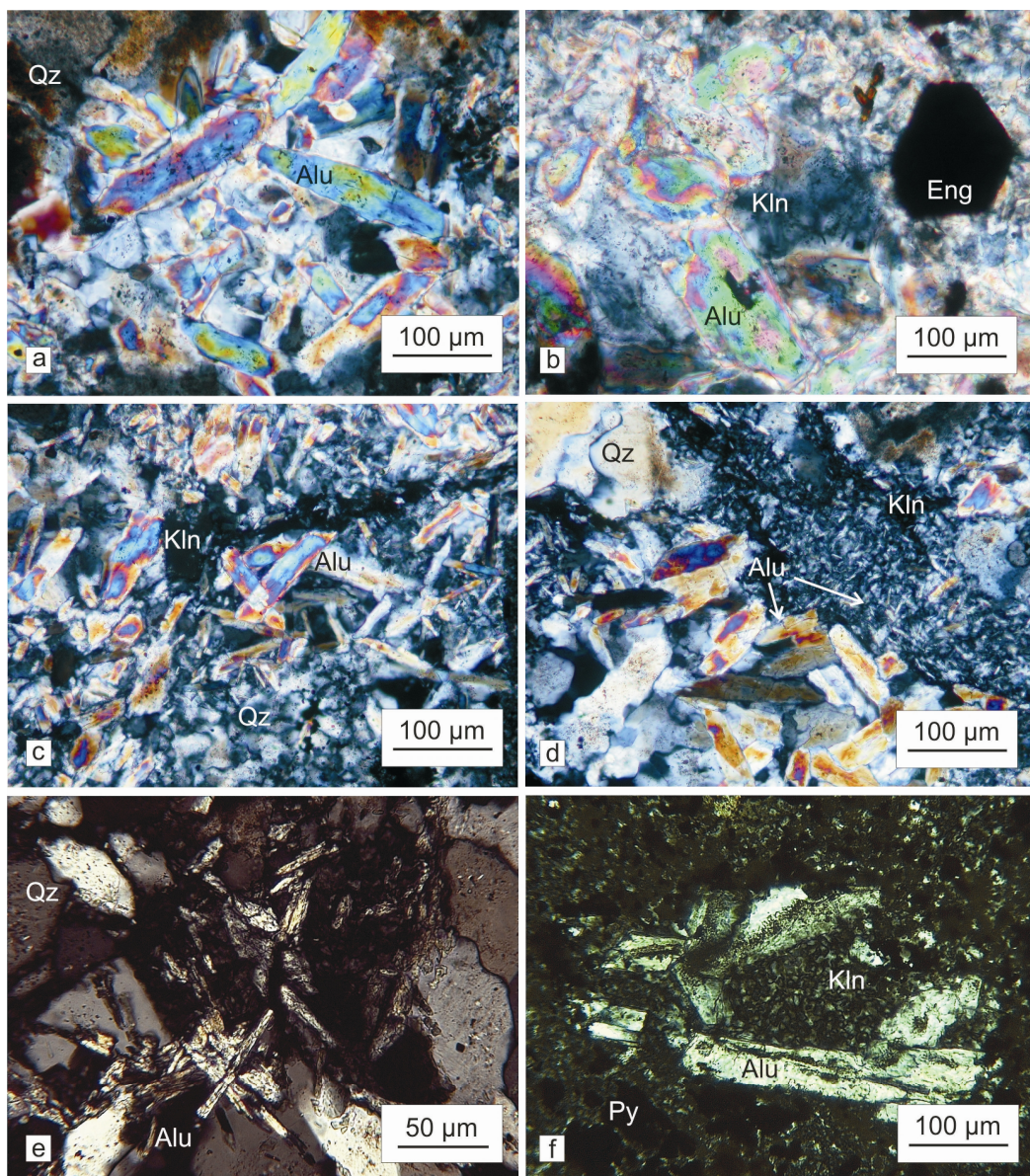


Fig. 1. Microphotographs of alunitic mineral associations with quartz (Qz), kaolinite (Kln), enargite (Eng) and pyrite (Py) from different levels: a-d) on the surface in the area of Sharlo Dere; e-f) in deeper levels of the deposit. The abbreviations for mineral names are used according to Whitney & Evans 2010

alunitic (Georgieva et al. 2002). The distribution of the mineral in the altered rocks is not uniform. The most abundant presence is in the area of Sharlo Dere occurrence, situated

approx. 1 km to the northeast of the Chelopech mine and considered as an exhumed part of the Chelopech deposit (Popov et al. 2000). At this location the alunitic contents is variable from 1

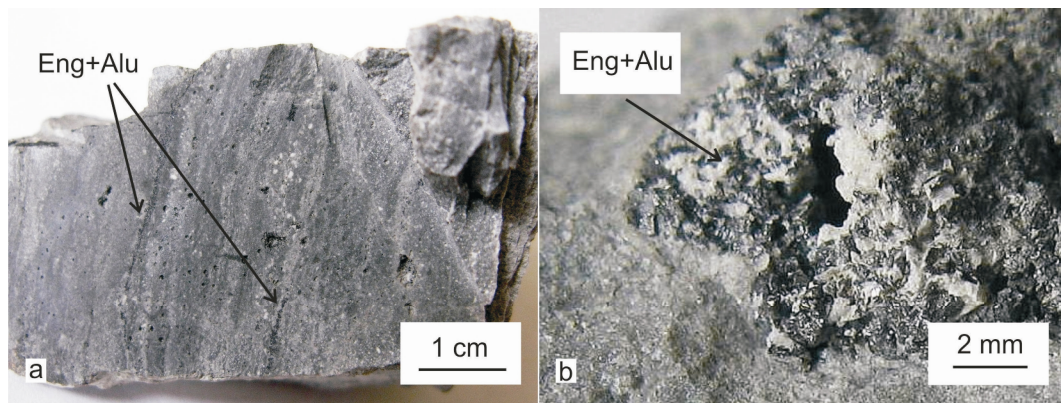


Fig. 2. Alunite (Alu) and enargite (Eng) from Sharlo Dere occurrence: a) as replacements in altered volcanic tuffs; b) in cavities

to 20%, where the mineral forms pseudomorphic replacements, veinlets or filled cavities (Fig. 2). In the underground levels the presence of this mineral is irregular and sporadic.

Alunite is usually present as medium- to fine-grained tabular 5–250 μm crystals with pinacoidal habit. The dominant form of the crystals is a combination of basal pinacoid $\{0001\}$ and rhombohedral faces (Fig. 3). The mineral is chemically heterogeneous. A distinct zoning was established with the BSE images. The zoning is due to variations, mainly in the K/Na content (Fig. 4). Generally, the chemical composition of alunite is mixed with K predominance, but sometimes approach natroalunite compositions, without reaching the end member (Fig. 5). There is no regular change in K/Na ratio from the center to the periphery of the crystals. In some samples K_2O content reach up to 9.75 wt.%, or up to 0.85 atoms per formulae unit (*apfu*), whereas the maximum Na_2O content reach up to 5.05 wt.%, or up to 0.69 *apfu* (Table 1). Small quantities of Ca (up to 0.289 *apfu*), Ba (0.125 *apfu*) and Sr (0.094 *apfu*) are often present (Table 2). The content of REE is very low, however is almost constant among the analyzed samples, for example Ce (up to 0.031 *apfu*), La (0.016 *apfu*), Nd (0.01 *apfu*). In some phases the content of P in (TO_4) position varies from 0.01

apfu up to 0.473 *apfu*. The increased content of P is connected with the increase of Ca, Ba, Sr and Ce. These probably represent solid solutions between alunite and APS minerals. In some analyses, small amount of F (up to 0.246 *apfu*) was detected also. As and Fe are indistinctive. EPMA elemental mapping shows hidden zoning in alunite with substitution of K–Na–Ca–Sr (Fig. 6). The mapping indicates the concentration of Ca and Sr in the central parts of the mineral. Sr is also slightly

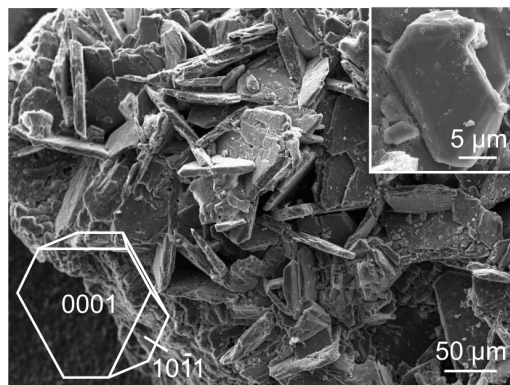


Fig. 3. SEM image of tabular alunite crystals showing combination of basal pinacoid $\{0001\}$ and rhombohedral faces

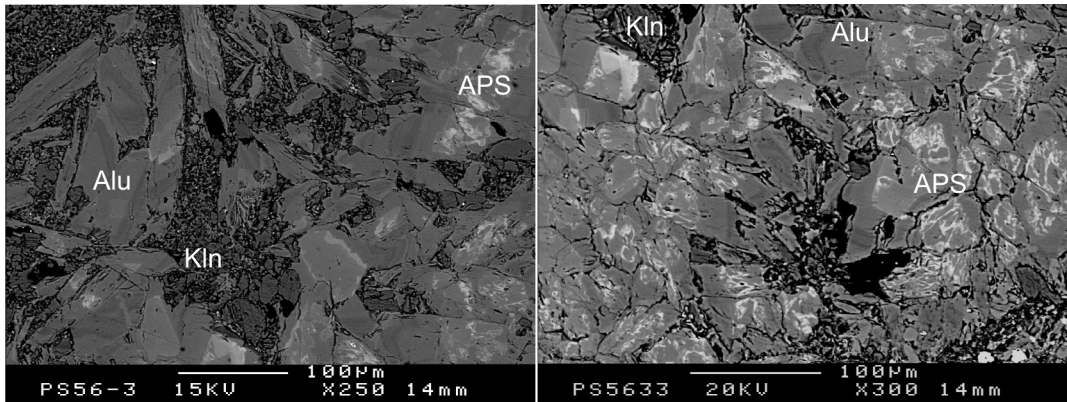


Fig. 4. BSE image of zonal alunite (Alu) with randomly shaped APS cores in association with kaolinite (Kln)

disseminated across the whole surface. The content of K is distributed throughout the entire section with increased concentration in the core of the crystal as well in some external parts. Na is scattered over the whole surface with a slight enrichment in the periphery.

APS minerals typically occur as zonal grains with pseudocubic or random shape in the central part of the alunite crystals. Commonly, this is an earlier formed solid solution of APS minerals followed by later precipitation of the

alunite. Generally, APS minerals are unhomogeneous with complicate zoning due to the variable concentrations of Ca, Sr, Ba, K REE and also PO_4^{3-} and SO_4^{2-} in the fluid. The chemical composition of the APS minerals is studied in earlier work that confirms mainly svanbergite-woodhouseite solid solution $(Ca,Sr)Al_3(PO_4,SO_4)_2(OH,H_2O)_6$ without reaching pure end-members. Except the presence in the central parts of the alunite crystals these minerals are found independently as isolated 5–150 μm pseudocubic crystals or irregular aggregates. APS minerals also occur in the sericitic zone of the AAA zone in association with quartz, illite, pyrite, halloysite and anatase (Georgieva et al. 2002).



Fig. 5. D-position diagram of alunite (Alu) and alunite-APS s.s. (Alu-APS)

Discussions

Alunite and its structural analogues aluminium phosphate-sulfate (APS) minerals occur in different environments, including metamorphic, igneous and sedimentary rocks. They are formed as well in hypogene as in supergene processes (Stoffregen & Alpers 1987; Dill 2001). Different chemical substitutions are possible in the alunite, forming a large group of structural analogues, mentioned above. These minerals are typical for the advanced argillic style of alteration connected with high-sulphidation epithermal deposits (Aoki et al. 1993;

Table 1. Representative microprobe analyses of alunite, wt. %

sample	P56		P56		P56		S7		S7		S3c		S3c		S3c		S3c			
	231	435	640	648	649	649	196	197	4106	18	29	212	216	1a23	4a34	7.53	6.90	7.17	7.17	
K ₂ O	5.59	5.88	3.56	3.82	5.26	6.63	6.67	6.67	5.99	9.75	7.17	6.90	7.53	7.66	8.43	7.53	6.90	7.17	7.17	7.17
Na ₂ O	3.58	3.79	5.05	4.92	4.02	2.61	2.41	2.93	2.93	0.71	2.38	2.86	2.22	2.05	1.65	2.22	2.86	2.38	2.38	2.38
SrO	0.20	0.14	-	0.01	0.22	0.12	0.05	0.03	0.03	0.21	0.06	0.15	0.15	0.20	0.02	0.15	0.15	0.06	0.06	0.06
CaO	0.04	0.03	0.05	0.12	-	0.01	0.01	0.01	0.02	0.01	-	-	-	-	0.01	-	-	-	-	-
BaO	0.18	0.36	-	-	-	-	-	-	0.28	0.06	-	-	-	-	-	-	-	-	-	-
Ce ₂ O ₃	-	0.08	-	0.11	0.05	-	0.04	-	0.04	0.06	-	-	-	-	-	-	-	-	-	-
La ₂ O ₃	-	0.27	0.05	-	-	0.15	0.01	0.27	0.01	0.01	0.63	0.23	0.20	0.05	-	0.20	0.23	0.63	0.63	0.63
Nd ₂ O ₃	0.16	-	-	-	0.24	-	0.06	-	-	-	-	0.14	-	0.04	0.36	-	0.14	-	-	-
Al ₂ O ₃	37.95	37.45	38.60	38.20	37.55	38.26	38.07	37.59	37.59	37.14	38.08	37.65	36.40	37.49	37.45	36.40	37.65	38.08	38.08	38.08
Fe ₂ O ₃	-	0.04	0.02	-	-	-	0.02	-	0.02	0.11	-	-	-	0.01	-	0.08	-	-	-	-
SO ₃	38.72	38.18	38.38	38.85	38.34	39.03	38.88	40.83	40.83	38.83	38.95	38.54	38.57	38.38	37.96	38.57	38.54	38.95	38.95	38.95
P ₂ O ₅	-	0.16	0.06	-	0.08	0.07	0.03	0.10	0.10	0.18	0.03	-	-	-	0.08	-	-	0.03	0.03	0.03
F	0.11	0.16	-	0.31	0.41	0.23	0.21	-	-	-	0.86	0.17	0.41	0.53	0.50	0.41	0.17	0.86	0.86	0.86
Cl	-	-	0.02	-	-	-	-	-	-	-	0.01	-	0.01	0.02	0.03	0.01	-	0.01	0.01	0.01
Σ	86.52	86.64	85.80	86.33	86.17	87.11	86.48	88.03	88.03	87.24	88.20	86.74	85.62	86.49	87.31	85.62	86.74	88.20	88.20	88.20
K	0.49	0.51	0.31	0.33	0.46	0.57	0.58	0.51	0.51	0.85	0.62	0.60	0.66	0.70	0.74	0.66	0.60	0.62	0.62	0.62
Na	0.47	0.50	0.69	0.64	0.53	0.34	0.32	0.38	0.38	0.09	0.31	0.38	0.30	0.27	0.22	0.30	0.38	0.31	0.31	0.31
Sr	0.01	0.01	-	-	0.01	0.01	-	-	-	0.01	-	0.01	0.01	0.01	-	0.01	0.01	-	-	-
Ca	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba	0.01	0.01	-	-	-	-	-	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-
Ce	-	0.002	-	0.003	0.001	-	0.001	-	-	0.002	-	-	-	-	0.003	-	-	-	-	-
La	-	0.01	0.001	-	-	0.004	-	-	0.01	-	0.02	0.01	0.01	0.001	-	0.01	0.01	0.02	0.02	0.02
Nd	0.004	-	-	-	0.01	-	0.001	-	-	-	-	0.003	-	0.001	0.01	-	0.003	-	-	-
Al	3.04	3.02	3.08	3.04	3.02	3.04	3.04	3.04	2.94	2.99	3.01	3.02	2.97	3.02	3.03	3.02	3.02	3.01	3.01	3.01
Fe	-	-	-	-	-	-	-	-	-	0.01	-	-	0.01	-	-	-	-	-	-	-
S	1.98	1.96	1.96	1.97	1.97	1.98	1.98	1.98	2.03	1.99	1.96	1.98	2.00	1.97	1.96	1.98	1.98	1.96	1.96	1.96
P	-	0.01	-	0.01	0.01	-	-	0.01	-	0.01	-	-	-	-	-	-	-	-	-	-
F	0.02	0.04	-	0.07	0.09	0.05	0.05	-	-	-	0.18	0.04	0.09	0.11	0.11	0.04	0.04	0.18	0.18	0.18
Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 2. Representative microprobe analyses of alumite and alumite-APS s.s., wt. %

sample	PS56 4 34	PS56 6 39	PS56 6 42	PS56 6 45	PS56 6 46	PS56 6 52	Shd7 1 94	Shd7 2 98	S7 299	Shd7 4 103	Shd7 4 104	Shd3c 1 6	Shd3c 1 7
K ₂ O	6.14	4.43	4.13	3.35	8.26	8.59	8.19	8.31	5.96	7.19	8.10	8.05	8.53
Na ₂ O	2.40	1.54	1.48	1.62	1.99	1.57	1.05	1.10	2.68	1.80	1.34	1.32	1.07
SrO	0.43	1.78	2.31	2.17	0.28	0.43	0.28	0.08	0.14	0.26	0.22	0.16	0.05
CaO	0.52	3.70	3.75	2.67	-	0.26	0.53	0.02	-	0.26	0.15	0.06	1.28
BaO	0.97	0.92	0.97	4.40	1.03	0.23	0.89	0.80	0.23	1.01	0.10	0.42	-
Ce ₂ O ₃	0.18	0.36	0.47	1.16	0.08	-	0.29	-	0.03	0.07	0.03	0.21	-
La ₂ O ₃	0.32	0.30	0.07	-	0.17	0.18	0.33	-	-	-	-	0.17	0.26
Nd ₂ O ₃	0.26	-	-	0.07	0.39	0.22	-	-	-	-	0.20	0.09	0.12
Al ₂ O ₃	36.77	35.15	36.24	35.09	36.63	36.39	37.10	36.90	37.52	38.56	36.99	36.79	36.83
Fe ₂ O ₃	0.01	-	-	-	-	0.01	-	0.01	-	0.17	-	0.34	0.12
SO ₃	35.70	28.37	30.12	28.08	36.71	37.84	36.48	38.59	38.73	38.20	36.94	37.20	37.64
P ₂ O ₅	1.98	7.02	6.89	7.72	0.51	0.77	1.57	0.33	0.21	0.62	0.64	0.35	0.62
F	0.19	-	0.04	-	-	-	0.27	-	-	0.24	-	0.05	-
Cl	0.11	-	0.02	0.04	0.14	-	0.02	0.09	-	0.06	0.02	-	0.02
Σ	86.06	83.62	86.57	86.47	86.19	86.54	86.99	86.23	85.49	88.43	84.72	85.32	86.62
K	0.55	0.41	0.37	0.31	0.74	0.76	0.72	0.73	0.52	0.62	0.73	0.72	0.75
Na	0.32	0.22	0.20	0.23	0.27	0.21	0.14	0.15	0.36	0.24	0.18	0.18	0.14
Sr	0.02	0.08	0.09	0.09	0.01	0.02	0.01	-	0.01	0.01	-	0.01	-
Ca	0.04	0.29	0.28	0.21	-	0.02	0.04	-	-	0.02	0.01	0.01	0.09
Ba	0.03	0.03	0.03	0.13	0.03	0.01	0.02	0.02	0.01	0.03	-	0.01	-
Ce	0.01	0.01	0.01	0.03	0.002	-	0.01	-	0.001	0.002	0.001	0.01	-
La	0.01	0.01	0.002	-	0.004	0.01	0.01	-	-	-	-	0.004	0.01
Nd	0.01	-	-	0.002	0.01	0.01	-	-	-	-	0.01	0.002	0.003
Al	3.02	3.01	3.00	2.99	3.03	2.97	3.02	3.00	3.02	3.06	3.05	3.03	2.99
Fe	-	-	-	-	-	-	-	-	-	0.01	-	0.02	0.01
S	1.87	1.55	1.59	1.53	1.93	1.97	1.96	2.00	1.99	1.93	1.94	1.96	1.95
P	0.12	0.43	0.41	0.47	0.03	0.05	0.09	0.01	0.01	0.04	0.04	0.02	0.04
F	0.04	-	0.01	-	-	-	0.06	-	-	0.05	-	0.01	-
Cl	0.01	-	0.003	0.005	0.02	-	0.002	0.01	-	0.01	-	-	0.002

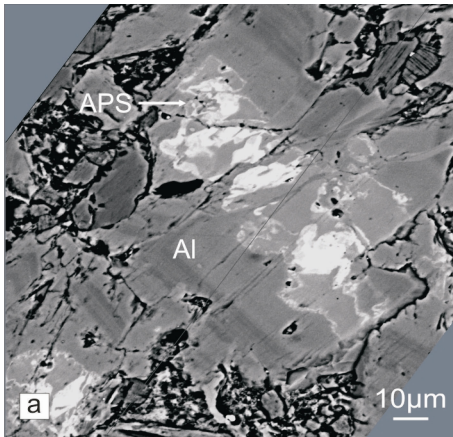
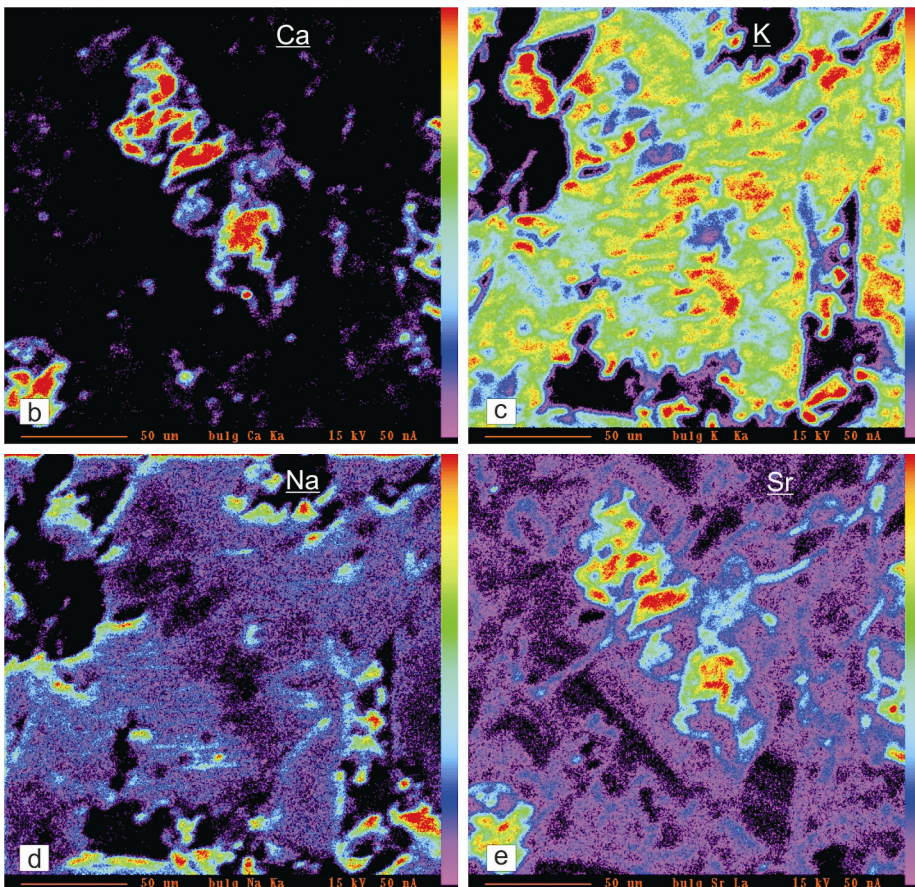


Fig. 6. SEM image (a) and EPMA elemental mapping (b-e) of alunite with APS minerals in the central parts, showing distribution of Ca, K, Na and Sr



Hedenquist et al. 1994; Arribas et al. 1995, etc.). Recently, alunite and APS minerals are considered as part of the most important

characteristic feature for the advanced argillic alterations. This increases their genetic importance regarding the physicochemical

condition of ore formation and particularly in ore prospecting.

According to Atlas der Kristallformen (Goldshmidt 1913) alunite is observed with pinacoidal and rhombohedral habit. With development of basal pinacoid {0001} with small {1011} faces the crystal obtains tabular appearance, whereas the development of single rhombohedron {1011} leads to formation of pseudocubic crystals. Based on the experimental study, as well after numerous field observations, many authors conclude that alunite with rhombohedral habit forms mainly under surface conditions with temperatures up to 200°C and a pressure 1–12 atm. At depth, with increasing of temperature and pressure only alunite with pinacoidal habit is encountered. Factors like pH, Eh and the relative concentration of Al³⁺ and SO₄²⁻ in the solutions are also considered as significant for development of the specific habit (Aslanian et al. 1976; Velinov et al. 1986; Kostov & Kostov 1999; Velinov et al. 2007).

Alunite from the Chelopech deposit is present as tabular crystals with development of basal pinacoid {0001} and small {1011} faces. At the upper parts of the deposit, alunite occurs together with APS minerals existing as cores in its 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 of the fluid composition as well the physical conditions during their formation, which determines the broad variety of chemical and textural differences. The chemical composition of alunite is change from K to Na with additional content of Ba Ca, Sr and REE. The joint growth APS s.s. are also with various chemical composition mainly with Sr, Ca, Ba, REE,

SO₄²⁻, PO₄³⁻. Small amount of F is detected as well. The spatial relationship between alunite and APS minerals suggest that full miscibility between them is not possible, probably due to some textural differences, as presumed by Hikov et al. (2010). Alunite forms at temperatures up to 500°C and sulphate fluids with high oxygen potential and low pH (0.8–5.3) (Hemley et al. 1969; Kashkai 1972). 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 from strong acid to neutral (3–8). Joint presence of these minerals suggests formation of the AAA zone in the Chelopech deposit in pH interval of 3–5. After Deyell & 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 condition of formation.

Stable isotopes of alunite and pyrite of two samples from the Chelopech deposit are given in Table 3. The high δ³⁴S values of alunite combined with mineralogical features of the deposit show characteristics classically described for magmatic-hydrothermal systems (Rye et al. 1992). Oxygen and hydrogen data on alunite confirm the dominant magmatic component of the fluid, but also indicate important participation of surficial waters, which can contribute by different ways to the sulphur content of the hydrothermal fluid.

Possible sources of sulphur in acid-sulphate alteration include dominantly

Table 3. Sulphur, oxygen and hydrogen isotopic composition of alunite and pyrite from the Chelopech deposit

Sample reference	δ ³⁴ S _{Pyrite} ‰ CDT	δ ³⁴ S _{Alunite} ‰ CDT	δ ¹⁸ O _{SO₄} _{Alunite} ‰ V-SMOW	δD _{Alunite} ‰ V-SMOW	T (°C)
SHD7		24.4	12.8	-25	200–250
SHD3c	-3.7	22.8	13.6	-15	213±7

magmatic/volcanic SO₂ and H₂S but also seawater sulphates and sulphur from the crustal basement. The coexisting alunite-pyrite pair in the sample SHD3c has alunite-pyrite sulphur isotope fractionations of 26.5‰, which imply formation temperatures of 213 ± 7°C, using the data of Rye et al. (1992) (Lerouge et al. 2006). The temperature of formation of alunite was estimated also in previous works using combined data of mineralogical assemblage from AAA zone and microthermometric data (Georgieva et al. 2002; Moritz et al. 2001, 2003). The alunite is stable with kaolinite/dickite and APS minerals. The predominance of dickite and the presence of APS minerals with alunite suggest temperatures ~200–250°C (Hemley et al. 1980; Corbett & Leach 1998; Hedenquist et al. 1998). The isotope temperatures from the pyrite-alunite pair (213 ± 7°C) (Lerouge et al. 2006) are in good agreement with the temperature range predicted from the mineral assemblage mentioned above and previous works (mineralogical data in Georgieva et al. 2002; microthermometry on enargite in Moritz et al. 2001, 2003). At deeper levels, alunite is stable with diaspore, pyrophyllite and zunyite. Kashkai & Babaev (1976) define the existence of diaspore in the alteration assemblage as a sign of relatively high temperatures of mineral formation. In the experimental systems as well in the nature, when the quantity of Si is enough, the temperature of formation of alunite is clearly recognized by the variety of associated aluminosilicates minerals. According to experimental data, alunite-kaolinite-muscovite association is typical for the temperatures up to 200°C. At temperatures higher than 300°C kaolinite is transformed into pyrophyllite (Hemley et al. 1969; Kashkai & Babaev 1976). The coexistence of pyrophyllite and diaspore suggest temperatures above 285°C and very low pH from 1–1.5 (Hemley et al. 1980). Dickite-pyrophyllite-zunyite assemblage might be stable at temperatures up to 375°C, according to Berman (1988). The range of the H₂S/SO₄ ratio calculated for the hydrothermal fluids at Chelopech deposit is 2–4 (Lerouge et

al. 2006). The presence of F-rich minerals such as zunyite in the hydrothermal system, the predominance of magmatic fluids and the H₂S/SO₄ ratio >1 are in accordance with the corresponding results obtained in high-sulphidation epithermal Cu-Au deposits such as Summitville (Rye et al. 1990), Pueblo Viejo (Vennemann et al. 1993), Nansatsu (Hedenquist et al. 1994), Rodalquilar (Arribas et al. 1995), Lepanto (Hedenquist et al. 1998), etc. These conditions are not sufficient but seem to be important to accomplish the development of mineralized systems in the high-sulphidation deposits (Lerouge et al. 2006).

Conclusions

Alunite from the Chelopech deposit occurs as tabular 5–250 µm crystals with pinacoidal habit in all studied samples. The isotopic signatures combined with mineralogical features show characteristics of magmatic-hydrothermal systems, according to Rye et al. (1992) with significant dilution of surficial waters and H₂S/SO₄ ratio about 2–4. The variable chemical composition of alunite and the presence of the APS s.s. reflect frequent change of chemical composition and concentration of elements in the hydrothermal fluid (K⁺, Na⁺, Ca²⁺, Sr²⁺, Ba²⁺, LREE³⁺, SO₄²⁻ and PO₄³⁻). The presence of the zunyite in the deeper part of the system as well the minor amount of F⁻ in alunite, indicates acid-fluorine-sulphate composition of the fluid that is considered as important feature for the mineralized systems. The combined mineralogical, microthermometric and isotopic data suggest temperatures of formation of the advanced argillic alterations ~200–250°C and pH interval of 3–5 in the upper levels and more than 300°C and pH less than 3 in the deeper parts of the hydrothermal system. The factual material collected recently, especially the isotopic features of alunite and mineralogical peculiarity, characterize Chelopech as typical high-sulphidation epithermal Cu-Au deposit and range it among the most representative deposits of this type in the world.

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