



LA-ICP-MS trace element study of alunite from the Chelopech high-sulphidation epithermal deposit, Bulgaria

LA-ICP-MS изследване на елементи-примеси в алунит от високосулфидизираното епитермално находище Челопеч, България

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Introduction

The epithermal high-sulphidation Chelopech deposit is known as one of the largest Cu-Au deposits in Europe. It is situated in the Panagyurishte metallogenic district along with still others porphyry-Cu and epithermal deposits (Moritz et al., 2004, and references therein). Considerable studies have been published so far for the deposit, focused on geological framework, hydrothermal and ore-forming processes. Recently, Marton et al. (2016) proposed a new genetic model for the ore-forming magmatic environment at Chelopech, based on a development of multiphase intrusive complex, intersected by vertically extended breccia bodies and at least one maar-diatreme eruptive center. The mineral chemistry of alteration minerals is used for prediction of proximity and direction to the mineralized intrusive center and consequently as geochemical exploration tools. In this regard, systematic studies on trace elements in alunite from the advanced argillic alteration in epithermal deposits have been conducted (e.g., Chang et al., 2011).

This work presents preliminary LA-ICP-MS data on trace elements in alunite from two different levels and locations in the advanced argillic zone of the Chelopech deposit. The data are used to discuss whether the trace elements in alunite by itself could be sufficient for vectoring and estimation of proximity to the shallow-intrusive center or to the ore bodies.

Geological setting

The genesis of the Chelopech deposit is related to the Late Cretaceous magmatism and the ore min-

eralization is hosted by Upper Cretaceous volcanic and volcano-sedimentary complex. The volcanic rocks are defined as andesite, trachydacite to dacite lavas, breccias and tuffs (Stoykov et al., 2004). Three main hydrothermal alteration zones are distinguished in the deposit: advanced argillic with siliceous core, surrounded by sericitic zone that grade outward into large propylitic alteration. The high-sulphidation Cu-Au mineralization occurs mainly as stockwork, veins and disseminations among volcanic breccia affected by intensive silicification or advanced argillic alteration composed of quartz, dickite, kaolinite, aluminium phosphate-sulphate minerals (APS), alunite and pyrite. In deeper levels pyrophyllite, diaspore, and zunyite occur (Georgieva, Velinova, 2012).

Materials and analytical methods

The samples represent intensively altered and ore-mineralized volcanic rocks with alunite, collected from exploration block 151 (elevation 100–150 m) in the western part of the deposit, as well as similar samples from the present-day surface Sharlo Dere area (a remote easternmost part of the deposit – elevation 750 m), where the ore mineralization is with non-economic significance. The vertical extent between both locations is around 600 m and their distance from each other is about 2 km.

The chemical composition of major elements was determined using Jeol “Superprobe 733” (EDS–HNU “System 5000”) at the Geological Institute, Bulgaria. The minor and trace element signature of alunite was analyzed by the LA-ICP-MS system in Geological Institute, Bulgaria, consisting

of New Wave Research (NWR) 193 nm Excimer laser UP-193FX attached to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma mass spectrometer. Aluminum content, determined by microprobe analyses was used as internal standard for LA-ICP-MS data reduction.

Results and discussion

The alunite mineralization is abundant in the area of block 151, western part of the deposit. It extends among and around the ore bodies from level 280 to level -120 or 400 m vertical spread out. Alunite occurs as pale to deep pink fine-grained aggregates in veins and nests with up to 3 cm thickness, as well as pseudomorphic replacements of clasts and phenocrysts among the advanced argillic altered and ore-mineralized volcanic breccia. The main mineral association in studied aggregates consists of alunite, dickite/kaolinite, quartz, pyrite and enargite.

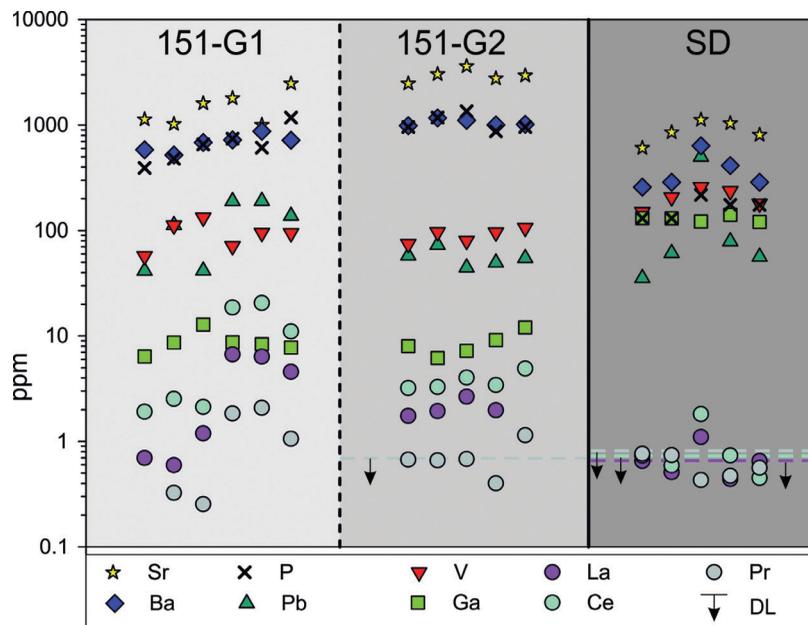
At least two generations of alunite are distinguished, according to the relations and intersections among the mineral aggregates. The first generation (G1) is presented mainly as clast and phenocryst replacement aggregates, and rarely as single crystals in the matrix of the altered volcanic rocks. This alunite associates with pyrite, rarely quartz, dickite/kaolinite and single rutile/anatase grains and it is normally brecciated or intersected by late pyrite and ore-mineralized veins. The mineral is well-shaped with bladed crystals of 5–600 μm in size. Aluminium phosphate-sulphate (APS) minerals are observed in the central parts of the alunite crystals. The second alunite generation (G2) forms thin veins and nests in association with clay minerals and quartz. The larger size of the crystals reaches up to 100–150 μm . This mineralization intersects previously formed pyrite veins clasts and disseminations. Early formed pyrite is often brecciated and involved among the second generation alunite aggregates. According to its macro- and microscopic characteristics, the alunite from Sharlo Dere (SD) refers to G1 (Georgieva, Velinova, 2012). The mineral forms 5–250 μm crystals and associates with pyrite, quartz, dickite/kaolinite, enargite, rutile/anatase and APS. The content of K_2O from G1 alunite varies between 4.91–9.83 wt%, where the highest value corresponds to 0.9 atoms per formulae unit (*apfu*). The Na_2O ranges from 1.01 to 5.04 wt%, or 0.7 *apfu* for the highest percentage that falls into natroalunite composition. In the analyzed points Ca (up to 0.31 wt%), Ba (up to 0.59 wt%) and Sr (up to 0.32 wt%) were detected, that generally substitute K and Na in the crystal structure (Bayliss et al., 2010). The chemical composition of APS phases found in the central part of alunite crystals is mixed and falls into woodhouseite-svanbergite field. Increased Ba content (up to 7.27 wt% or 0.23 *apfu*) was

also established which could be due to the presence of a gorceixite-walthierite component. The G2 alunite has similar chemical composition but K_2O and Na_2O vary in more limited range. K_2O content falls in scope between 6.57–8.38 wt%, whereas Na_2O is between 2.17–3.04 wt%. Strontium up to 0.43 wt% and Ba up to 0.13 wt% were established. APS minerals in the studied samples were not observed. The chemical composition of SD alunite, indicates K_2O content between 3.56–9.75 wt% and Na_2O from 0.71 to 5.05 wt% (Georgieva, Velinova, 2012), that matches well with the composition of the G1 deeper levels alunite. Concerning the major elements, statistically Na_2O content is slightly higher in the G1 and G2 alunite of bl. 151, compared to its content in the SD alunite.

The detected minor and trace elements in alunite using LA-ICP-MS analytical technique are P, Sc, V, Fe, Zn, Ga, Ge, As, Sr, Zr, Sn, Ba, REE, Au, Pb, Bi, Th and U. The LREE (La, Ce, Pr, Nd, Sm) prevail clearly over the HREE (Eu, Gd, Tb, Dy, Ho, Er and Tm), the latter being detected only in samples with increased Sr, P, Ba and Pb content. This is probably due to APS inclusions in alunite crystals. The Pb shows slightly increased values in the G1 alunite, bl. 151 (up to 190.7 ppm) in comparison with G2 (79 ppm) and SD alunite (73.2 ppm) (Fig. 1). The Sr and Ba contents in alunite show very good correlation. The values of both elements are higher in G1 and especially in G2 alunite, bl. 151, compared to SD alunite, as can be seen on Fig. 1. The same tendency is observed for the P with maximum value up to 1353 ppm for bl. 151 and up to 218 ppm for SD samples. The incorporation of La, Ce, Pr, Nd and Sm also shows significant variations. The G1 alunite, bl. 151 is enriched in Nd (up to 7.7 ppm), La (6.7 ppm), Pr (2.1 ppm), Sm (2.1 ppm) and particularly Ce (20.5 ppm). In G2 alunite, bl.151 only Ce (4.9 ppm) and La (2.7 ppm) are regularly detected, whereas Pr (1.1 ppm) was above the detection limit (DL) in single points only. The obtained results from SD alunite show substantial decrease or even absence of lanthanides with a single data for La (1.1 ppm) and Ce (1.8 ppm). The Sr/Pb ratio is 5.3–38.5 for G1 alunite, bl. 151 and significantly higher for G2 (33.6–85.3), compared to SD alunite (2.2–22.9). The elements as Fe, Zn, Ge, As, Sn, Sc, Au, Bi, Th and U are sporadically presented in single analyses for both locations or are below detection limit.

There is a great difference in the concentrations of V and Ga in alunites from both locations. These elements substitute Al in the crystal structure (Bayliss et al., 2010). It is remarkable that the contents of V and Ga are up to ten times higher in SD alunite compared to the alunite from bl. 151. The values of V in SD samples are between 150.2–258.6 ppm, whereas in the bl. 151 between 57.4–133 ppm for G1 alunite and 74.9–106.2 ppm for G2 respectively. The content

Fig. 1. Distribution chart of minor and trace elements in alunites of the first (G1) and second (G2) generations in bl. 151 samples, and the first generation in the Sharlo Dere (SD) samples. DL, detection limit.



of Ga in SD alunite is between 121.8–141 ppm, in contrast to bl. 151 samples with 6.4–12.8 ppm in G1 and 8–12 ppm for G2 alunite. The significant enrichment of the two elements could be explained with hydrothermal fluid transition through stratigraphic sequences locally containing coal-bearing sedimentary rocks. This is in agreement with the assumption of Sahlström et al. (2017) about the possible factor for enrichment of some critical elements in high-sulphidation deposits. The presence of coal-bearing sandstones and conglomerates, commonly known as coal-bearing formation is characteristic for the Chelopech geological environment (Moritz et al., 2004, and references therein). The involvement of meteoric waters in the system, convecting through sedimentary country rocks is also in accordance with the isotopic features of the alunite (Lerouge et al., 2006). Moreover, the content of these elements in the SD alunite is higher than in the hosting volcanic rocks (Georgieva, Hikov, 2016). However, the different magnitude of V and Ga incorporation in alunite from both locations requires further research.

In summary, according to this study the minor and trace elements composition in alunite from two different levels and locations in Chelopech deposit show significant variations especially regarding Sr, Ba, REE, P, Pb, V and Ga. In deeper levels of the deposit (bl. 151) where alunite is in association with economic ore the contents of Sr, REE and Sr/Pb ratio increase. According to Chang et al. (2011) these features could be used as an indication for proximity to the intrusive center. In Sharlo Dere area, where the ore mineralization is scarce, alunite chemistry is characterized by lower REE, Sr, Ba and P content and higher V and Ga. These data suggest that the alunite minor and trace element composition could

be used as signatures for vectoring to the ore mineralization or causative intrusive center.

References

- Bayliss, P., U. Kolitsch, E. H. Nickel, A. Pring. 2010. Alunite supergroup: recommended nomenclature. – *Mineral. Mag.*, 74, 5, 919–927.
- Chang, Z., J. W. Hedenquist, N. C. White, D. R. Cooke, M. Roach, C. L. Deyell, J. Garcia, Jr., J. B. Gemmill, S. Mcknight, A. L. Cuisson. 2011. Exploration tools for linked porphyry and epithermal deposits: Example from the Mankayan intrusion-centered Cu-Au District, Luzon, Philippines. – *Econom. Geol.*, 106, 1365–1398.
- Georgieva, S., A. Hikov, 2016. Geochemistry of hydrothermally altered rocks from the Chelopech high-sulphidation Cu-Au deposit, Bulgaria. – *C. R. Acad. Bulg. Sci.*, 69, 6, 761–768.
- Georgieva, S., N. Velinova. 2012. Alunite from the advanced argillic alterations in the Chelopech high-sulphidation epithermal Cu-Au deposit, Bulgaria: Chemistry, morphology and genetic significance. – *Geochem., Mineral. and Petrol.*, 49, 17–31.
- Lerouge, C., A. Kunov, C. Fléhoc, S. Georgieva, A. Hikov, J.-L. Lescuyer, R. Petrunov, N. Velinova. 2006. Constraints of stable isotopes on the origin of alunite from advanced argillic alteration systems in Bulgaria. – *J. Geochem. Explor.*, 90, 166–182.
- Marton, I., Y. Dintchev, M. Trifonova, N. Hadzhieva, M. Grigорова, A. Aleksieva, G. Ivanov, S. Milinković, A. Szakács, M. Knaak, K. Kunchev, R. Gosse. 2016. A new geological model for the Chelopech Au-Cu deposit in Bulgaria: exploring a maar-diatreme system within an intrusive environment. – In: *SEG-MJD 2016 Conference* (electronic abstracts).
- Moritz, R., K. Kouzmanov, R. Petrunov. 2004. Late Cretaceous Cu-Au epithermal deposits of the Panagyurishte district, Srednogorie zone, Bulgaria. – *Schweiz. Mineral. Petrogr. Mitt.*, 84, 79–99.
- Sahlström, F., A. Arribas, P. Dirks, I. Corral, Z. Chang. 2017. Mineralogical distribution of germanium, gallium and indium at the Mt Carlton high-sulphidation epithermal deposit, NE Australia, and comparison with similar deposits worldwide. – *Minerals*, 7(11), 213, 1–28.
- Stoykov, S., I. Peytcheva, A. von Quadt, R. Moritz, M. Frank, D. Fontignié. 2004. Timing and magma evolution of the Chelopech volcanic complex (Bulgaria). – *Schweiz. Mineral. Petrogr. Mitt.*, 84, 101–117.