

Rare earth element (REE) mobility during advanced argillic alteration in Asarel porphyry copper deposit, Central Srednogie, Bulgaria

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The Asarel porphyry copper deposit is located in Panagyurishte ore region, Central Srednogie, part of the Late Cretaceous Apuseni-Banat-Timok-Srednogie (ABTS) magmatic and metallogenic belt defined by intensive magmatic and volcanic activity and formation of many porphyry and epithermal deposits. The volcanic activity in the Asarel magmatic center successively formed andesites to latites, basaltic andesites, andesites to dacites, followed by comagmatic porphyritic plutons (quartz-diorite to quartz-monzodiorite, quartz-monzonite to granodiorite and granite porphyry). Intensive hydrothermal alterations of propylitic, argillic, sericitic and advanced argillic alteration (pyrophyllite, dickite, diaspore and alunite) types had affected volcanic and porphyritic rocks within and around the deposit. K-silicate alteration is weakly developed in the deeper part of the system. Alteration zoning is expressed by successive replacement of advanced argillic alteration, sericitization, argillization and propylitization from the center to the periphery and from the top to the bottom of the deposit.

REE concentration in the unaltered volcanic rocks from the Asarel region is about 110 ppm. Their chondrite-normalized REE patterns are characteristic for island-arc subduction-related magmas with enrichment of LREE in relation to HREE ((La/Yb)_{cn}: 7,38–11,5) and comparatively flat HREE patterns ((Gd/Yb)_{cn}: 1,58–2). REE patterns of propylitic, weak K-silicate, argillic and sericitic altered rocks are similar to those in fresh volcanic rocks. Visible mobility of MREE and HREE is seen with increasing alteration degree, especially in argillic and sericitic alteration types. LREE do not show differences with respect to parent rocks, only weak mobility is visible in sericitic alteration.

Significant changes in the behaviour of REE are observed in advanced argillic altered zones. REE patterns in pyrophyllite altered rocks show MREE and HREE fractionation, which is stronger in dickite- and diaspore-bearing rocks. REE behaviour in alunitic rocks is very similar to the dickite- and diaspore altered types. LREE are relatively immobile (sometimes with slight enrichment). This is due to the presence of alunite and APS minerals, which contain some amounts of La, Ce and Nd (usually low up to 1%, sometimes with high LREE content). Silicic alteration, which forms small bodies at the top of the alteration zone, is characterized by strong extraction of all REE.

REE concentration in altered rocks from the Asarel deposit show comparatively inert behaviour of REE during the propylitic, intermediate argillic and sericitic alteration of volcanic rocks and slight fractionation with weak mobility of HREE in argillic and sericitic altered types. This is due to the nearly neutral pH of the fluids and the low water/rock ratio during these types of alteration. Starting of mobility in LREE is registered in the sericitic rocks, which is connected to the dissolution of apatite.

During advanced argillic alteration in low-pH environment, high water/rock ratios and high activity of SO₄²⁻ (for the alunitic rocks) or of Cl⁻ and F⁻ (for the pyrophyllite, dickite and diaspore rocks) strong fractionation of REE occurs. The mobility of MREE and HREE is connected with the high activity of F⁻, low pH of the fluids and their ability to form stable complexes in these conditions (Fulignati et al., 1999). LREE are relatively immobile (with slight enrichment in some samples) due to their entrance in the lattice of appropriate minerals like alunite, APS minerals and clay minerals (Kikawada et al., 2004; Aja, 1998). Decreasing of pH leads to apatite dissolution. Liberated LREE immediately take part in the new-forming APS minerals – mainly svanbergite and woodhouseite. Sometimes florencite-svanbergite solid solutions may form as cores in svanbergite (Hikov et al., 2010). High activity of F⁻ ions and the lack of new minerals to accommodate REE are the main reasons for their depletion from the silicic altered zones.

S, O and H stable isotope data show that alunite and APS minerals in Asarel are formed from magmatic-hydrothermal fluid between 200 and 300°C with significant dilution (up to 50%) of superficial waters (Hikov et al., 2010). This REE behaviour probably is characteristic of a high-sulphidation style epithermal environment in the upper part of the porphyry copper system and illustrates the main stages in the evolution of the hydrothermal fluids.