



Mobility of major and trace elements during hydrothermal alteration of volcanic rocks from the Chelopech high-sulphidation epithermal Cu-Au deposit, Central Srednogie, Bulgaria

Мобилност на главните и редките елементи при хидротермалните изменения на вулканските скали от високосулфидизираното епитермално Cu-Au находище Челопеч, Централно Средногорие, България

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The Chelopech high-sulphidation epithermal Cu-Au deposit is located within the northern part of the Panagyurishte ore region belonging to the Late Cretaceous Apuseni–Banat–Timok–Srednogie (ABTS) magmatic and metallogenic belt (Popov et al., 2000). The deposit is hosted in Upper Cretaceous volcanic and volcano-sedimentary complex which volcanic products are subdivided by Popov et al. (2002) into 3 units: (I) dome-like volcanic bodies with andesitic and trachydacitic composition; (II) lava and agglomerate flows ranging from latitic-trachydacitic to dacitic with age of 91.3 ± 0.3 Ma according to Stoykov et al. (2004); (III) Vozdol volcanic breccias and volcanics (basaltic andesites and andesites to latites).

The Chelopech Cu-Au deposit is characterized by an alteration style typical for epithermal high-sulphidation systems. Three main alteration zones are distinguished (Georgieva et al., 2002). The most intensive alteration that hosts the ore bodies is the advanced argillic zone with “vuggy” and massive silica areas. The advanced argillic alteration assemblage (AAA) is composed of quartz, dickite, kaolinite, pyrite, alunite and APS (aluminium phosphate-sulphate) minerals mainly of svanbergite-woodhouseite solid solutions (s.s.). This zone is spatially followed by zones of sericitic and external propylitic alteration.

Surface and underground samples of fresh and altered rocks from the Chelopech deposit were analyzed by X-ray fluorescence in University of Lausanne, Switzerland and by LA-ICP-MS in Geological Institute, Bulgaria. Some whole rock analyses of unaltered and AAA rocks from Stoykov et al. (2004) and Chambefort (2005) were used as well.

Significant chemical changes of volcanic rocks have taken place during the hydrothermal alteration in Chelopech deposit. The loss of ignition (LOI) at 1050 °C is used as a monitor for alteration. Most of elements show considerable variations of their concentrations in altered rocks therefore only general trends of elements behaviour are discussed. SiO₂ is scattered in propylitic and sericitic rocks while in AAA rocks it is weakly concentrated. The increasing of alteration intensity is accompanied with depletion of Ca, Mg, Na, Mn, Co, Y, MREE and HREE. The contents of K and Rb increase in sericitic and partially in propylitic rocks while these elements are strongly depleted in AAA rocks. Sr is leached from propylitic and especially from sericitic altered rocks and is concentrated in AAA zones. Rb/Sr ratio increases in propylitic (1.66) and sericitic (2.66) rocks while in AAA rocks strongly decreases to 0.006. Relatively inert behaviour during the hydrothermal alteration is observed for P, Zr, V (with partial leaching from AAA zones), Ba and Ga (with high contents in single samples), Sc, Th, U, Nb, Ta, LREE, and Ti (with slight depletion in most intensively altered rocks). Cu and Pb have high concentrations in single samples from all altered types especially in AAA rocks, while Zn increases mainly in propylitic and sericitic ones. The data about Au are not sufficient. Considering that most of the ore bodies are hosted in AAA rocks, it is suggested a higher Au concentration therein.

Chondrite-normalized REE patterns of unaltered volcanic rocks display LREE enrichment and relatively flat MREE and HREE patterns, typical for subduction-related magmas (Stoykov et al., 2004; Chambefort, 2005). REE concentrations in propylitic rocks are very

similar to those in unaltered rocks. Similar REE patterns are seen in sericitic rocks but with slight mobility of LREE in some samples probably as a result of the ongoing dissolution of apatite. REE patterns in AAA rocks show strong MREE and HREE fractionation and depletion. LREE are relatively stable (immobile or with slight enrichment in the most of samples).

MORB normalized multi-element patterns for unaltered magmatic rocks indicate an enrichment of LILE and low values for HFSE with a strong negative Nb and Ti and positive Sr and Pb anomalies (Stoykov et al., 2004) which is typical for subduction-related magmatic sequences. The mobility of chemical elements during the formation of propylites is not significant, except depletion of Sr and increasing of Rb, K and to a lesser extent Ba. Important depletion in Sr and less Ba, P, LREE and MREE are established in sericitic altered rocks while Rb, K, Pb and insignificantly Th and U are enriched. The AAA zone is characterized with depletion of the most elements, especially Rb, K, Y, MREE and HREE; Ba, Nb, Ta, Th, U, P, Zr, Ti are comparatively inert. Only Sr, Pb and occasionally Ba and LREE are enriched in these zones.

The distribution and behaviour of elements in hydrothermally altered rocks from Chelopech deposit are very similar to other deposits from Central Srednogie as Asarel, Pesovets and Petelovo where the same alteration types are developed. Most characteristic is the behaviour of Sr, which is leached from external areas of alteration and is concentrated in the inner zones of AAA (Hikov, 2004). In these conditions Sr forms its own minerals as svanbergite and svanbergite-woodhouseite s.s. and/or it is included in alunite. These minerals are distinctive for advanced argillic alteration and control the geochemistry of Sr. K and Rb have the opposite behaviour compared to that of Sr. They are concentrated in sericitic rocks and are depleted in AAA zones. Rb/Sr ratio reflects the different distribution of both elements and has good potential for identifying the alteration zones.

REE patterns of the studied volcanics show characteristic features for similar hydrothermal systems (Fulignati et al., 1999; Hikov, 2011). The mobility of the MREE and HREE occurring only during advanced argillic alteration is related to higher F^- activity in low pH of the hydrothermal fluids and their ability to form stable complexes in these conditions. LREE are relatively inert with enrichment in some samples. Their immobility is connected with the formation of appropriate minerals that accommodate LREE as alunite and APS minerals (Georgieva et al., 2002, 2011) especially florencite established recently (Georgieva, Velinova, 2012, this volume) and clay minerals as well (Hikov, 2011). Slight depletion of LREE is registered in some AAA samples. It is probably due to the low values of REE in the initial rocks, or to the

redistribution of LREE within the AAA zone. This redistribution is possible at low pH (0.8–5.3) values where “vuggy” and massive silica areas are formed in the AAA zones with absence of APS minerals. These minerals are the main hosts of LREE and occur at higher pH (3–8) conditions.

Contrary of our conclusions Chambefort (2005) considers that the altered rocks from the Chelopech deposit are depleted in Sr and P and enriched in K and Rb compared to fresh andesitic rocks whereas REE remain immobile during the hydrothermal processes. This contradiction results from the fact, that this author divided the rocks only into fresh and altered, excluding the AAA samples. The advanced argillic alteration is most intensive and generally hosts the ore mineralization. The geochemistry of this zone should be taken into account for better interpretation and prospecting.

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