



New data for REE and other trace elements in hydrothermally altered rocks from Petelovo deposit, Central Srednogorie

Нови данни за редкоземните и други елементи-следи в хидротермално променените скали от находище Петелово, Централно Средногорие

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Key words: REE, trace elements, alunite, APS minerals, advanced argillic alteration, Central Srednogorie.

The low grade Petelovo Au-Cu porphyry deposit is located in Panagyurishte ore region, part of the Late Cretaceous Apuseni–Banat–Timok–Srednogorie (ABTS) magmatic and metallogenic belt (Popov et al., 2002). Panagyurishte ore region is defined by development of intensive magmatic and volcanic activity and formation of many porphyry copper and Cu-Au epithermal deposits. Tsonev et al. (2000) described volcano-plutonic structure with andesite effusive rocks (lava flows, lava breccias and agglomerate tuffs), subvolcanic dacite and subvolcanic-hypoabyssal granodiorite to quartz-diorite porphyry.

Hydrothermal alteration was studied by Radonova (1969), and completed by Chipchakova and Stefanov (1974) and Hikov (2005). The following altered rocks which form good expressed lateral zoning are distinguished: propylitic, sericitic and advanced argillic (dickite-kaolinite, pyrophyllite, alunite, monoquartz and multiply advanced argillic altered rocks). Tsonev et al. (2000) supposed that there is a close spatial relationship between porphyry copper system in depth and high sulphidation epithermal mineralization in the upper part of the system.

Significant redistribution of trace elements is accompanying intensive hydrothermal alteration in the region of Petelovo deposit (Hikov, 2005). Sr has the most characteristic behavior. It is extracted during propylitization and sericitization of the parent rocks and concentrates in the inner zones of advanced argillic alteration. Sr is redistributed during hydrothermal alteration. It forms own mineral svanbergite and svanbergite-woodhouseite solid solutions (s.s.) while part of Sr includes in alunite and alunite-svanbergite-woodhouseite s.s. Rb, opposite to Sr, concentrates in sericitic rocks and decreases in advanced argillic. Ba is comparatively inert between different zones but there is a high barite accumulation on the Petelovo peak probably part of ore mineralization (Hikov, 2005). Ti,

Zr, V and Cr have immobile behaviour. Highly mobile are Mn, Zn, Ni and Co which are depleted in the altered rocks, while Li is slight enriched in the dickite-kaolinite zone. Many samples from all altered rocks have slight increased Au concentration but this cannot be connected with distinct type of alteration. Study of stable isotope composition of S, O and H in alunite has shown that the alunite from Petelovo has magmatic-hydrothermal origin.

New ICP-MS data were obtained for the REE and other trace elements which throw additional light on the geochemistry of Petelovo hydrothermal alteration. The results for their concentration and distribution are presented below.

The chondrite-normalized REE pattern in unaltered diorite porphyry from the region is characteristic for island-arc subduction-related magmas with enrichment of LREE in relation to HREE ($(La/Yb)_{cn} = 5.02$) and comparatively flat HREE pattern ($(Gd/Yb)_{cn} = 2.09$), as well as weak expressed negative Eu anomaly. REE concentration in propylitic rocks and their chondrite-normalized pattern is very similar with those in unaltered rocks. Visible mobility of MREE and HREE is seen in sericitic altered rocks ($(La/Yb)_{cn} = 23.42$), while the fractionation is stronger expressed near the advanced argillic rocks. Weak mobility of LREE is probably as a result of starting the apatite dissolution.

REE patterns in pyrophyllite altered rocks show MREE and HREE fractionation which is stronger in dickite and kaolinite rocks. LREE are relatively immobile (with slight addition in pyrophyllitic rocks) which is connected with the presence of APS minerals containing some amounts of La, Ce and Nd. REE behaviour in alunitic and multiply advanced argillic rocks is very similar as in the dickite and kaolinite rocks while the depletion of MREE and HREE is stronger than in the pyrophyllite altered rocks. Relative stability of LREE is connected with the entrance of these elements into

the lattice of alunite and APS minerals (Fulignati et al., 1999; Kikawada et al., 2004). Small amounts of La, Ce and Nd (together up to 1–2 wt.%) are detected in alunite and alunite-svanbergite-woodhouseite s.s. There are no differences in REE patterns between the samples of alunitic rocks from different temperature associations.

Strong depletion of all REE in monoquartz (silicic) rocks can be explained by their extracting from the rocks by the extremely low-pH hydrothermal fluid and the lack of secondary minerals which can take them in their lattice.

The results of ICP-MS analysis for other trace elements from Petelovo altered rocks are as follows:

1) U, Th, Nb, Ta and Hf (just like Zr), which are high field strength elements (HFSE), are comparatively inert during hydrothermal alterations being extracted only from the monoquartz zone. This is due to the relatively stability of their source minerals (zircon, titanium minerals, apatite). Ga is comparatively inert but it decreases in dickite-kaolinitic and multiply advanced argillic altered rocks. At the same time there are high Ga contents in single samples from alunitic and pyrophyllitic rocks.

2) Y, Sc and Cs are mobile and are depleted in different degree in advanced argillic rocks. The behaviour of Y is very similar to that of HREE. Mo, Sn and

W have variable concentrations with accumulation trend toward the most altered rocks. Maximal values are detected in sericitic (Sn), alunitic (W) and multiply advanced argillic rocks (Mo, Sn). High concentrations of As, Sb and Bi are registered in a sample with barite (probably related to ore mineralization) and in less degree in other samples from advanced argillic rocks.

Significant mobilization of REE is taken place during advanced argillic alteration of rocks from Petelovo epithermal system. It consists in leaching of MREE and HREE and comparatively inert behaviour of LREE. This is due to the low pH of hydrothermal fluids, high water/rock ratios and abundant complexing ions (F^- , Cl^- , PO_4^{3-} , SO_4^{2-}). The presence of appropriate minerals which can accommodate LREE is of vital importance. These are alunite and APS minerals (svanbergite, svanbergite-woodhouseite s.s., woodhouseite, and probably florencite). These minerals are characteristic for advanced argillic alteration and determine the geochemistry of other elements like Sr (which concentrates in these zones) and probably some other immobile elements. Such behaviour of REE is described for the altered rocks from active magmatic-hydrothermal system of Vulcano (Fulignati et al., 1999), Rodalquilar gold alunite deposit (Arribas et al., 1995) and Asarel porphyry copper deposit (Hikov, 2011).

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