



## Geochemistry of trace elements in hydrothermally altered rocks from Pesovets epithermal system, Central Srednogorie

### Геохимия на редки и разсеяни елементи в хидротермално променените скали от епитермалната система Песовец, Централно Средногорие

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The Pesovets epithermal system is located in Panagyurishte ore region, part of the Upper 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 between 92 and 78 Ma (von Quadt et al., 2005) and formation of many porphyry copper and Cu-Au epithermal deposits.

The hydrothermally altered rocks form about 1 km<sup>2</sup> of the area of Pesovets peak, 2 km NW of Popintsi Village, Panagyurishte area. Structurally the zone is located in the core of Pesovets anticline, formed by Upper Cretaceous rocks of the Pesovets volcano, being referred to the last stage of volcanic activity in the region. The volcanic rocks and their pyroclastic products (mainly volcanic breccia and minor tuffs) are with andesite to latite composition (Hikov, 2001).

The Pesovets epithermal system has been object of practical interest since 1936 and a lot of exploration works for Cu and Au ore mineralization as well as for decorative and facing stone have been done. Hydrothermal alteration studied by Radonova (1966) and Hikov (2001) are of advanced argillic, propylite-argillic and propylitic type. Advanced argillic alteration is of acid-sulphate type (alunitic rocks in the central parts) and acid-chlorine type (kaolinitic rocks with transitions to topaz-quartz varieties in some places and zunyite containing diaspore-pyrophyllite rocks in the deeper parts of the system). The transition to unaltered volcanic rocks is marked by zones of propylite-argillic and propylitic alteration.

Significant redistribution of trace elements is taken place during the intensive hydrothermal alteration of volcanic rocks in the Pesovets epithermal

system (Hikov, 2001). Many elements (Y, Mn, Zn, Ni, Co, Cs) are highly mobile and are extracted from the rocks especially during advanced argillic alteration. Comparatively immobile behaviour have Zr, Cr, V, Ga and Ti. Other elements show specific distribution: they are leached from the most of alteration zones but they are enriched in some ones (for example Rb in propylite-argillic zone, Li in kaolinitic zone, Pb in alunite zone). Sr has characteristic behaviour. The element is extracted from outer zones of alteration and concentrates in the inner zones of advanced argillic alteration (alunitic, kaolinitic and pyrophyllitic). Increased contents of Sr in these altered rocks are connected with the formation of aluminium-phosphate-sulphate (APS) minerals, mainly svanbergite-woodhouseite solid solution series (Hikov, 2004).

New data were obtained for the rare earth elements (REE) which throw additional light on the geochemistry of Pesovets hydrothermal alteration.

Recent investigations of REE concentration in hydrothermal fluids and hydrothermally altered rocks have shown that, under particular conditions, REE can be mobilized by hydrothermal alteration. REE mobility is favoured by low pH, high water/rock ratios and abundant complexing ions (CO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>) in hydrothermal solutions, being preferentially complexed by Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in acid conditions (Fulignati et al., 1999, and references therein).

REE patterns in unaltered latite and in propylitic rock from Pesovets are flat with clear fractionation of light REE with respect to the heavy REE and weak expressed negative Eu anomaly. Such behaviour is described by Fulignati et al. (1999) for the propylitic rocks from the active magmatic-hydrothermal system of Vulcano (Aeolian Islands, Italy). The chon-

drite-normalized REE pattern in propylite-argillic altered rock is similar to the fresh rocks with slight impoverishment in all REE.

Significant changes in the behaviour of REE are observed in advanced stage of acid-chlorine and acid-sulphate argillic alteration. REE patterns in pyrophyllitic and kaolinitic rocks show strong fractionation of medium and heavy REE. The mobility of medium and heavy REE is related to increased  $F^-$  ions activity and low pH of fluids (Fulignati et al., 1999), and their possibility to form stable complexes in these conditions. Similar conditions are presumed during the acid-chlorine advanced argillic alteration in Pesovets (Hikov, 2001). Relatively slight mobility of the light REE is explained not only with the instability of their complexes, but also with the presence of APS minerals (Hikov, 2004) which contain some amounts of La, Ce and Nd (our unpublished data). Aja (1998) shows the ability of light REE for sorption in kaolinite group minerals, which can also explain the relative immobility of light REE in these altered types.

In the alunite altered rocks as well as the kaolinitic and pyrophyllitic ones is observed strong depletion of medium and heavy REE. Relatively immobility of the light REE is connected with the presence of alunite and ability of entrance of these elements into the alunite lattice in the place of potassium (Fulignati et al. 1999; Kikawada et al., 2004).

## References

- Aja, S. U. 1998. The sorption of the rare earth element, Nd, onto kaolinite at 25°C. – *Clays, Clay Miner.*, 46, 103–109.
- Fulignati, P., A. Gioncada, A. Sbrana. 1999. Rare-earth element (REE) behaviour in the alteration facies of the active magmatic-hydrothermal system of Vulcano (Aeolian Islands, Italy). – *Journ. Volc. Geoterm. Res.*, 88, 325–342.
- Hikov, A. 2001. Metasomatic zonation and trace element geochemistry in hydrothermally altered Late Cretaceous volcanics at Pesovets Hill, Panagyurishte area. – *Geochem., Mineral., Petrol.*, 38, 101–111 (in Bulgarian).
- Hikov, A. 2004. Aluminium phosphate-sulphate minerals in advanced argillic alteration zones in Petelovo and Pesovets deposits, Central Srednogorie. – *C. R. Acad. bulg. Sci.*, 57, 12, 61–68.
- Kikawada, Y., M. Uruga, T. Oi, T. Honda. 2004. Mobility of lanthanides accompanying the formation of alunite group minerals. – *Journ. Radioanal. Nucl. Chem.*, 261, 3, 651–659.
- Popov, P., T. Berza, A. Grubic, D. Ioane. 2002. Late Cretaceous Apuseni-Banat-Timok-Srednogorie (ABTS) magmatic and metallogenic belt in the Carpathian-Balkan orogen. – *Geologica Balc.*, 32, 2–4, 145–163.
- Radonova, T. 1966. Zoning of hydrothermal metamorphites and location of alunite quartzites in them near Popintsi village, district of Panagyurishte. – *Bull. Geol. Inst.*, 15, 129–143 (in Bulgarian).
- Von Quadt, A., R. Moritz, I. Peytcheva, C. Heinrich. 2005. Geochronology and geodynamics of Late Cretaceous magmatism and Cu-Au mineralization in the Panagyurishte region of the Apuseni-Banat-Timok-Srednogorie belt, Bulgaria. – *Ore Geol. Rev.*, 27, 95–126.
- Wood, S. 1990. The aqueous geochemistry of the rare earth elements and yttrium: 2. Theoretical prediction of speciation in hydrothermal solutions to 350°C at saturation water vapor pressure. – *Chem. Geol.*, 88, 99–125.

APS minerals in the alunite zone (Hikov, 2004) also contain small amounts of light REE.

Strong depletion of medium and heavy REE as well as light REE is observed in topaz-quartz altered rocks, which is owed to the higher activity of  $F^-$  ions and the sharp decrease of REE containing minerals in this rock type. Relatively higher concentration of light REE probably can be explained by the presence of limited amounts of kaolinite and dickite.

The possibility to form complexes is considered to be the main reason for the mobility of rare earth elements. In acid environment REE form complexes preferentially with  $Cl^-$  and  $SO_4^{2-}$  (Wood, 1990). From La to Lu (light-heavy REE) the complex stability increase, as a result of lanthanide contraction and concentration of electric charge on smaller volume and the bond with the negative ligand (complex-forming agent) become more and more strong. Thus logically is explained the higher mobility of medium and heavy REE during the intensive chlorine and sulphate advanced argillic alteration. On the other hand the relatively immobility of the light REE is defined by the presence of secondary minerals, which include these elements in their lattice, such as alunite, APS minerals and kaolinite.

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