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Trace elements in hydrothermally altered rocks from Asarel porphyry copper deposit, Central Srednogorie

Редки и разсеяни елементи в хидротермално променените скали от меднопорфирното находище Асарел, Централно Средногорие

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Geological setting

The Asarel porphyry copper 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). The Asarel magmatic center represents a volcano-plutonic edifice emplaced in Paleozoic metamorphic and plutonic basement. The following volcanic rocks are distinguished: andesites to latites, basaltic andesites, andesites to dacites. The volcanics are intruded by comagmatic porphyritic bodies of quartz-diorite, quartz-monzonite to granodiorite porphyrites and granite porphyry dated 90–90.23 Ma (Kamenov et al., 2007, and references therein).

Propilitic, propilite-argillic, argillic, argillic-sericitic, sericitic and advanced argillic alteration types are established (Popov et al., 1996). Advanced argillic alteration is divided in two subtypes: pyrophyllite (acid-chlorine) and alunite (acid-sulphate). Alteration zoning is expressed by successive replacement of advanced argillic alteration, sericitization, argillization and propilitization from the center to the periphery and from the top to the bottom of the deposit. This succession is complicated by local zones of different permeability as well as by telescoping of pre-, syn- and post-ore hydrothermal and/or supergenic events.

Geochemistry

This study includes evaluation of element mobility versus loss of ignition (LOI), distribution of elements in the different alteration zones and MORB-normalized trace element patterns. The loss of ignition (LOI) can be used as a monitor of alteration (Chambefort, 2005). The SiO_2 content shows significant variations from 42.5 to 90 wt.%. MgO and CaO are leached from the rocks during argillization and sericitization, and particularly during advanced argillic alteration. Na_2O has similar behaviour with the difference that it is partly enriched in alunitic rocks. K_2O increases in sericitic and partly in alunitic altered rocks.

Sr is depleted in the propilitic, intermediate argillic and sericitic alteration types and accumulates in advanced argillic ones. Phosphorus has similar distribution in the alteration zones. Rb is leached from most of the alteration zones whereas it increases only in sericitic rocks, coherently with the K_2O behaviour. Ba concentration varies in a wide range from 200 to 2000 ppm, the highest contents being in the advanced argillic rocks as a result mainly of barite mineralization. Pb shows slight tendency to enrichment in the advanced argillic zone, which is possibly due to its low mobility in acid-sulphate environment and fixing in sulphate minerals. Some elements like Mn, Co, Zn and Li are very mobile during alteration and are totally depleted in all alteration types. The behavior of Y is like that of Ba.

The elements Ti and Zr are relatively immobile during propilitization, intermediate argillization and sericitization. Their concentrations vary significantly during advanced argillic alteration being relatively immobile as compared to other elements. The distribution of V is similar showing positive correlation with Ti. The distribution of these elements in the different alteration zones confirms their relatively immobility. On the other hand the total chemical changes of volcanic rocks occurred during advanced argillic alteration, which also reflect to the classical inert elements. Some redistribution is evident with slight tendency to enrichment of Ti and Zr and depletion of V concentrations. Ti and Zr have positive correlation only in the fresh and weakly altered volcanic rocks.

The general trace element characteristics of the volcanic rocks studied are clearly expressed in MORB-normalized (Pearce, 1983) multi-element patterns. All patterns of analysed fresh rocks are enriched in LILE and depleted in HFSE and compatible (Sc and Cr) elements (Kamenov et al., 2007; Chambefort, 2005). These specific features are characteristic of subduction-related magmas. The MORB-normalized patterns are also enriched in smaller degrees in all elements from Ce to Sm, observed in the rocks from the same region by Kamenov et al. (2007). The later is typical for some transitional and anomalous volcanic-arc suites. Distinct negative Ti-anomalies and depletion of Sc and Cr are present in trace element speidergrams.

The MORB-normalized trace element patterns of altered (propilitic, sericitic, argillic, alunitic and pyrophyllitic) rocks are enriched in LILE and depleted in HFSE, like the patterns of fresh rocks. A peculiarity of the MORB-normalized patterns in altered rocks is the wide range of normalized P abundances, especially in argillic and sericitic rocks. Although in smaller extent, similar variations of normalized Yb abundances are observed in alunitic and pyrophyllitic rocks.

In order to compare altered and fresh rock patterns, the trace elements of altered rocks have been normalized to average fresh composition. The normalization shows slight LREE depletion in propilitic rocks and almost the same LREE abundances in alunitic and pyrophyllitic rocks. In argillic and sericitic rocks LREE, HFSE and compatible Sc and Cr are enriched in different degrees.

Discussion and conclusion

The copper mineralization in Asarel porphyry copper deposit is accompanied by intensive hydrothermal alteration of propilitic, argillic, sericitic and advanced argillic alteration types. Significant chemical changes of volcanic rocks occurred during hydrothermal alteration. Even inert elements, such as Ti and Zr, become partly mobile during advanced argillic alteration. The other elements, including trace elements are strongly mobile and are leached from the altered rocks or redistributed. Very characteristic behavior has Sr, which is depleted in the outer alteration zones and accumulates in the inner zones of advanced argillic alteration. This element forms own aluminium-phosphate-sulphate (APS) minerals, first of all svanbergite and woodhouseite (Velinov et al., 1990). Such behavior of Sr is observed in other deposits from the Srednogorie zone and the Rhodopes (Hikov, 2004) and it becomes a characteristic feature of advanced argillic alteration in volcanic rocks. Rb has opposite behavior than Sr and the Rb/Sr ratio may be used as a geochemical indicator.

The porphyry copper mineralization is later than intensive hydrothermal alteration. It is observed mainly in sericitic, argillic and propilitic alteration zones and rarely in advanced argillic ones. Supergenic enrichment has an important role for the secondary concentration of copper.

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