



## Behaviour of inert (immobile) elements in extremely acid leaching: an example from Asarel porphyry copper deposit

## Поведение на инертните (неподвижни) елементи при екстремно киселинно извличане: пример от меднопорфирно находище Асарел

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**Key words:** alunite, rutile, geochemistry, trace elements, advanced argillic alteration, Asarel porphyry copper deposit.

### Introduction

Advanced argillic altered (AAA) rocks or the rocks of metasomatic secondary quartzite formation result from highly intensive hydrogen (acid) metasomatism (Meyer, Hemley, 1967; Zharikov, Omel'yanenko, 1978). Mineral associations with dickite, kaolinite, pyrophyllite, sericite, quartz, alunite, diaspore, pyrite, tourmaline, topaz, zunyite, etc. are formed which build up to nine natural mineral types (zones, facies) (Nakovnik, 1968). The most intensively altered rocks are built of almost pure  $\text{SiO}_2$  – monoquartz rocks, massive silica, vuggy quartz. During the extremely acid leaching ( $\text{pH} < 2$ ) rock-forming minerals are destroyed and the majority of elements become mobile and are extracted. On the other hand these rocks mark the central parts of the hydrothermal systems and may concentrate Au mineralizations (Hedenquist et al., 2000).

The Asarel porphyry copper deposit is located in Panagyurishte ore region, part of the Upper Cretaceous Apuseni–Banat–Timok–Srednogorie magmatic and metallogenic belt. The Asarel magmatic center is emplaced in Paleozoic metamorphic and plutonic basement. The following volcanic and porphyritic rocks are distinguished: andesites to latites; basaltic andesites; andesites to dacites; quartz diorite, quartz monzonite to granodiorite porphyry and granite porphyry (Nedialkov et al., 2007). Propylitic, argillic, sericitic and advanced argillic alteration types are described in the deposit. AAA consists of alunite, pyrophyllite, dickite and diaspore bearing rocks and the most intensively altered monoquartz (silicic) rocks.

### Characteristic of monoquartz (silicic) rock

The monoquartzites had formed two small lens-like bodies (5–10 m thick) among the alunite quartzites at the top of Razslatitsa Peak (Ignatovski, 1981). This is the top of the Asarel porphyry copper system where high sulphidation epithermal style is developed

(Petrunov et al., 1991). These rocks are built mainly by quartz (>90%), rutile, Fe-oxides/hydroxides, sometimes alunite, kaolinite, pyrophyllite. The “gain–loss” diagram shows enrichment of  $\text{SiO}_2$  and  $\text{TiO}_2$ , inert behaviour of  $\text{Fe}_2\text{O}_3$  and total depletion of other components. Even  $\text{Al}_2\text{O}_3$  is almost totally depleted (–95%). REE patterns show strong depletion of all REE. Strong depletion of the most elements is seen on multicomponent diagrams: only Nb, Ta, Zr, and Ti are immobile.

In order to compare the mobility of all elements in monoquartz rocks the trace elements of altered rocks have been normalized to unaltered granodiorite porphyry. The normalization shows strong depletion of Ba, Sr, Rb, Mn, Zn, Co, Li, Y, U, Th, LREE, MREE and slight depletion of V, Pb, Ni, Sc and HREE. Immobile are Zr, Cu, Nb, and Ta. Enrichment is registered for Ti, Cr and Ag markedly for W, Sn, As, Hf, Au, and Mo.

Some LA-ICP-MS analyses of minerals alunite, rutile and Fe-oxides/hydroxides show the distribution of inert elements in the extremely altered monoquartz rocks. Alunite is very rare and fine-grained, usually in small cavities. Besides K and Na, alunite contains (ppm) Sr (3873), Ba (1336), La (43), Ce (87), Pb (562), rarely Ti (~700), V (~100), Ga (~50) etc. Sr, Ba, La, Ce and Pb are characteristic admixtures in alunite and in AAA rocks as a whole but they lack in monoquartzites. The very small quantity of alunite concentrates remnants of these elements. Ti, V and Ga do not registered by all analyses. They are typical inert elements – Ti and V include mainly in rutile, while Ga takes part only in alunite.

Rutile occurs as small crystals. This mineral is a typical product of AAA and is the main mineral phase of Ti, which is inert and is common even in monoquartz rocks. The following elements are registered in rutile with LA-ICP-MS (mean values in ppm): V (2116), Zr (2780), Nb (1264), Sn (1100), Hf (87), Ta (54), W (146), Th (~26), U (~20), rarely Y (~40), Mo (~130),

sometimes HREE. These results show that rutile contains up to 100% of Sn, Nb and Ta, from 50 to 70% of V and W, about 20% of Th and U. The concentration of Zr varies significantly from 521 to 12 289 ppm due to the presence of Zr-phase inclusions (<5 µm), which are registered in some rutile crystals during the analyses. Thus rutile contains from 5 to 50–60% of Zr according to the presence of some inclusions or not. Till now this Zr-phase is unknown despite of its existing independently out of rutile crystals being registered during whole rock analyses. It contains Zr, Hf, Y, MREE, HREE, Th, U (qualitative analysis). It is possible that these are fine residua of dissolved zircon crystals, or fine-grained baddeleyite (ZrO<sub>2</sub>) hosting liberated Zr and accompanying elements after zircon dissolution. In both cases there is partial or full zircon dissolution.

Preliminary data for Fe-oxides/hydroxides show that they can accumulate Mo, possibly Th, U, etc.

## Discussion and conclusions

The deposition of porphyry copper mineralization in Asarel deposit was accompanied by the development of intensive hydrothermal alteration of propylitic, argillic, sericitic and advanced argillic types. AAA resulted from the action of extremely acid (pH <2), rich of volatiles (CO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) magmatic-hydrothermal fluids mostly between 200 and 300 °C. Significant to complete changes of mineral and chemical composition of the parental rocks became during hydrothermal alteration. Hikov (2013) found out that Sr concentrates in AAA rocks while Ti, Zr, V, Ta, Nb, Th, U and LREE are immobile. The highly altered monoquartz (silicic) rocks are characterized with depletion of almost all elements studied and even Sr and LREE are depleted since the rock is free of proper minerals.

Inert elements in these rocks are hosted mainly by rutile and in a small degree by alunite and Fe-oxides/hydroxides. Rutile hosts V, Zr, Hf, Nb, Ta, Sn, W, Mo, partially U and Th, which are comparatively inert at these conditions. Part of Zr occurs as unknown fine-grained Zr-phase, possibly ZrO<sub>2</sub> (Hikov, 2013).

Enrichment of some elements as Cr, Ag, W, Sn, As, Hf, Au and Mo is registered in monoquartz rocks. Despite of strong acid leaching, the enrichment of these elements indicates high sulphidation epither-

mal environment. Such environment is feasible in the uppermost parts of the porphyry copper systems (Hedenquist et al., 2000; Sillitoe, 2010). The presence of complex hydrothermal alteration and geochemical anomalies of these trace elements is thought to be important criteria for the development of porphyry copper mineralization at depth (Halley et al., 2015).

There is visible enrichment of Hf while Zr has inert behavior in monoquartz rocks. The Zr-Hf fractionation may result from different stability of chemical complexes of Zr and Hf with Cl and SO<sub>4</sub> ligands in strong acid environments (Inguaggiato et al., 2015).

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