## **Accessory mineral assemblage and their dependence on the melt character in the S‐type granites: an example from the Western Carpathians**

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Volatile-rich S-type granite melts during their cooling and fractionation may significantly change the accessory mineral assemblage. Moreover, such granite systems strongly modify also the composition of some accessory phases. Therefore, the accessory minerals can be used as an important discriminative parameter for revealing circumstances or PTX conditions in such type of granite evolution. Generally the fluids and especially the presence of boron in the felsic melt significantly decrease the melt viscosity (e.g. Dingwell et al. 1993), minerals have more time for their growth, and unusual chemistry conditions during long fractionation give them special compositional features.

The Permian S-type granites from the Alpine Gemeric unit in the Western Carpathians are an excellent example of specialised accessory mineral evolution (Broska et al. 2002). Because of high concentration of boron the granites commonly contain schorlitic tourmaline and due to specific volatile and trace element contents (F, B, Rb, Nb, Ta, W, Sn) they are named specialised S-type granites. The content of tourmaline increases upwards changing also its form of occurrence - tourmaline in the deeper granite part forms scattered grains but within upper part it can be also nodular and dendritic.

The count of typomorphic minerals in the S-type granites, represented mainly by zircon, monazite, xenotime- $(Y)$  ± garnet and tourmaline, is significantly enlarged in the differentiated upper part of granite body or in the granite cupolas. There is strong alteration of granites, including greisenisation. The granites in cupolas are tin-bearing because the extended S-type accessory mineral assemblage includes also Sn, Nb, Ta, W mineral phases or various Nb-Ta oxides, wolframites and economically important cassiterite, but on the contrary there is the decrease of frequency of REE accessory minerals. The apex granites can be qualified as rare-metal granites. Zircon in the raremetal granite compared to deeper seated biotite granites shows a larger xenotime- $(Y)$ molecule and also a different morphology, which result in lower IT parameter. Zircon composition or  $Zr/Hf_{wt}$  ratio in zircon from deeper biotite granite varies from 29 to 45, for upper rare-metal granites an increase in Hf contents toward  $Zr/Hf_{wt}$  results in a ratio of 5. The cheralite component in monazite from biotite granites does not exceed 12 mol.  $%$ , but in rare-metal granites the monazites contain up to 14 to 20 mol.  $%$  of cheralite and in some places even more than 40 mol. %. Accumulation of P along with high activity of  $F$ in granite cupolas stabilised aluminophosphates and topaz instead of primary apatite and albite (Petrík et al. 2011). Tiny, late pure apatite precipitates by exsolution of  $P$  from albites. 

The very high flux regime in the differentiated granite cupolas which influences on frequency of the accessory mineral paragenesis, documents a formation of the tetrad effect on REE`s chondrite normalised patterns (Fig. 1). According to Bau (1996) the tetrad effect is caused by complexation of the REE's with  $H_2O$ ,  $CO_2$ ,  $F^2$ , and Li. In such circumstances the behaviour of the REE's is not more dependent on the ionic radii, but on filling of 4f orbitals. Thus, the REE`s with  $0/4$  (La),  $1/4$  (Nd, Pm),  $2/4$  (Gd),  $3/4$  (Ho, Er) and  $4/4$  (Lu) filling 4f orbitals can be fractionated from the other REE`s resulting in the

tetrad pattern. Generally, the tetrad effect occurs in highly evolved igneous rocks as an indicator of the transition between magmatic to high-temperature hydrothermal systems.

The relationship between accessory mineral paragenesis and the extreme volatile richgranite system documents the tetrad effect or significant increase of the frequency of accessory mineral phases also in the granites from the Gemeric unit in Western Carpathians. The normalised REE pattern of the basic (undifferentiated) S-type granite with paragenesis represented by monazite-(Ce), xenotime-(Y), tourmaline  $\pm$  garnet without bulk rock tetrad effect. On the other hand, rare metal granites in upper part of granite body are almost free of the REE accessory minerals which is in contrary to the more variable other accessory minerals including cheralite-(Ce), Nb-Ta-W minerals (Nb-Ta rutile, ferrocolumbite, manganocolumbite, ixiolite, Nb-Ta ferberite), cassiterite, topaz, molybdenite, arsenopyrite and rare accessory aluminophosphates (arrojadite, lacroixite, goyazite, gorceixite and viitaniemiite).



*Fig. 1. Comparison of REE chondrite normalised patterns in deeper seated granites and upper rare‐ metal granites. The tetrad effect (open marks) in chondrite normalised granites indicates the high flux of volatiles in rare‐metal granite cupolas which is connected with high frequency of accessory minerals with exception of REE minerals. Secondary albitites show the lowermost content of REE`s (locations are in brackets)*

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