## Secondary zircon-group minerals originating by recrystallization of Sc,Y,U,P-rich zircon and complex W-Nb-Fe-Sc oxide from the pegmatite No. 3, Dolní Bory, Czech Republic.

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Zircon-group minerals are very important as indicators of geochemical fractionation, for age determinations, thermometry (zircon saturation thermometry, Ti in zircon) and they are considered as potential matrices for high level nuclear waste storage. Dolní Bory pegmatites provide excellent natural laboratory for investigation of their properties, such as compositional variability and behavior during recrystallization.

Pegmatite No. 3, about 5 m thick and several tens of meters long dyke, belongs to large population of NNW-SSE trending dykes, cross-cutting granulites of the Gföhl unit of the Moldanubian zone, Bohemian Massif. The pegmatite consists from contact inwards of: 1) granitic zone (microcline + quartz + oligoclase + biotite  $\pm$  muscovite), 2) graphic zone (microcline + quartz), 3) blocky microcline, 4) quartz core, 5) albitic unit (albite + andalusite + schorl + sekaninaite) and 6) andalusite-diaspore nodule.

Both investigated mineral assemblages occur in about metersized andalusite-diaspore nodule enclosed in quartz core. Novák *et al.* (2008) determined the p-T conditions of crystallization of primary diaspore and andalusite at 400°C and 2 kbar. The nodule also contains younger pyrophyllite and kaolinite partially replacing andalusite and accessory schorl-foitite, ferberite-wolframoixiolite, rutile, ilmenite, monazite-(Ce), xenotime-(Y), zircon, autunite and pyrite.

Zircon rich in Sc, Y, U, P initially formed in association with monazite-(Ce). xenotime-(Y) and ilmenite. Subsequent hydrothermal alteration left the xenotime intact, partially replaced the monazite to REE-rich crandallite and caused complete recrystallization of the zircon (Fig. 1). Contrary to nearby located dyke No. 4, (Výravský & Novák, 2013) no primary zircon domains were found. Recrystallised zircon contains in average 9.7 mol% of pretulite (ScPO<sub>4</sub>) component, 0.7 mol% of xenotime component, 0.003 apfu U and Zr/Hf 35. The recrystallised zircon hosts numerous tiny pores, inclusions of secondary xenotime (0.021 apfu Sc, 0.036 apfu U, 0.006 apfu Zr) and inclusions of secondary pretulite (0.05 apfu Zr, 0.018 apfu Y, 0.0004 apfu U) all  $\leq \approx 10 \ \mu m$ . Absence of uraninite inclusions in recrystallised zircon, which were found in similar zircon in dyke No. 4 (Výravský & Novák, 2013) indicates that excess of the released U, which did not fit to structures of forming secondary zircon-group minerals, was leached out by oxidizing fluids in the form of  $U^{6+}$  and precipitated away as common autunite.

Complex W-Nb-Fe-Sc oxide, ranging in composition from wolframoixiolite to ferberite ( $\leq$ 4.36 wt.% Sc<sub>2</sub>O<sub>3</sub>,  $\leq$ 2.84 wt.% ZrO<sub>2</sub>; Novák *et al.*, 2008), is another mineral, which underwent partial recrystallization. It is partially replaced by fine-grained mixture of various minerals including Nb-wolframite, W-columbite, Nb-rutile, scheelite and pretulite-zircon solid solution. The pretulite-zircon solid solution contains 0.09-0.77 apfu Zr, 0.89-0.22 apfu Sc, 0.005-0.066 apfu Y, 0.001-0.029 apfu U and Zr/Hf 40. Similar solid solution was also described from epizonal metamorphosed sedimentary iron ore by Moëlo *et al.* (2002). Zr-rich compositions

tend to have increased concentrations of Y and U, indicating better solubility of large ions in zircon, than in pretulite structure and they also show elevated amounts of Ca, Al and Fe, low analytical totals and deviations from ideal stoichiometry, which are all signs of metamictization and hydration.

Composition of secondary zircon-group minerals from Dolní Bory (zircon, xenotime-(Y) and pretulite), which formed by recrystallization of different precursors is influenced by composition of their precursors and redistribution of elements between recrystallization products. Xenotime strongly prefers larger cations (Y, U, REE), whereas zircon prefers smaller ones (Zr, Hf, Sc).

In the assemblage of primary Y-rich zircon, the pretulite contains higher amounts of Y and REE, than secondary zircon and secondary xenotime is the main host of Y, REE and U.

On the other hand, in the assemblage of primary wolframoixiolite, no secondary xenotime is present because of low initial concentration of Y. In absence of the secondary xenotime, Y, REE and U are hosted in Zr-rich compositions of the pretulitezircon solid solution, which therefore have higher con concentrations of these elements than Sc-rich ones.

Our data also supports the existence of complete solid solution between pretulite and zircon, as proposed by Moëlo *et al.* (2002).



Fig. 1: Recrystallised zircon full of pores and inclusions of xenotime and pretulite. It is associated with homogenous primary xenotime (medium grey) and monazite (bright) partially replaced by crandallite. BSE.

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