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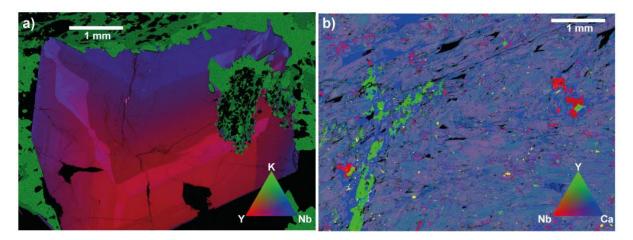
## Local controls on mineral transformations: replacement of (Y-Nb-REE)-rich titanite by rutile

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Although Ti, Nb and REE are assumed to be immobile during most hydrothermal and metamorphic processes, many examples of (mostly) small-scale mobility of these elements have been reported [1,2]. Large (> 1 cm), idiomorphic titanite-(I) crystals growing in deformed quartz-feldspar veins within quartz-feldspar-muscovite±biotite gneisses from the Penninic nappes of the Binntal Valley, Switzerland, at amphibolite-facies peak metamorphic conditions are enriched in Y, Nb, REE ± As [3]. Some of these crystals have broken down into assemblages of titanite-(II)+gramaccioliite-(Y)+calcite±(Nb-rich-rutile). The host gneiss shows little evidence of alteration. It is common to observe fresh titanite-(I) in close proximity to titanite-(II). Titanite-(II) displays a patchy distribution of Y and Nb, and gramaccioliite-(Y) forms exsolution-like lamellae within these crystals. However, EBSD reveals that there is no crystallographic relationship between gramaccioliite-(Y) and the host titanite. The titanite-(II) assemblages often further decay to Nb-rich-rutile+gramaccioliite-(Y)±minor phases.

This new pathway of titanite composition [4] illustrates the importance of *local conditions* and *small amounts of fluids* for controlling rare metal mineralogy and geochemistry. The unusual reaction pathways of the Binntal titanite-(I) results from the crystallization of titanite probably under the influence of metamorphic fluids enriched in Y, Nb, REE ± As, resulting in an unusual chemistry. During retrograde alteration, the high levels of rare metals become unstable within the crystal structure of



titanite. However, due to relatively low diffusion rates of Y + REE + Nb in titanite, titanite-(I) can survive

metastably unless it interacts with small amounts of  $CO_2$ -rich fluids. Importantly, despite textures reminiscent of a solid-state, diffusion-driven process (exsolution), the gramaccioliite-(Y) lamellae are clearly formed via a fluid-driven process. Once initiated, the process usually proceeds to a final assemblage of Nb-rich-rutile+gramaccioliite-(Y).

*References:* [1] JANOTS E, BERGER A AND ENGI M (2011) *Lithos* 121: 1-11; [2] LOTTERMOSER B (1992) *Ore Geology Reviews* 7: 25-41; [3] CUCHET S, CRUMBACH MA AND BURGT A 2014. *Schweizer Strahler* 48: 2-55; [4] MIDDLETON AW, FÖRSTER HJ, UYSAL I T, GOLDING SD AND RHEDE D (2013) *Chemical Geology* 335: 105-117.

*Figure 1: RGB elemental distribution showing a) primary titanite in a quartz (black), feldspar (light green) vein, hosted by a muscovite-biotite (dark green) gneiss, and b) titanite breaking down into gramaccioliite-(Y) (green). Other products are Nb-rich rutile (red) and calcite (blue).*