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W-Nb-bearing zirconolites from metasomatic veins in marbles from the Stubenberg Granite contact aureole (Styria, Austria)

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The occurrence of accessory phases like baddeleyite and zirconolite has long been recognized to be related to metasomatic activity during contact metamorphism accompanied with metasomatism of carbonate rocks. The Stubenberg Granite belongs to the lower Austroalpine basement nappe system of the Eastern Alps. A Rb-Sr whole rock isochron suggests a Permian age of the intrusion. During Eo-Alpine metamorphic overprint, the secondary assemblage garnet₂(Alm₅₃Pyr₂Gro₄₂Sps₃) + biotite + muscovite + albite \pm K-feldspar formed. The unusually high Cl-contents in biotites of up to 1.3 wt. % are thought to be an inherited primary igneous feature. Thermobarometric calculations indicate a high-pressure overprint of 1.2 - 1.5 GPa at $530 - 600^{\circ}$ C. Application of calcite-dolomite thermometry to a texturally older generation of calcite (Mg = 0.1 a.p.f.u.) in the marbles leads to temperatures of ca. 530° C. Texturally later calcite contains less MgO (Mg = 0.03 a.p.f.u.) and hence leads to lower temperatures of ca. 300° C due to subsequent re-equilibration after the temperature peak.

Contact metamorphism during emplacement of the granite lead to the formation of the assemblage olivine (Fo_{95}) + calcite + Ti-clinohumite (≤ 8 wt. % TiO₂) \pm phlogopite \pm chlorite in the adjacent marbles. During the intrusion of the granite, veins, rich in Ti, Zr, REE and actinides (ACT) formed. These veins show a distinct mineralogical zoning sequence with three zones from the center to the margin: (1) Mg-rich ilmenite + baddeleyite + zirconolite + apatite + calcite + chlorite \pm magnetite \pm pyrrhotite assemblage, (2) calcite + chlorite and (3) olivine + Ti-clinohumite + calcite \pm phlogopite. The mineral assemblage of the veins is similar to veins from the Adamello

contact aureole (Gire, 1992). Baddeleyite is always replaced by zirconolite, possibly along the model reaction baddeleyite + 2 geikielite + 3 calcite + CO_2 = zirconolite + 2 dolomite. Zirconolite shows strong oscillatory zoning with U- and Nb-rich rims. The U-contents reach up to 2.1 wt.% UO₂ in the rims, whereas Th is below 0.5 wt.% ThO₂. These rims occur as distinct overgrowths with a different chemical composition, thus probably reflecting later re-mobilization during a subsequent Eo-Alpine metamorphic overprint. The chemical variation between cores and rims can be explained with the two main substitutions: ACT + Fe²⁺ = Ca + Ti and REE + Nb = Zr + Ti. In contrast to other zirconolites from metacarbonates from contact aureoles, the analyses show elevated Nb contents of up to 4.5 wt.% Nb₂O₅ and unusually high W contents of 1 – 2 wt.% WO₃ (Gire, 1998) The occurrence of scheelite in adjacent calcsilicate rocks also points to the interaction of a W-rich fluid phase most likely during the contact metamorphic overprint.

Occasionally, baddeleyite has been replaced by zircon and uraninite (UO₂), indicating locally an increase in the activity of $a(SiO_2)$ relative to ZrO_2 – $ZrSiO_4$. Textures suggest that the HFSE- and REE-rich assemblages formed during Permian emplacement of the Stubenberg granite and as a result of the subsequent high-P Eo-Alpine metamorphic overprint, HFS- and RE-elements probably were locally re-mobilized leading to U and Nb-rich overgrowths on zirconolites.

References:

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