Electron microprobe dating of zirconolite: an additional tool for unravelling complex metamorphic histories and a case example from the eastern, lower Austroalpine nappes (Stubenberg Granite contact aureole, Styria, Eastern Alps, Austria)

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Contact metamorphism during emplacement of the Permian Stubenberg Granite has led to the formation of the assemblage forsterite + calcite + titanian clinohumite ± phlogopite ± chlorite in the adjacent marbles. During intrusion of the granite, veins, rich in Ti, Zr, REE and actinides (U + Th) formed. These veins show a distinct mineralogical zoning sequence with four zones. Going from the center of the vein to the margin, these zones include: (1) geikielite + baddeleyite + zirconolite + apatite + calcite + chlorite ± magnetite ± pyrrhotite assemblage, (2) calcite + chlorite, (3) forsterite + titanian clinohumite + chlorite + calcite ± phlogopite and (4) calcite ± forsterite. Baddeleyite is always replaced by zirconolite, possibly via the model reaction baddeleyite + 2 geikielite + 3 calcite + CO_2 = zirconolite + 2 dolomite. Zirconolites (Zirc I) show a strong internal oscillatory zoning and distinct overgrowths (Zirc II), which have a different chemical composition. The chemical variation between the cores (Zirc I) and the rims (Zirc II) can be explained by the substitutions: Me^{5+} + Me^{2+} => Ti + Me^{3+} and REE + Me^{5+} + Me^{2+} => Ca + 2Ti. In contrast to zirconolites from metacarbonates associated with contact aureoles, these analyses show elevated Nb contents of up to 4.5 wt. % Nb_2O_5 and unusually high W contents of 1–2 wt. % WO_3. The Zr-mineral sequence baddeleyite – zirconolite – zircon implies an increasing $a(SiO_2)$ and fCO_2 during the growth of these minerals. A strong Eo-Alpine metamorphic overprint led locally to the formation of the assemblage chlorite + dolomite + calcite ± ilmenite ± zirconolite II ± geikielite + Fe-sulfides. Late zircon grew locally, presumably as the last Zr-mineral in the carbonates during the Permian contact metamorphism.

Although zirconolite has been noted as a potential U-Pb geochronometer (Heaman and LeCheminant, 1993), it has rarely been dated (Andersen and Hinthorne, 1972; Hinthorne et al., 1979; Rasmussen and Fletcher, 2004). When attempted, these studies were performed using a SHRIMP ion microprobe as opposed to electron microprobe analyser (EMPA). Two of the polished thin sections contain zirconolite grains, which show a particularly coarse zoning under BSE imaging. In an attempt to derive rough age constraints on the basis of EMPA Th-U-Pb dating (Suzuki et al. 1991; Montel et al. 1996), lighter and darker domains were systematically analysed in three grains. U, Th and Pb analyses for EMPA dating were performed on a JEOL JX 8600 at the Department of Geography, Geology and Mineralogy at the University of Salzburg. In order to obtain precise Th, U and Pb concentrations, long counting times were used (Th Ma: 20s, U Ma: 30s and Pb Ma: 140 s), at a high beam current of 200 nA and 15 kV accelerating voltage (Finger and Helmy, 1998). Under these conditions the typical 2s errors for Th, U and Pb are 0.05 wt. %, 0.04 wt. % and 0.007 wt. % respectively. The beam diameter was slighly defocused to about 2 μm to avoid beam irradiation effects. Slight interferences of Th on U, and Y and Th on Pb, were empirically corrected with standards. Electron microprobe U-Th-Pb dating of zirconolites (Zirc I) yields weighted average ages of 263 ± 16 Ma and indicates that the HFSE- and REE-rich assemblages formed during Permian emplacement of the Stubenberg granite. As a result of the subsequent high-*P* Eo-Alpine metamorphic overprint (111 ± 15 Ma), zirconolite recrystallization occurred, leading to dissolution of zirconolite I and re-precipitation of the REE and Nb-rich overgrowths of zirconolite II.

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