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The decoupling of the Zr- and U-Pb systematics in rutile during cooling from HT conditions

Ellen Kooijman (1), Klaus Mezger (2), Jasper Berndt (1), and Matthijs Smit (1)

(1) Institut für Mineralogie, Westfälische Wilhelms-Universität, Münster, Germany (e.kooijman@uni-muenster.de), (2) Institut für Geologie, Universität Bern, Bern, Switzerland

Rutile ($\mathrm{TiO_2}$) is a common accessory mineral in igneous and metamorphic rocks. It is stable over a wide range of $P-T$ conditions and is the main Ti-bearing phase in high-grade metamorphic rocks. It shows temperature-dependent partitioning of Zr, providing a potentially reliable single-mineral thermometer [1]. Because rutile can incorporate up to 200 ppm U, it can be dated with excellent analytical precision using the U-Pb system. This makes the mineral highly suitable for constraining the history of metamorphic rocks.

Under metamorphic conditions the U-Pb system in rutile may (re-)equilibrate with the matrix by volume diffusion. The same may be expected for Zr and other trace elements. This complicates interpretation of results from rutile thermometry and geochronology, because Zr-in-rutile temperatures may neither represent peak conditions nor correspond to the U-Pb ages determined in the same mineral grain. Although diffusivities of Zr and Pb in rutile have been experimentally constrained [2,3], the relative behaviour of these elements in natural metamorphic rutile is not well-characterized. To better understand the Zr- and U-Pb systematics in rutile, we performed an EPMA (Zr) and LA-ICP-MS (U-Pb) study on rutile grains from Archaean granulites from the Superior Province, Canada.

Zirconium contents were determined along profiles through—and in cores and rims of—15 rutile grains (120-280 μm) from 4 samples. The profiles show largely homogeneous Zr concentrations and, with the exception of 3 grains, no significant difference in Zr content between cores and rims. Some profiles display either a Zr decrease or increase of up to 200 ppm in the outermost 10-45 μm of grains, showing the effects of marginal volume diffusion. Variations among grains within one thin section are large (600-3400 ppm). If these concentrations are pristine, they would indicate highly variable crystallization temperatures (690-870 ˚C) for grains of the same mineral paragenesis, which is unlikely.

Laser ablation ICP-MS of 35-μm spot transects across the grains analyzed for Zr yielded concordant U-Pb ages with core ages of ca. 2450 Ma and core-to-rim younging towards ca. 2280 Ma. In contrast to the Zr profiles, age profiles show no core plateaus, indicating that volume diffusion of Pb occurred throughout the grains. The ages were used to construct closure temperature profiles ($T_c(x)$; [4]), representing the temperature of insignificant Pb diffusion as a function of position within the grains. The T_c estimates show a core-to-rim decrease from ca. 640 ˚C (depending on grain size) to an extrapolated value of ca. 490 ˚C. These estimates provide valuable insight into the closure behaviour of the U-Pb system in rutile and allow a more effective use of U-Pb rutile dating in constraining cooling histories of metamorphic rocks.

This study shows that the U-Pb system and Zr distributions in rutile behave differently during cooling from high temperature conditions and are to a variable degree affected by volume diffusion. This decoupling indicates that U-Pb ages and Zr-in-rutile temperatures cannot be correlated directly. Our study confirms the difference between Pb- and Zr diffusion in rutile as predicted by experimental studies [3]. Zirconium contents are likely to be pristine, but may vary significantly for cogenetic minerals due to currently unknown causes. Therefore, care must be taken when applying Zr-in-rutile thermometry. In contrast, U-Pb dating of rutile is a robust method for providing reliable time constraints on various stages of cooling.

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