Trace element systematics in HT metamorphic rutile: The robustness of the Zr geothermometer

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The Zr-in-rutile thermometer [1] has been successfully applied to a wide range of high-grade metamorphic rocks. However, experimental data indicate that rutile may be only moderately retentive to Zr [2]. Some field-based studies reported a large range of Zr concentrations from granulite facies metamorphic rocks suggesting post-peak diffusional resetting during slow cooling [3]. Further investigation into the Zr systematics in rutile is needed to improve the interpretation of Zr-in-rutile temperature estimates.

For this purpose, we analyzed rutile grains from zircon-bearing granulite-facies metapelites of the Archaean Pikwitonei granulite domain, Canada. The Zr concentrations were evaluated by acquiring compositional profiles and maps by electron probe micro-analysis. Profiles of Nb, Cr and V, which diffuse faster in rutile than Zr [4], were analyzed simultaneously. The variation in the concentrations of all elements is small within individual rutile grains (120-280 µm) from 3 different samples, but large differences are observed between grains only millimeters apart in the same sample.

The lack of diffusion profiles for all analyzed elements indicates that Zr concentrations are pristine. Zoning of high-Zr rutile (3000-4600 ppm) demonstrates Zr undersaturation during growth under dry UHT conditions in spite of the presence of zircon. Therefore, several rutile grains should be analyzed in a sample to obtain a useful minimum peak temperature estimate. The highest Zr-in-rutile temperatures for the samples from the Pikwitonei granulite domain are ca. 900 °C and thus exceed previous estimates of 820 °C based on two-feldspar thermometry [5], demonstrating the advantage of Zr-in-rutile thermometry for constraining peak temperatures of UHT rocks.

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In situ analysis of U-Th disequilibria in titanite by fs-LA-MC-ICPMS

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A new technique for *in situ* analysis of U-Th disequilibria in titanite by fs-LA-MC-ICPMS is presented. An in-house titanite glass ([U] = 215 ppm), determined to be in secular equilibrium by solution mode MC-ICPMS, is used to correct for U-Th elemental fractionation by sample standard bracketing. SEM-Faraday gain and abundance sensitivity are determined on solution standards interspersed every 15 laser ablation analysis.

The effect of instrument settings to the accuracy and precision of (^{230}Th/^{238}U) ratios was investigated by multiple analyses of secondary titanite standards. The laser analysis mode (scanning or spot), laser energy and wavelength, and titanite material properties were all found to variably influence the U-Th elemental fractionation and compromise the accuracy of the data to different extents.

During spot analyses using near infra-red (NIR) wavelength and high laser energy, time-dependent elemental fractionation is observed, resulting in relatively large standard errors on the (^{230}Th/^{238}U). Decreasing the laser energy significantly reduces the time-dependent elemental fractionation but does not eliminate it completely, e.g. 2RSE on (^{230}Th/^{238}U) are 5.2% instead of 19%. NIR scanning mode analyses are not compromised by time-dependent elemental fractionation (2RSE on (^{230}Th/^{238}U) are 3.2%), but the absolute amount of fractionation between analyses of different materials (e.g. glass versus minerals) is variable.

Ultra violet (UV) mode LA analyses are significantly less affected by time-dependent elemental fractionation compared to NIR analyses, but are limited by counting statistics due to lower signal intensities. Furthermore, differences in fractionation behaviour between various titanite materials are still observed. The effect of adjusting plasma conditions, with the aim to reduce the elemental fractionation, is currently investigated.