## In-situ oxygen isotope and trace element geothermometry of rutilated quartz from Alpine fissures

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## ABSTRACT

Finely acicular rutile intergrown with host quartz (rutilated quartz) is commonly found in hydrothermal veins, including the renown cleft mineral locations of the Swiss Alps. These Alpine cleft mineralizations reportedly formed between ~13.5 and 15.2 Ma (based on ages of rare hydrothermal monazite and titanite) at temperatures (T) of  $\sim$ 150–450 °C (based on fluid inclusions and bulk guartz-mineral oxygen isotope exchange equilibria), and pressures (P) of 0.5-2.5 kbar (estimated from a geothermal gradient of 30 °C/km). The potential of rutilated quartz as a thermochronometer, however, has not been harnessed previously. Here, we present the first results of age and T determinations for rutilated quartz from six locations in the Swiss Alps with vein country rocks that cover peak-metamorphic conditions between  $\sim 600$  and <350 °C. Samples were cut and mounted in epoxy disks to expose rutile ( $\sim 30$  to 1400 µm in diameter) and its host quartz. Cathodoluminescence (CL) and backscattered electron (BSE) imaging of host quartz and rutile inclusions, respectively, shows internal zonations, which are nevertheless isotopically homogeneous. Newly developed secondary ionization mass spectrometry (SIMS) oxygen isotopic analysis protocols for rutile were combined with those established for trace elements (including Zr) and U-Pb ages in rutile, and Ti abundances in the host quartz. U-Pb rutile ages average  $15.1 \pm 1.7$  Ma ( $2\sigma$ ), in excellent agreement with previous accessory mineral geochronometers. Pressure-independent T estimates, calibrated for low-temperature conditions, from oxygen isotope fractionation between rutile and quartz in touching pairs are 310-576 °C. Individual rutile needles vary in Zr abundances beyond analytical uncertainties, but average Zr-in-rutile inversely correlates with oxygen isotopic fractionation between quartz and rutile. Linear regression of the data yields:

$$T(^{\circ}\mathrm{C}) = \frac{26(\pm 9)}{0.07(\pm 0.01) - \mathrm{R}\ln x} - 273$$

with x = Zr ppm and R = 0.008314 (uncertainties scaled by the square root of the mean square of weighted deviates MSWD = 11; n = 9). This relationship supports previously recognized temperaturedependent Zr uptake in rutile, although widely used Zr-in-rutile thermometer calibrations based on high-*T* experiments are at variance with oxygen isotope exchange temperatures. By contrast, Ti-inquartz lacks systematic relations with oxygen isotope temperatures. The discrepancy between low-*T* Ti-in-quartz thermometry on one side, and oxygen isotope and Zr-in-rutile thermometry on the other, suggests that Ti-in-quartz thermometry should be applied with caution for low-*T* (<500 °C) rocks.

**Keywords:** Rutilated quartz, Ti-in-quartz thermometer, Zr-in-rutile thermometer, Alpine fissures, Swiss Alps