Mapping trace element zoning in rutile

Mona Lüder[1], Pierre Lanari[1], Jörg Hermann[1]

[1] Institut für Geologie, University of Bern, 3012 Bern, Switzerland.

Rutile is a major accessory mineral in eclogites and Zr-in-Rutile thermometry is one of the most frequently used single-grain thermometers. Intra grain variations of Zr contents in rutile are rarely reported and systematic investigations of trace element zoning in Rutile are missing. We performed LA-ICP-MS mappings of rutile in eclogite samples from the Alps (Pfulwe and Capoli). All grains show strong compositional zoning in several trace elements. Here we present Zr maps with different zoning patterns and their possible implications for Zr-in-rutile thermometry. A rutile aggregate from Pfulwe (Fig. 1) shows isolated cores with 22 ppm Zr surrounded by rims with up to 40 ppm Zr. This could be related to prograde rutile growth from 520 to 550 °C, at 2.1 GPa using the calibration of Tomkins et al. (2007). Alternatively, as rutile forms a large cluster of serval 100 grains, it can be questioned if Zr-supply is efficient enough to ensure Zr-saturation, even as Zircon is present in the sample. Highly speckled patterns as seen in Nb-, Ta- or Cr-maps support the hypothesis of limited trace element supply towards the inner part of the cluster. We propose that local under-saturation in Zr and thus variable Zr-activity (Δa_{Zr}) is responsible for the Zr-zoning observed. Assuming constant temperature, pressure, silica activity during Rutile growth and a Zr activity of 1 at the highest Zr concentration measured, we calculated a map of Δa_{Zr}. The isolated cores show values as low as 0.4. Another example from Capoli, with a similar rutile cluster shows less pronounced, but still visible Zr zonation. Zr contents vary between 440-490 ppm, with corresponding temperatures of 750-760°C at 2.6 GPa, showing a much more constant supply of Zr at higher temperatures.

Similar zonings can be observed for a variety of trace elements (*e.g.*, Nb, Ta, U, Zr, Hf, Sn, W, Mo, V, Si, Sb, Sc, Ga, Cr, Ni, Fe, Al, Zn, Mg). In all investigated samples, Nb and Ta show distinctly different zonings, resulting in intra-grain variations of Nb/Ta ratios. Those variations correlate mainly with the Ta content, indicating higher variability of Ta in metamorphic fluids. Performing random spot analysis on a zoned sample like this would lead to large spread of Nb/Ta-ratios that are difficult to interpret. Additionally, systematic variations in trace element contents such as Al, Cr, Fe, Sc or V could potentially be utilized to infer rutile-forming reactions.

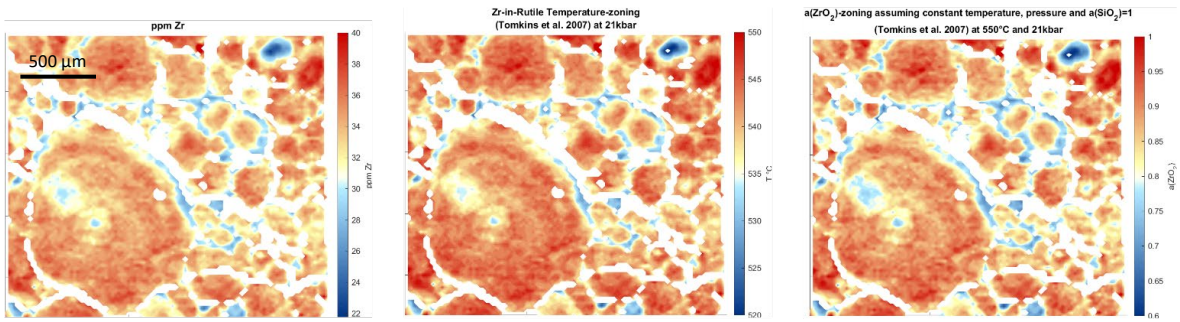

Figure 1- Zr zonation in Rutile from Pfulwe with equivalent temperature zoning according to Tomkins et al. 2007 and calculated Zr activity variations with assumed Zr saturation at maximum Zr content, constant temperature and pressure.

Tomkins, H.S., Powell, R., Ellis, D.J., 2007. The pressure dependence of the zirconium-in-rutile thermometer. *Journal of metamorphic Geology* 25, 703-713.