

The Ti content of zircon and the Zr content of rutile as a function of temperature and pressure

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The Ti content of zircon coexisting with rutile and quartz is strongly dependent on temperature and can be used as a geothermometer [1]. Knowledge of crystallisation temperatures is important for interpreting geological histories, yet previous calibrations have not identified a pressure dependence on the Ti content of zircon, despite the importance of pressure, in addition to temperature, for Zr in rutile [2] and Ti in quartz [3]. A pressure effect is expected for the substitution of Ti⁴⁺ for either ⁴⁴Si⁴⁺ or ⁸⁸Zr⁴⁺ in zircon, due to the different sizes of the cations. Ti occupies the ⁴⁴Si⁴⁺ site in zircon at atmospheric pressure [4] but is expected to change to ⁸⁸Zr⁴⁺ with increasing pressure [5].

Synthetic zircons, coexisting with rutile and a silica melt were crystallised at 1200 - 1400 °C and 5 – 60 kbar. These experiments also allow the Zr content of rutile to be determined. In addition, zircon crystals were grown using a Na₂WO₄ flux over the same P-T range to produce crystals of sufficient size to allow the coordination of Ti to be determined by XANES spectroscopy.

The Ti contents of the flux-grown zircons decreases from 1200 ppm at 5 kbar to 225 ppm at 60 kbar at 1400 °C. The results suggest a change in Ti coordination at 10 kbar, which is much lower than previously estimated (3.5 GPa) [5]. This has implications for the application of the existing Ti-in-zircon geothermometer, which may overestimate the temperature of some crustal zircons. NanoSIMS analysis of the Ti content of zircon coexisting with rutile will shed further light on the effect of pressure.

The Zr content of rutile at > 30 kbar was found to be less than predicted [2], suggesting that a recalibration of this thermometer for high pressures may be required. Therefore the accuracy of both the Ti-in-zircon and Zr-in-rutile thermometers may be compromised when applied to pressures outside the range used for the calibration.

[1] Ferry & Watson (2007), *Contrib. Mineral. Petrol.* **154**, 429-437. [2] Tomkins *et al.* (2007), *J. Metamorph. Geol.* **25**, 703-713. [3] Thomas *et al.* (2010), *Contrib. Mineral. Petrol.* **160**, 743-759. [4] Tailby *et al.* (2011), *Geochim. Cosmochim. Acta* **75**, 905-921. [5] Ferriss *et al.* (2008), *Eur. J. Mineral* **20**, 745-755.