

## Accuracy of Ti-in-zircon thermometry improved by isotope dilution determinations of Ti in zircon reference materials

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The temperature-dependence of Ti incorporation into zircon has been exploited as a powerful tool to estimate zircon crystallisation temperatures (Ti-in-zircon thermometer; Watson et al. 2006; Ferry and Watson 2007). The accuracy of calculated zircon temperatures derived using this method depends on assumptions made about the activity of TiO<sub>2</sub> and SiO<sub>2</sub> in the chemical environment (in particular in the absence of co-crystallising rutile or quartz) as well as, potentially, crystallisation pressure. However, given informed choices of chemical potentials and an adequate pressure correction can be made, the absolute accuracy of model Ti-in-zircon temperatures ultimately hinges on the ability to accurately determine low Ti concentrations in zircon.

Depending on the Ti content of the zircon, the analytical techniques applied to determining the Ti concentration include secondary ion mass spectrometry (SIMS), laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and electron probe microanalysis (EPMA). The applicability of EPMA is limited to only the highest-T zircons (>>10 µg/g Ti); Ti concentrations pertinent to most zircon-saturated rocks (<1 to ~50 µg/g Ti corresponding to crystallisation temperatures of ~500–900 °C) are most commonly determined by SIMS or LA-ICP-MS. However, matrix effects associated with these two analytical techniques require the use of adequate matrix-matched primary reference materials. Currently, despite the growing popularity of *in situ* trace element and isotopic analyses of zircon, there is an evident lack of zircon reference materials that are suitably homogeneous with an independently determined and fully traceable value for Ti concentration that could be used for relative trace element determinations via SIMS or LA-ICP-MS.

To improve the accuracy of future *in situ* analyses of Ti in zircon, we have identified zircon reference materials that are sufficiently homogeneous with respect to Ti to serve as primary reference materials for SIMS and LA-ICP-MS. We present traceable and independent determinations of Ti concentration in multiple aliquots of these zircon crystals using isotope dilution (ID)-ICP-MS employing a precisely calibrated <sup>47</sup>Ti–<sup>49</sup>Ti double spike. We then describe a method for quantifying Ti contents in unknown zircons based on the newly-derived standard compositions and determine Ti contents of a range of other standard zircons to be used as either primary or secondary reference materials.

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### References:

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