Redox conditions of Hadean magmas: Insight from Ce-in-zircon oxygen barometry

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Positive Ce anomalies on chondrite normalized REE abundance diagrams are a nearly ubiquitous feature of zircon. This is the result of the presence of trace amounts of Ce^{4+} in natural systems and the higher compatibility of Ce^{4+} over Ce^{3+} in zircon. Using experimental determinations of the Ce^{4+}/Ce^{3+} in the melt as a function of fO_2 and melt composition, we have calibrated a Ce-in-zircon oxygen barometer independent from that of Trail et al. [1]. Our method takes the approach of Ballard et al. [2], applying the lattice strain model to measured D(zircon/melt) trace element distribution coefficients for both the REEs and a suite of 4+ cations (Zr, Hf, Th, U) which allows the estimation of the end-member D values for Ce^{3+} and Ce^{4+}. Measured "bulk" D_{Ce} values, which plot on a mixing curve between these end members, can then be related to the fraction of Ce as 4+ in the melt. Our calibration then allows for this to be linked directly to fO_2.

Evaluation of this technique has been carried out on zircons from three different lithologies whose fO_2 (expressed as Δ FMQ) has been estimated independently: rhyolite from the Bishop tuff, California (FMQ +1.1 ± 0.6), dacite from the Toba tuff, Indonesia (FMQ +0.9 ± 0.6), and monzodiorite from the Umiakovik pluton, Nain plutonic suit, Labrador (FMQ -2.4 ± 1.4). Trace element concentrations of zircon and host glass were measured by LA-ICP-MS. Values of Δ FMQ calculated by our method are +1.6 ± 0.4 (Bishop tuff), +0.8 ± 0.7 (Toba tuff) and -3.9 ± 0.5 (Umiakovik pluton), which are within error of the independent estimates.

Using D(zircon/melt) values for the REEs from Sano et al. [3] and empirical estimates for the 4+ cations, we have applied our oxygen barometer to Hadean zircons from the Jack Hills, Australia. Calculated values of Δ FMQ for zircons whose $\delta^{18}O$ is in the mantle range yield a bimodal distribution with peaks at –2.4 (n = 4) and +2.0 (n = 7). This appears to be connected to the crystal chemistry as light REE enriched samples consistently give lower estimations of fO_2. In addition to fO_2 we have also observed considerable dependence in Ce^{4+}/Ce^{3+} on melt composition. For the likely range in composition of zircon crystallizing melts this would affect the calculated fO_2 by at most 1 Δ FMQ unit. Therefore, the range in fO_2 observed is beyond that which can be explained by melt composition alone. This suggests that heterogeneities in fO_2 persisted in the source region for the zircon-producing magmas during the Hadean.

[1] Trail et al. (2011) *Nature* **480**, 79-82. [2] Ballard et al. (2002) *Contrib. Mineral. Petrol.* **144**, 347-364. [3] Sano et al. (2002) *Chem. Geol.* **184**, 217-230.

Atomic scale imaging of U, Th and radiogenic Pb in zircon

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Radiometric dating of a mineral depends on the assumption that the parent radionuclides and daughter radiogenic Pb have remained together within the analyzed volume. Isotopic dating techniques continue to evolve from bulk methods towards *in situ* techniques with ever smaller analyzed volumes such as afforded by LA-ICPMS and SIMS. The use of small sample volumes in zircon minimizes common Pb from microinclusions, but increases the importance of knowing if there has been any spatial redistribution of the radiogenic Pb relative to its parents.

In Atom Probe Tomography (APT) a specimen with dimensions of a few hundreds of nanometers is evaporated atomic layer by atomic layer. The original position of each atom is identified, along with its atomic species, and in most cases its isotope. The result is a reconstruction allowing quantitative three-dimensional study of the specimen at the atomic scale, with very low detection limits and high mass resolution.

A zircon specimen in garnet from recently identified possible UHP rocks from the Taconian of Western Massachusetts, USA [1] was selected for study by APT. WDS mapping and quantitative analysis by FE-EPMA had revealed high concentrations of Th and U in a submicron envelope between a resorbed zircon core, and a subsequent metamorphic overgrowth.

Guided by FE-EPMA trace-element mapping, a sample of this envelope was extracted by FIB and milled into 200nmX100nm conical tips appropriate for APT. A dataset of ~11 million atoms was obtained, revealing a 25nm wide band of zircon between core and overgrowth containing >0.25 at% each of U and Th.

Sufficient radiogenic Pb had accumulated within the specimen to be detectable by APT, consistent with the high concentrations of radionuclides and the expected 4-500my age of the specimen,. Strong spatial covariance was observed between U and 206Pb, without apparent migration or agglomeration of the radiogenic Pb atoms.

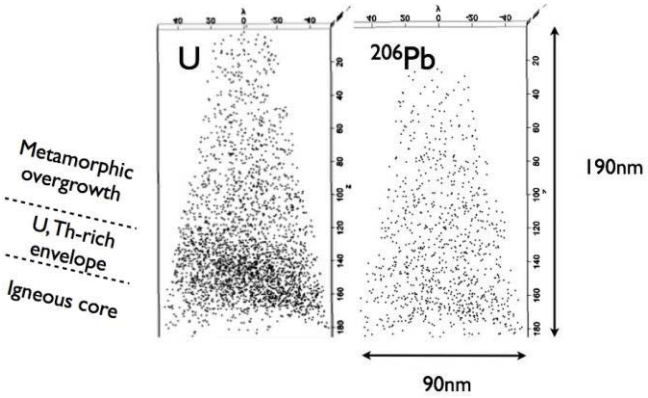

Figure 1: Ion image of U(total) and 206Pb atoms detected by APT.

[1] Snoeyenbos, Koziol, Russell, Ebel and Valley (2011) *EOS Trans. Fall meeting Suppl.* **Vol 92**, Abstract V21G-04