

Insights into the Hadean Earth from zircon experimental studies

by

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ABSTRACT

Part I: An experimental calibration of oxygen isotope fractionation between quartz and zircon is reported. Data were collected from 700-1000°C, 10-20 kbar, and in some experiments the oxygen fugacity was buffered at the fayalite-magnetite-quartz equilibrium. Oxygen isotope fractionation shows no clear dependence on oxygen fugacity or pressure. Some high-temperature data (900°C – 1000°C) show evidence for disequilibrium oxygen isotope partitioning. This is based in part on ion microprobe data from these samples that indicate some high-temperature quartz grains may be isotopically zoned. Excluding data that probably represent non-equilibrium conditions, the preferred calibration for oxygen isotope fractionation between quartz and zircon can be described by: $1000\ln\alpha_{\text{qtz-zrc}} = (2.33 \pm 0.24) \times 10^6/T^2$. This relationship can be used to calculate fractionation factors between zircon and other minerals. In addition, results have been used to calculate whole-rock/melt-zircon fractionations during magma differentiation. Modeling demonstrates that silicic magmas show relatively small changes in $\delta^{18}\text{O}$ values during differentiation, though late-stage mafic residuals capable of zircon saturation contain elevated $\delta^{18}\text{O}$ values. However, residuals also have larger predicted melt-zircon fractionations meaning zircons will not record enriched $\delta^{18}\text{O}$ values generally attributed to a granitic protolith. These results agree with data from natural samples if the zircon fractionation factor presented here or from natural studies is applied.

Part II: The incorporation of hydrogen into zircon at 1650°C and 1550°C, and pressures of 2.5 and 1.5 GPa under water saturated conditions in a piston cylinder apparatus was investigated. Concentrations were determined by polarized Fourier transform infrared spectroscopy using the zircon absorption coefficient $\epsilon_i = 36,241 \text{ cm}^{-2}$ per mol $\text{H}_2\text{O}/\text{L}$ and range from ~90 to 200 ppm H_2O by weight. Crystals grown in the presence of Ti^{4+} or Th^{4+} do not differ significantly in their H_2O content. I also synthesized zircons with various concentrations of Lu_2O_3 and Al_2O_3 to characterize changes in band positions and hydrogen concentrations related to coupled substitutions in zircon. Trivalent cations correlate in a nearly 1:1 fashion (by mole) with hydrogen highlighting a potentially important coupled substitution in high water activity environments. Bands from undoped

and doped zircons in the OH stretching region of the infrared spectrum show broad agreement when compared to spectra from natural samples. Heating experiments at 1 atm and 1000 °C produce a decrease in the integrated area; while some bands disappeared entirely, others are particularly stable with little decrease in integrated area after 128 hrs at 1000 °C. Results presented here help eliminate uncertainties that arose from Fourier transform infrared studies of natural zircons and provide further clarification for the origin of band positions in natural samples. In addition to the water activity of the crystallizing medium, the H₂O content of natural grains will likely be significantly influenced by trivalent cation concentrations. In crustal zircons especially, trivalent atomic contents generally exceed those of phosphorus, meaning that hydrogen may be particularly important for trivalent cation charge compensation.

Part III: The dependence of Ce and Eu anomalies in zircon on temperature, melt composition, and oxygen fugacity are presented for 29 experiments. Crystals were synthesized in hydrous peralkaline, metaluminous, and peraluminous melts (~72 wt% SiO₂) at 10 kbar and 800-1300°C. Melts were doped with La, Ce, Pr or Sm, Eu, Gd and the oxygen fugacity buffered at conditions near IW to ~HM+1; the run products were analyzed by electron microprobe to obtain crystal/melt partition coefficients. Results show a systematic correlation in zircon Ce anomalies (Ce/Ce*) that increase with higher oxygen fugacities and lower crystallization temperatures; Eu anomalies are more negative at lower oxygen fugacities, but with no resolvable temperature dependence. It is also demonstrated that Eu²⁺ and Ce⁴⁺ may co-exist in terrestrial melts; this implies that melt depletion of Eu by plagioclase fractionation prior to (or during) zircon crystallization is not a prerequisite for the presence of zircon Eu anomalies. The following empirical relationship has been fit to describe the dependence of Ce/Ce* on oxygen fugacity and temperature for peralkaline melts:

$$\ln\left(\frac{Ce}{Ce^*}\right) = (0.038 \pm 0.007) \times \ln(fO_2) + \frac{7062 \pm 1149}{T(K)} - 3.21 \pm 0.94$$

The importance of melt composition/structure is especially evident for peraluminous melts which yielded larger Ce anomalies and can be described by the following empirical relationship

$$\ln\left(\frac{Ce}{Ce^*}\right) = (0.107 \pm 0.005) \times \ln(fO_2) + \frac{13143 \pm 830}{T(K)} - 5.9 \pm 0.58$$

Application of this equation to a suite of natural zircons with reasonably constrained temperatures and oxygen fugacities (e.g., Bishop Tuff, mid-ocean ridge, and lunar zircons) predicts oxygen fugacities in good agreement with expected results. Application of this calibration to pristine (i.e., >95% concordant) Hadean zircons, yields average calculated oxygen fugacities for zircon source melts are \sim QFM \pm 2; this extends the record of the oxidation state of terrestrial magmas 500-800 Ma further back than previously possible to \sim 4.4 Ga.