

Zircon as an oxybarometer

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The redox variability of Ce (3+, 4+) and Eu (2+, 3+) results in the preferential uptake of Ce⁴⁺ and exclusion of Eu²⁺, relative to the other exclusively trivalent rare earth elements (REE), by zircon crystallising from a melt. This results in Ce and Eu "anomalies". The magnitudes of these anomalies will depend on the amounts of Ce⁴⁺ and Eu³⁺ in the melt. The amount of an oxidation state is controlled by both the overall abundance of the element (e.g. depletion of Eu by prior crystallisation of plagioclase) and the Ce⁴⁺/Ce³⁺ and Eu³⁺/Eu²⁺ ratios, which reflect the oxygen fugacity (fO_2).

Ce⁴⁺/Ce³⁺ and Eu³⁺/Eu²⁺ will vary at constant fO_2 due to differences in melt composition, temperature, and pressure. Partitioning experiments as a function of these variables should allow the magnitude of the anomalies to be calibrated for fO_2 . However, it is experimentally difficult to produce crystals of zircon of sufficient size for analysis by LA-ICPMS, which has appropriate detection limits and allows the full REE pattern to be determined.

We have undertaken over 350 zircon-melt REE partitioning experiments using nine synthetic compositions ranging from andesitic to granitic (ASI of 0.2-1.15), at temperatures from 800-1400 °C, pressures from 0.001-4 GPa, and fO_2 s from QFM-3 to QFM+12 (where QFM is the fO_2 in log units relative to the quartz-fayalite-magnetite buffer). The concentrations of REE in zircon crystals less than the size of the LA-ICPMS analysis spot were determined using a two component regression method. The resulting data set was fit to a multi-component model to produce an expression that relates the magnitude of the Ce anomaly to all the experimental variables. Thus, if the composition of the host rock and zircon crystallisation temperature are known, then fO_2 can be determined from the zircon REE pattern. Our expression allows fO_2 to be predicted within 2 log units. This is a new geochemical tool for estimating the fO_2 of intermediate to felsic melts.

We also determined the partitioning of REE between melt and different sectors of sector zoned zircon. The partition coefficients of Ce⁴⁺ are independent of sector, whereas those for REE³⁺ vary by over an order of magnitude. This results in differences in the Ce anomaly and hence estimated fO_2 s, which can vary by up to 4 log units between sectors. The major limitation of zircon as an oxybarometer is zoning in REE concentrations, the effect of which may be reduced by whole crystal analyses.