

An experimental study of the effects of temperature, pressure, oxygen fugacity, water content and composition on trace-element partitioning between zircon and melt

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Excursions in the chondrite normalised concentrations of Ce and Eu in zircon relative to the other rare earth elements (REE) are attributed to changes in redox state and are controlled by oxygen fugacity (fO_2) [1]. Ce^{4+}/Ce^{3+} ratios in zircon can be used as an indicator of mineralisation in magmatic-hydrothermal porphyry-Cu rocks, provenance and provide insight into early crustal magmatism [2].

However, the effect of temperature, pressure, fO_2 , water content and melt composition on Ce^{4+}/Ce^{3+} and Eu^{3+}/Eu^{2+} in zircon is largely unknown and has limited the applicability of this tool to natural samples. This provides an opportunity to experimentally investigate the partitioning of the REE between zircon and melt as a function of each variable.

Synthetic zircons, doped with the REE, were grown from a series of hydrous silicate melts at 1 GPa and 800 – 1500 °C. The compositions formed a mixing line between an andesite (ASI = 1.14) and granite (ASI = 1.00). The Zr concentration was varied to ensure saturation at each temperature and composition. The fO_2 was controlled using internal metal-metal oxide buffers and double capsule methods to give a range of 13 log units in fO_2 (QFM-4 to QFM+9). Zircon crystals ranged from 2 – 20 microns and were thus smaller than the smallest practical LA-ICP-MS spot. Instead, zircon concentrations were determined by a least-squares regression from zircon-melt mixed analyses. Ce^{4+}/Ce^{3+} ratios were calculated using the lattice strain model, where end-member D values for Ce^{3+} and Ce^{4+} were estimated from REE³⁺ and ⁴⁺ cation (Zr, Hf, Th) arrays.

The results indicate Ce^{4+} uptake in zircon is favoured by low-temperatures, high fO_2 , low ASI and is independent of pressure. These results will improve the calibration for constraining fO_2 in crustal melts. This has most importance for evaluating the economic potential of mineralised rocks and unraveling petrological conditions of pre-Archaeon melts from detrital zircons.

[1] Burnham & Berry (2012) *Geochim. Cosmochim. Acta.* **95**, 196-212. [2] Smythe & Brenan (2016) *EPSL*, **453**, 260-266.

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