Zircon as an oxy-barometer

A.J. BERRY AND A.D. BURNHAM

Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia (*correspondence: Andrew.Berry@anu.edu.au)

The Ce anomaly in zircon, Ce/Ce* = (Ce^{4+} + Ce^{3+})/Ce^{3+}, arises from the preferential partitioning of Ce^{4+} relative to the neighbouring rare earth elements (REE), which occur exclusively as REE^{3+}. The magnitude of the anomaly relates to Ce^{4+}/Ce^{3+} in the melt and hence the oxygen fugacity (fO_2) at the time of crystallisation. An empirical expression relating the anomaly to fO_2 has been proposed [1]. Here we determine Ce/Ce*, and hence estimate fO_2, for a number of I- and S-type granites from the Lachlan Fold Belt of Eastern Australia.

Ce/Ce* was calculated for 13 I-type and 10 S-type granites. The concentrations of the REE were determined by LA-ICPMS. Ce* was estimated by fitting the data for the trivalent REE to a lattice strain model. The average value of Ce/Ce* was 115(107) for the I-types and 20(18) for the S-types. Using the expression in [1] this equates to values of fO_2 relative to the fayalite-magnetite-quartz (FMQ) buffer of 4.3(2.6) and -2.6(3.3), respectively.

Ce/Ce* is clearly larger for the I-type than S-type granites, suggesting that the melts were more oxidised. This is consistent with differences in mineralogy and bulk rock values of $Fe^{3+}/(Fe^{3+} + Fe^{2+})$. The more reduced nature of S-type granites is attributed to the presence of graphite in the metasedimentary source.

The difference in the calculated average values of fO_2 between the two granite types, and the standard deviation, is too large to be correct. The equation in [1] does not have the correct theoretical form. ln(Ce/Ce*), strictly ln(Ce/Ce*-1), must have a 0.25 dependence on ln(fO_2), rather than the value of 0.1156(50) quoted, due to the stoichiometry of the redox reaction $CeO_{1.5} + 0.25O_2 = CeO_2$. The error is probably the result of fitting to a very limited data set. The fO_2 difference between the two suites is exaggerated by the incorrect coefficient and the range of values is so large as to be of limited us as an oxy-barometer. This is further illustrated by application of the oxy-barometer to the Bishop Tuff, for which an average value of 2.4 ± 3.0 is obtained, compared to the value of 1.3 ± 0.3 determined from Fe-Ti oxides. Extreme caution should be used when interpreting fO_2s obtained using this equation and further work is needed to calibrate Ce/Ce* as an oxy-barometer.

[1] Trail *et al.* (2012) *GCA* **97**, 70-87.