Zircon as a probe of the oxidising environment of magmas

A.P. Burnham & A.J. Berry

Department of Earth Science and Engineering, Imperial College London, South Kensington SW7 2AZ, UK

Introduction

Zircon is arguably the most important mineral in geology due to its use in radiometric dating and its preservation of trace element signatures that record geological processes. One such signature is defined by the rare-earth elements (REE). Anomalous abundances of Ce and Eu, usually both, are a feature of all igneous zircons. The presence of a positive Ce anomaly (Ce^{4+}) suggests an oxidised magma while a coexisting negative Eu anomaly (Eu^{2+}) indicates reduced conditions. This suggests a new potential role for zircon as a recorder of the oxidising environment of a melt, allowing insight into ancient magmas that have long since eroded away.

Figure 1: Cathodoluminescence image of synthetic zircon crystals in silicate glass, typical of the samples analysed in this study. The field of view is 500 µm.

Experimental Conditions

A limitation in our ability to interpret the geochemical significance of these Ce and Eu anomalies is the difficulty in growing zircons from melts of sufficient size for Ion Micro-Probe analyses.

We have recently been successful in growing large zircon crystals (>100µm) from Zr-rich "natural" melts at one-atmosphere pressure using a gas mixing furnace where the oxidising environment and temperature can be accurately controlled and varied over a wide range of conditions that simulate the crystallising conditions of natural zircons.

Results

The concentration of trace elements in the zircon and glass of each sample was determined using the NERC Cameca ims-4f ion probe at Edinburgh University.

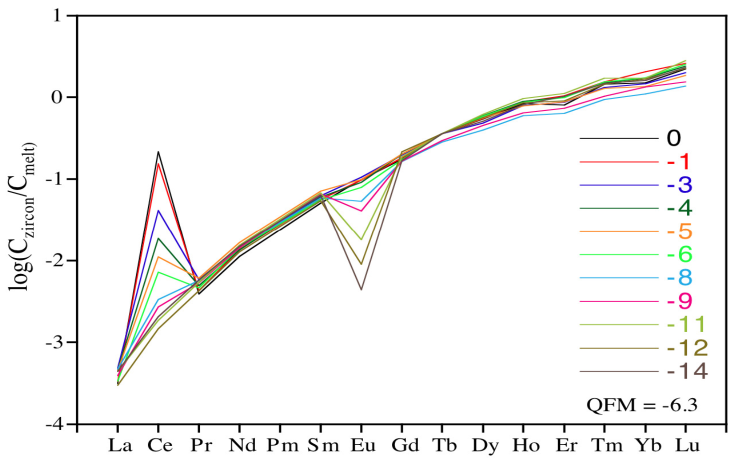

Figure 2: Average REE zircon-melt partition coefficients as a function of oxidising conditions (scale on right of graph) of the experiment.

The resulting average zircon-melt partition coefficients for the REE are shown in Figure 2. The magnitude of the Ce and Eu anomalies varies systematically with the magnitude of the oxidising conditions of the experiment. Both anomalies coexist between within a small window of conditions, although the anomalies are less than seen in many natural samples. The coexistence indicates that there is a window in natural systems where zircon will crystallise with both Ce and Eu anomalies.

However, the decreased magnitude of the anomalies compared to natural samples suggest that temperature or melt composition may have a significant effect on either the partition coefficients or the dependence of Ce^{3+}/Ce^{4+} relative to Eu^{2+}/Eu^{3+} on the oxidising conditions. Alternatively, changes in the relative abundance of the Eu and Ce relative to the other REE due to partitioning into earlier crystallising phases may be important in natural systems.

The zircon-melt partitioning of U and Th was also determined and D_U/D_{Th} was found to decrease smoothly with increasing oxidising conditions. Th occurs exclusively as Th^{4+} whereas U can occur as U^{4+}, U^{5+}, and U^{6+}. The range over which D_U/D_{Th} changes suggests that all three oxidation states of U occur in silicate melts under geological conditions.