



	Experiment title: The origin of Eu and Ce anomalies in the rare-earth element patterns of igneous melts	Experiment number: EC-657
Beamline: BM29	Date of experiment: from: 01/04/2010 to: 05/04/2010	Date of report: 28/02/2011
Shifts: 12	Local contact(s): Matthieu Chorro	<i>Received at ESRF:</i>
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Report:

The relative abundance of the Rare Earth Elements (REE) are often used in the earth sciences to provide insight into geological processes. Relative to the smoothly varying (normalised) concentrations of the other REE, anomalous abundances of Ce (enriched) or Eu (depleted) are a feature of many minerals and rocks. These anomalies are almost certainly related to the fact that Eu and Ce exhibit oxidation state variability ($\text{Eu}^{2+}/\text{Eu}^{3+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$), unlike the other REE. To interpret the significance of these anomalies it is necessary to understand how $\text{Eu}^{2+}/\Sigma\text{Eu}$ and $\text{Ce}^{3+}/\Sigma\text{Ce}$ vary in silicate melts as a function of the redox conditions (or oxygen fugacity, $f\text{O}_2$). The calibration of the magnitude of Eu and Ce anomalies with $f\text{O}_2$ would provide a new geochemical tool.

The samples were homogeneous Ca-Mg-Al-Si±Fe oxide glasses containing 0.5 wt% of Eu or Ce that are synthetic analogues of natural melts. The glasses were quenched from melts equilibrated at different values of $f\text{O}_2$ to produce samples in which $\text{Eu}^{2+}/\Sigma\text{Eu}$ and $\text{Ce}^{3+}/\Sigma\text{Ce}$ are expected to systematically vary. The glasses are typically 5 mm in size and were presented as polished surfaces in epoxy resin.

Eu and Ce L_3 edge XANES spectra were recorded in fluorescence mode at room temperature. The relative signal to noise of spectra recorded using a single element Si-drift and a ten-element Ge detector were compared and the Ge detector was found to be better for these samples. Approximately 90 Eu and 75 Ce spectra were obtained. The spectra were compared after subtracting a constant offset and normalising to the fluorescence intensity above the edge. For both the Eu and Ce samples the spectra exhibit systematic differences with the $f\text{O}_2$ of equilibration corresponding to changes in the average oxidation state (see Figure). The spectra were parameterised using features such as the intensity of the Eu^{2+} peak (6.97 keV), the intensity of the Eu^{3+} peak (6.98 keV), the peak ratio, and the edge energy. The oxidation state and hence a spectral feature should vary with $f\text{O}_2$ according to a thermodynamically predicted function. The fit of our

parameterised spectral data to this function is good but not entirely convincing and we are currently correlating the XANES data with results obtained using other methods.

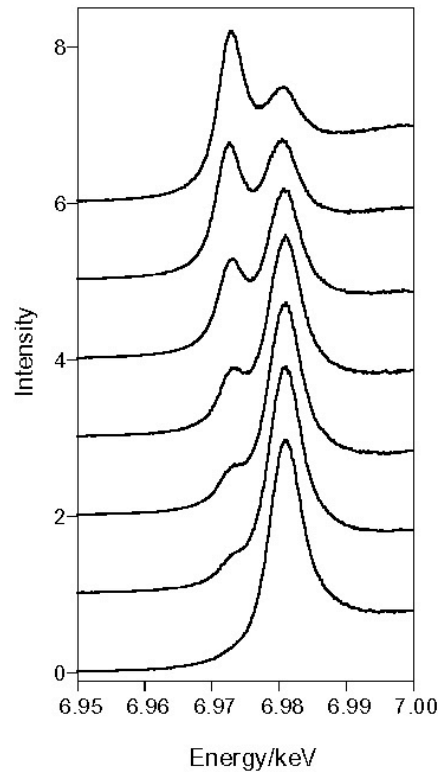


Figure: Eu L₃ edge XANES spectra of synthetic glasses equilibrated as a function of oxygen fugacity (decreasing from bottom to top) showing systematic changes in the oxidation state.

In related work we have experimentally grown the mineral zircon (ZrSiO₄) from melts similar to those used in the XANES experiments as a function of fO_2 . Zircon incorporates trace amounts of all the trivalent REE but preferentially includes Ce⁴⁺ and excludes Eu²⁺. The relative abundance of the REE in zircon and melt will hence depend on the oxidation state and fO_2 . In November 2010 we determined these abundances using an ion probe and will obtain more data using laser ablation ICPMS in March 2011. The results show systematic changes in the magnitude of the Eu and Ce anomalies with fO_2 . We are currently integrating the XANES and ion probe results in an attempt to properly understand the geochemical behaviour of Eu and Ce.

This work forms part of the PhD project of Antony Burnham who is due to submit his thesis in March 2012. Publications arising from this beamtime are to be expected around this time.