

**Experiment title:****Effects of the oxygen fugacity on the geochemical behaviour of europium (Eu) and cerium (Ce) in silicate glasses.****Experiment****number:**

HD-318

Beamline:

BM08

Date of experiment:

from: 06 February to: 10 February 2009

Date of report:

-02-09

Shifts:

12

Local contact(s):

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In spite of the low concentrations present in natural rocks, trace elements play an important role in studying the genesis of a magma. All the processes that occur during the uprising of the magma from the source region to the external surface of the Earth (like fractional crystallisation, magma mixing and crustal contamination) are responsible for the generation of the wide variety of rare earth abundance patterns in terrestrial igneous rocks. Accurate knowledge of Eu and Ce structural role in silicate glasses/melts is of key importance in Earth sciences for a better understanding of the Eu and Ce geochemical behaviour during the crystallisation of magma. However, despite Eu importance as a petrogenetic indicator, still no studies have been published on its structural role in silicate glasses.

XAS spectra at the Eu L₃-edge have been successfully collected for a group of silicate glasses representing different melt compositions, spanning from granitic to basaltic and synthesised at different oxygen fugacities: from very low redox conditions (Iron-Wüstite, IW buffer) to higher redox conditions (Fayalite-Magnetite-Quartz, FMQ buffer) up to oxidising conditions (air) and analysed in order to investigate the effect of reducing conditions on Eu oxidation state.

Collection of up to 5 scans per sample and the use of high purity Ge detector, allowed to obtain spectra with a very good signal to noise ratio even for the most diluted europium bearing glasses (0.1% wt. Eu₂O₃). We used a micro-beam in order to analyse the samples smaller than 1 mm, but this procedure implied very long measuring time and then the impossibility to change the machine set-up in time to be able also to analyse the cerium-bearing glasses.

Europium bearing glasses

Detectable changes in the XANES spectra were observed in the studied glasses, synthesised in air, as a function of bulk composition (report 37785_A, experiment EC-242). Absorption peaks located at ca. 6975 eV and ca. 6983 eV are attributed to the presence of Eu⁺² and Eu⁺³, evidenced by 7.5-8 eV difference in the energy (Rakovan *et al.*, 2001; Takahashi *et al.*, 2005). Significant changes in the intensity of these peaks can be observed when passing from basaltic to granitic glass compositions (DiAn and HPG8-Na respectively): these changes were interpreted as variations in the Eu²⁺/(Eu²⁺ + Eu³⁺) ratios (fig.1).

Now, interesting considerations can be carried out observing the spectra of the samples synthesized at low and very low redox conditions: FMQ buffer (Fayalite-Magnetite-Quartz) and IW buffer (Iron-Wüstite); the amount of Eu⁺² increases visibly respect to Eu⁺³ in all the glasses, as expected (fig. 2) but the equilibrium kinetics for granitic and basaltic compositions is very different (fig. 3 and 4). The granitic composition reaches the equilibrium after 60 hours, whereas the basaltic composition after only 6 hours.

Interesting is the presence of divalent Eu still found in the samples synthesised in air, despite all the previous works (Schreiber 1986, Carmichael & Ghiorso, 2000; Shearer *et al.*, 2006), identify the limit Eu⁺²/Eu⁺³ near the IW buffer.

Moreover, we collected spectra for basaltic composition doped with different amount of Eu oxide and Fe oxide, in order to understand the interactions between the two elements.

The data suggests that at both oxidising and reducing condition in the basaltic composition, the amount of divalent europium decrease if Fe is present, following a redox reaction described by *Schreiber et al. (1982)* for the iron metal production. Fig. 5 shows XANES spectra for simple basaltic composition, doped with 1.0% Eu_2O_3 e with different amounts of Fe_2O_3 (from 0 to 5%) synthetised in air (fig. 5A) and at very low oxygen fugacity (fig. 5B). We can observe as the amount of divalent Eu decreases with the increase in Iron oxide.

During this run we collected successfully data for most of the Eu-bearing samples. However, to lower beam intensity, compared to an undulator beam line (ID 26) and due to the long acquisition time needed, we couldn't analyse all the samples we planed to measure.

The theoretical analysis of the experimental data so far acquired will allow to publish data on the kinetics of Eu reduction and on the interaction between Eu and Fe.

However, in order to complete the project on the europium oxidation state and structural role, we need to perform other experiments. We plan to submit a continuation proposal, to collect the remain Eu-bearing glasses and all the Ce-bearing samples.

FIGURES

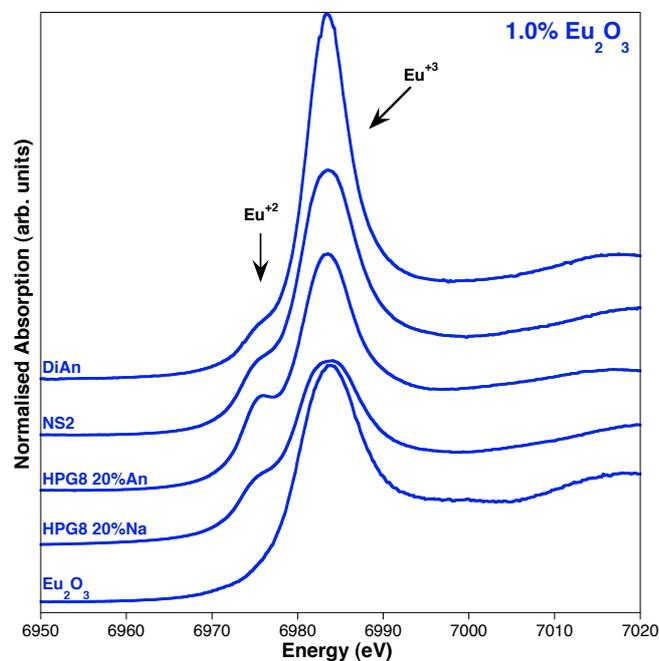


Fig.1 – Experimental spectra (XANES region) for silicate glasses of different compositions, synthetised in air and doped with 1.0% wt. Eu_2O_3 and the model compound Eu_2O_3 . Arrows indicate the different absorption peak attributed to the presence of Eu^{+2} and Eu^{+3} , respectively. Significant changes in the intensity of these peaks can be observed when passing from basaltic to granitic glass compositions (DiAn and HPG8-Na respectively)

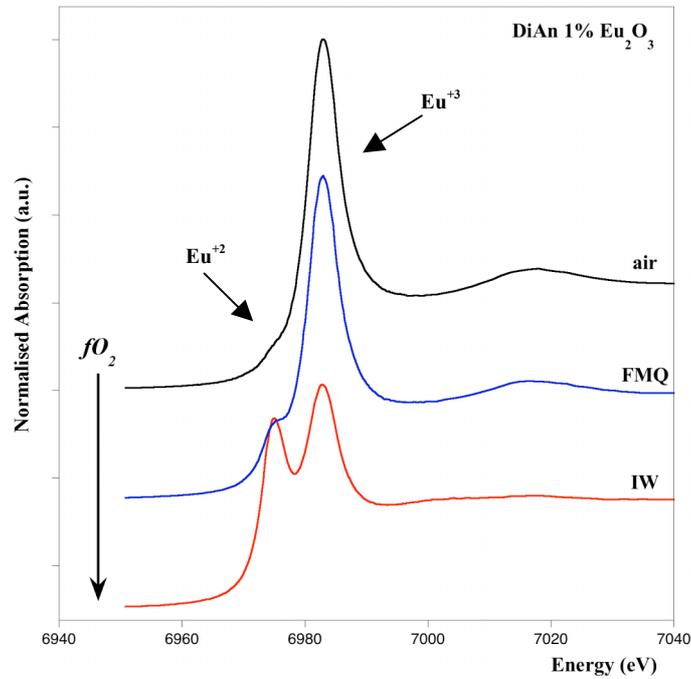


Fig.2 – Comparison between experimental spectra (XANES region) for silicate glasses of diopside-anortite composition (DiAn), doped with 1.0% wt. Eu_2O_3 and synthesised in air, at low oxygen fugacity – Fayalite-Magnetite-Quartz buffer (FMQ) and at very low oxygen fugacity - Iron-Wüstite buffer (IW). We can observe the change in the $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio for different redox conditions.

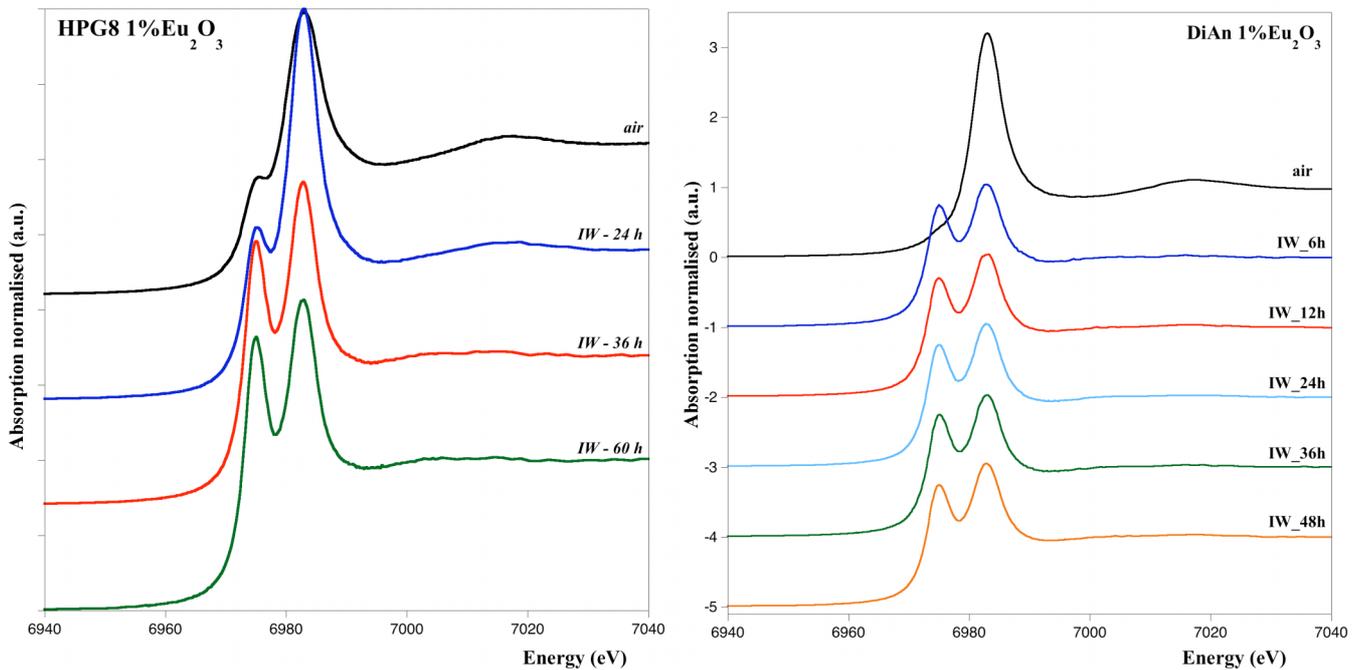


Fig.3 and 4 - Experimental spectra (XANES region) for silicate glasses of granitic composition (left) and basaltic composition (right), synthesised in air and at very low fO_2 (IW buffer) and doped with 1.0% wt. Eu_2O_3 . We can observe the different kinetics of the glasses. The granitic composition reaches the equilibrium after 60 hours, whereas the basaltic composition after only 6 hours.

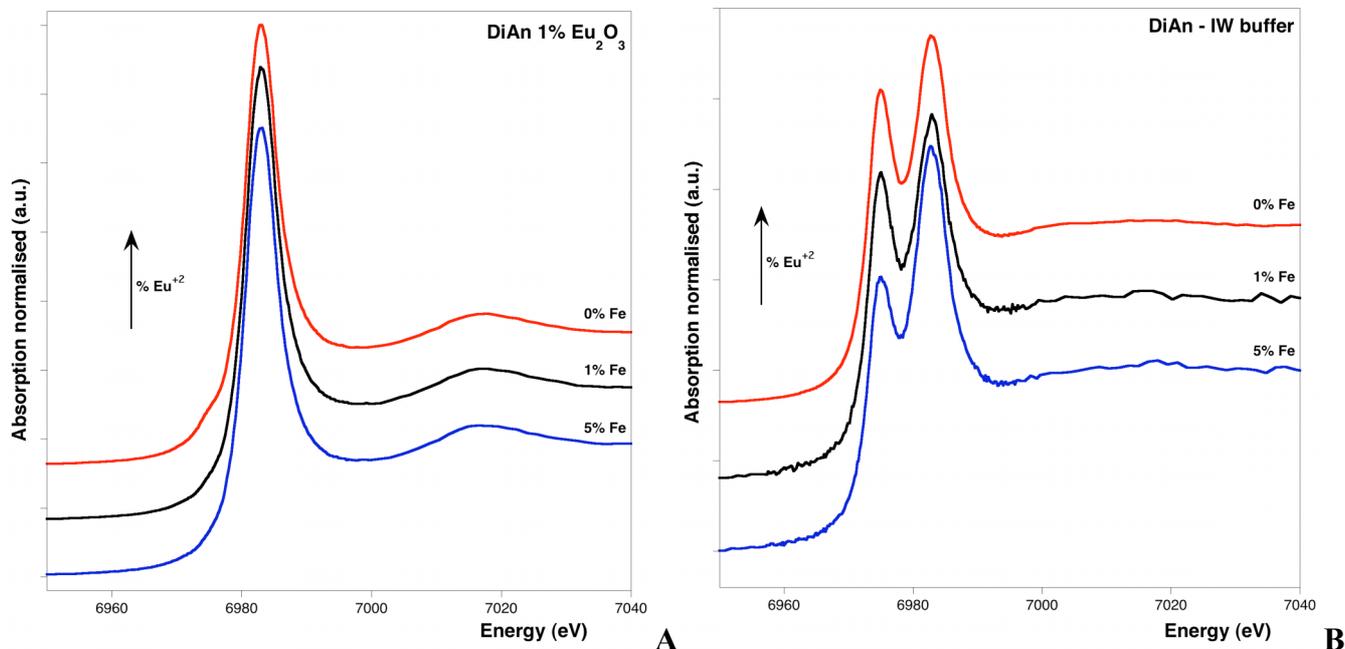


Fig.5 – Experimental spectra (XANES region) for silicate glasses of basaltic composition, doped with 1.0% wt. Eu_2O_3 and with different amounts of Fe_2O_3 , synthesised in air, on the left (5A), and at very low fO_2 , corresponding to the IW buffer, on the right (5B). We can observe as the amount of divalent Europium decreases with the increase in Iron oxide both for oxidizing and reducing conditions.

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