



**Experiment title:**  
**Geochemical behaviour of europium (Eu) and cerium (Ce) in silicate glasses.**

**Experiment number:**  
EC 242

**Beamline:**  
ID 26

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12

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### **Report:**

XAS spectra at the Eu and Ce L3-edge have been successfully collected for a group of silicate glasses representing different melt compositions, spanning from granitic to basaltic. Also, two glass samples doped with 1.0% wt.  $\text{Eu}_2\text{O}_3$ , were synthesized at very low redox conditions (Iron-Wüstite buffer) and analysed in order to investigate the effect of reducing conditions on Eu oxidation state.

The use of up to 30 scans per sample and the 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. Eu or Ce).

Eu bearing glasses

Detectable changes in the XANES spectra are observed in the studied glasses as a function of bulk composition (fig.1). Absorption peak located at ca. 6975 eV and ca. 6983 eV are attributed to the presence of  $\text{Eu}^{+2}$  and  $\text{Eu}^{+3}$ . Numerous other studies (*Baba et al. 1995; Tanaka et al. 1995; Antonio and Soderholm 1996; Rakovan et al. 2001*) have shown these peak positions to be due to  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ , with a separation of approximately 8 eV.

Significant change in the intensity of these peaks can be observed when passing from basaltic to granitic glass compositions (DiAn and HPG8-Na respectively). Moreover, even within samples of granitic compositions, the introduction of Ca produces small but still detectable changes as compared to Ca-free samples (HPG8-An and HPG8-Na respectively). These changes can be interpreted as variations in the  $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$  ratios which appear to be related by the glass composition. Furthermore, interesting considerations can be carried out observing the spectra of two samples synthesized at very low (Iron-Wüstite buffer) oxygen fugacities (fig.2); the amount of  $\text{Eu}^{+2}$  increases visibly respect to  $\text{Eu}^{+3}$  and also a phase shift is observed in the EXAFS region, which means a change in the Eu-O distances in the first coordination shell. It is evident that the change in the  $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$  ratio is much more pronounced for basaltic compositions than for granitic compositions despite both glasses have been produced under the same redox conditions. This is a topic, which needs to be investigated in details given the strong consequences on the behaviour of Eu in melts.

## Cerium bearing glasses

Ce in the analyzed glasses, all synthesized in air, is mostly in the 3+ state, but it appears to have a minor contribution from  $\text{Ce}^{4+}$ . Also cerium XANES data show important changes in the spectra as a function of composition (fig.3). Considerable variations are observed between the different compositions (NS2 and HPG8 An, which represent disilicate and granitic compositions, respectively) both in the XANES and EXAFS spectra. The composition seems therefore to influence not only the presence of  $\text{Ce}^{+4}$ , but also the local geometry around Ce in the different glasses.

XAS data of Ce model compounds,  $\text{Ce}_2\text{O}_3$  and Ce-pyrochlore  $(\text{Na,Ca,Ce})_2(\text{Nb,Ti,Fe})_2\text{O}_6\text{F}$ , have been collected as well, in order to interpret some spectral features (presence/absence of a pre-edge peak, and variations of the white-line intensity and energy position).

Theoretical XANES calculations will be performed by the MXAN code in order to reproduce the spectral features found in the experimental data, whereas theoretical EXAFS calculations have been already performed using the GNXAS package.

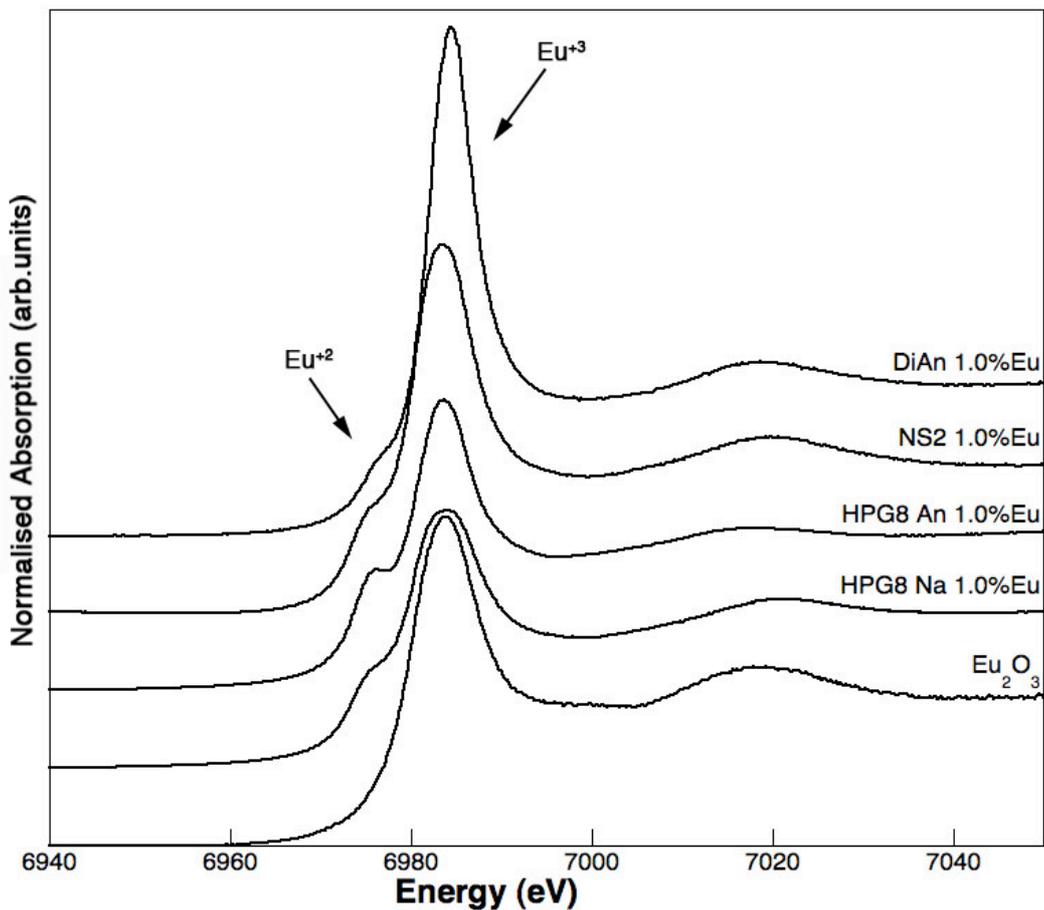


Fig.1 – Experimental spectra (XANES region) for silicate glasses of different compositions, synthesised in air, and doped with 1.0% wt.  $\text{Eu}_2\text{O}_3$  and the model compound  $\text{Eu}_2\text{O}_3$ . Arrows indicate the different absorption peak attributed to the presence of  $\text{Eu}^{+2}$  and  $\text{Eu}^{+3}$ , respectively.

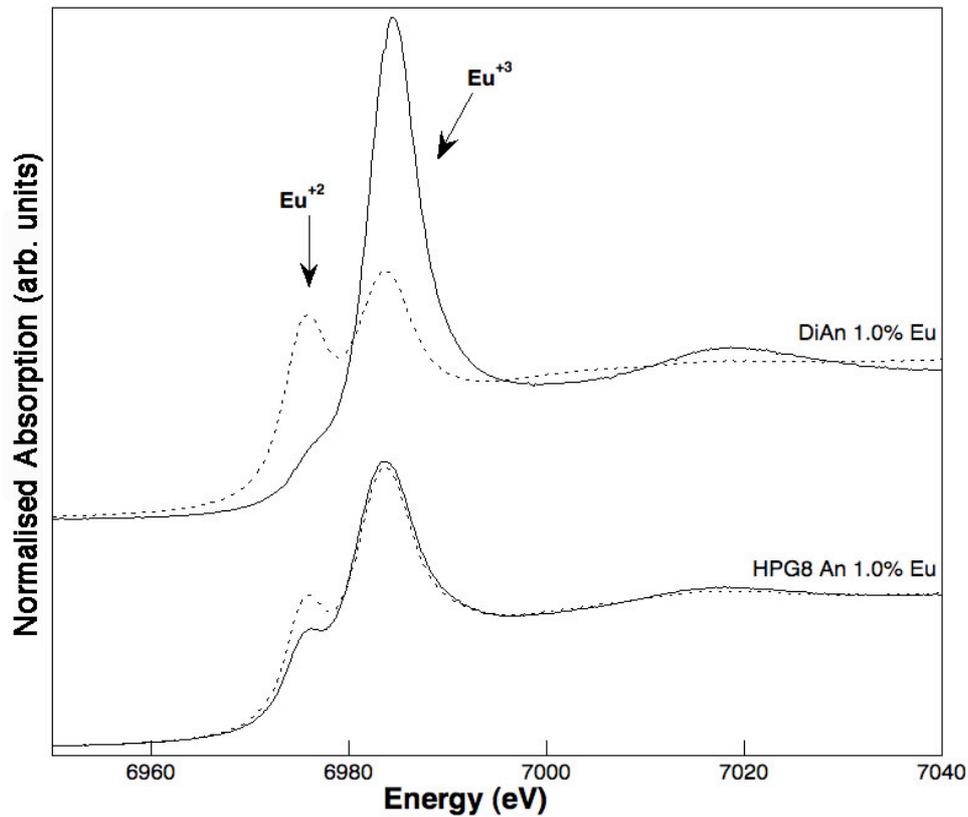


Fig.2 – Comparison between experimental spectra (XANES region) for silicate glasses of haplogranitic composition (HPG8 An) and diopside-anortite composition (DiAn), doped with 1.0% wt.  $\text{Eu}_2\text{O}_3$ , synthesised in air (solid lines) and at very low oxygen fugacity - Iron-Wüstite buffer (dotted lines).

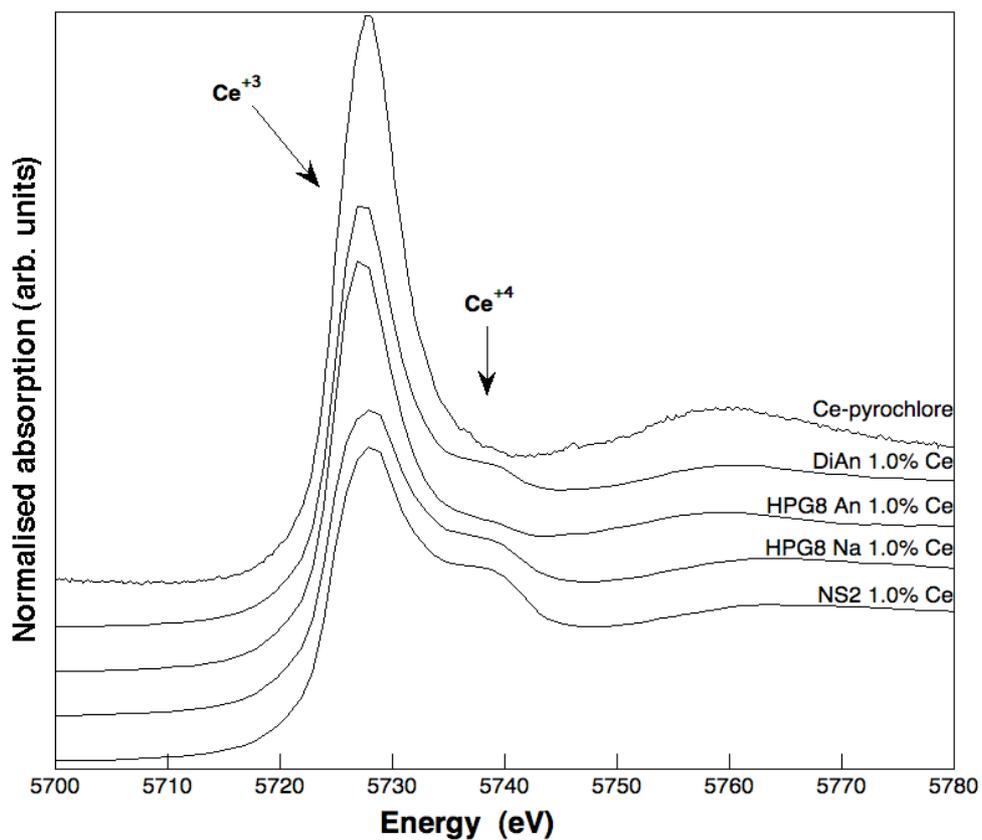


Fig.3 - Experimental spectra (XANES region) for silicate glasses of different composition, synthesised in air, and doped with 1.0% wt.  $\text{Ce}_2\text{O}_3$  and the model compound Ce-pyrochlore. Arrows indicate the different absorption peak attributed to the presence of  $\text{Ce}^{+3}$  and  $\text{Ce}^{+4}$ , respectively.

## References:

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