

EUROPIUM (Eu) IN SILICATE GLASSES: XAS STUDY OF OXIDATION STATE AND LOCAL ENVIRONMENT

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Accurate knowledge of europium (Eu) structural role in silicate glasses/melts is of key importance for a better understanding of the trace elements geochemical behaviour during magma crystallization. In spite of the interest for trace elements in magmas there are no direct measurements of their structural role in glasses/melts, and the data available in the literature are limited or based on thermodynamic calculations.

The aim of this study is to determine the structural role of Eu (oxidation state, coordination, bond distances) in silicate glasses of compositions corresponding to major magma compositions (from haplogranitic to basaltic). The synthesis of several sets of glasses has been carried out for each different composition, taking also into account the presence or absence of iron and the excess of alkalis. Variable redox environments have been considered via synthesis both in oxidizing and controlled reducing atmosphere conditions. The experiments allowed to produce a variety of glass samples that could permit to understand how the structural and geochemical role of these elements varies according to the physical and chemical conditions existing in a magma chamber.

The structural study has been performed by XAS spectroscopy. XAS is a useful technique in Earth Sciences because provides direct measurements of a selected element even at very low concentration both on crystalline and amorphous materials. XAS spectra of Eu-bearing glasses and model compounds have been collected at ESRF (European Synchrotron Radiation Facility, Grenoble, F), in order to obtain the needed structural information (oxidation state, coordination number and bond distances). The study of experimental Eu L_{III}-edge XANES and EXAFS spectra has been combined with theoretical calculations to reproduce the structural environment around Eu. XANES data allowed to distinguish between Eu²⁺ and Eu³⁺ and to estimate the Eu²⁺/(Eu²⁺ + Eu³⁺) ratio in all the glasses with an estimated error of ± 0.06. All the Eu-bearing glasses synthesized in air show the prevalent presence of trivalent Eu (peak B in Fig.1), but also, unexpectedly at these oxidizing conditions, the presence of a small amount of Eu²⁺ in the basaltic glasses and up to 20% of Eu²⁺ in the haplogranitic (HPG8 An) sample (peak A in Fig. 1). Then, we observe the presence of Eu³⁺ in all the glasses and of

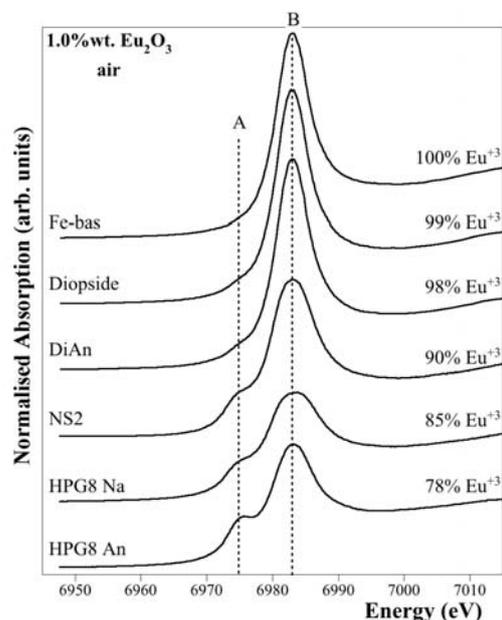


Fig. 1 - XANES spectra for all the glasses doped with 1wt.% Eu₂O₃ and synthesized in air. Peaks A and B are relative to the divalent and the trivalent europium, respectively. The estimated Eu³⁺ amount is reported for each spectrum.

Eu^{2+} increasing in going from basaltic to granitic composition and this suggests an effect played by the bulk composition of the glass on the Eu oxidation state. To understand how the composition affects Eu oxidation state we considered both the NBO/T ratio and the alkaline cations contents (as $\text{Na}+\text{K}+\text{Ca}/\Sigma\text{cations}$), however, neither alkalis content of the glasses or the calculated NBO/T ratio show a significant correlation with the $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio of the samples synthesized in air.

The glasses of different compositions have been synthesized also in reducing atmosphere (FMQ, IW, IW-2) to investigate how the redox conditions affect the $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio. The preliminary study of Eu reduction kinetics at low oxygen fugacity (IW buffer) allowed to ascertain that equilibrium in the $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio is attained within only 6 hours for a basaltic melt (DiAn) but after 60 hours for a haplogranitic melt (HPG8An). The different behaviour of these two glasses depends on the diffusivity of oxygen within these melts, which, in turn, depends on the melt viscosity (Cicconi *et al.*, 2009).

At low oxygen fugacity (FMQ and IW buffer), as expected, the XANES spectra show that there is an increase of the $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio both in the simple basaltic (DiAn) and in the haplogranitic compositions (HPG8 An) (Fig. 2a and 2b, respectively). However, at IW buffer, the amount of Eu^{2+} is not more than 55% of the total Eu (Fig. 2). An almost purely divalent europium glass (HPG8 An, $\text{Eu}^{2+} = 96\%$)

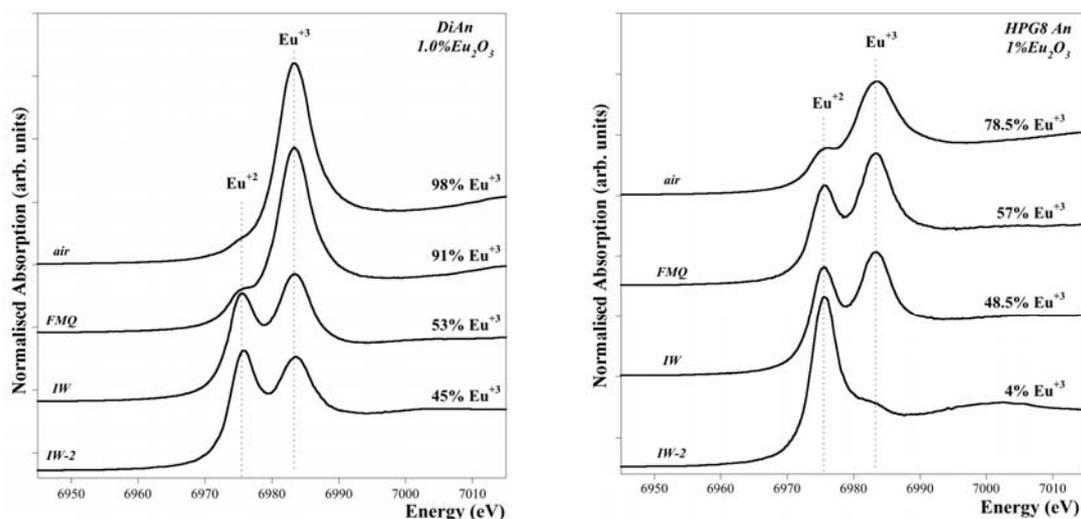


Fig. 2 - XANES spectra for the basaltic, DiAn (a) and for the haplogranitic glasses, HPG8 An (b) doped with 1 wt.% Eu_2O_3 and synthesized at different oxygen fugacity conditions (from air to IW-2). The estimated Eu^{3+} amount is reported for each spectrum.

was obtained only at more reducing conditions (IW-2) (Fig. 3). However, at these conditions (IW-2) syntheses were carried out using H_2/CO_2 as gas mixtures, which required a longer time for quenching and the slower quenching rate possibly produced a partial oxidation during vitrification. In fact, glasses produced at IW-2 conditions display a much larger spread of the $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio compared to the samples synthesized at IW buffer (Fig. 3). In order to understand how the composition affects Eu oxidation state we considered again both the NBO/T ratio and the alkaline cations contents (as $\text{Na}+\text{K}+\text{Ca}/\Sigma\text{cations}$). There is a strong correlation between Eu^{2+} and NBO/T and also a correlation with the alkalis content, suggesting also a possible correlation with melt viscosity. This implies that, at IW-2,

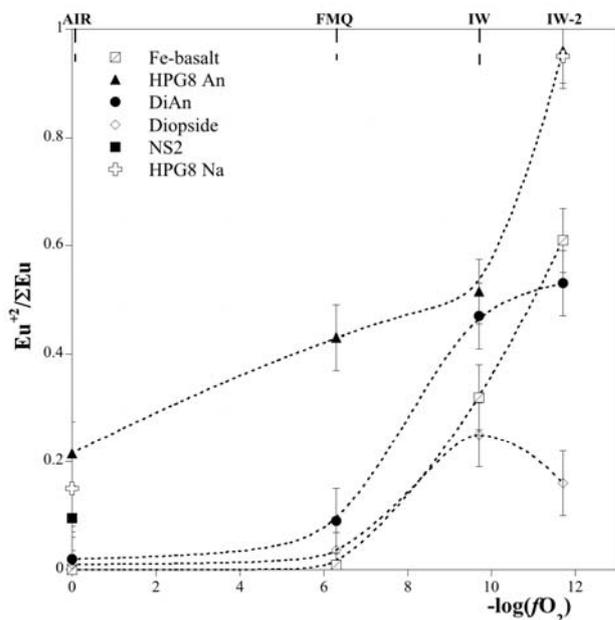


Fig. 3 - $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+})$ ratio vs. $-\log(f\text{O}_2)$ for glasses synthesized at different oxygen fugacity conditions (error bar = 0.06).

partial oxidation occurred during quenching in the basaltic glasses, whereas the haplogranitic composition was the least affected by oxidation thanks to its higher viscosity.

To verify the possible influence of other multivalent elements, like Fe, on Eu oxidation state, a set of glasses of basaltic composition (DiAnFe), doped with different amounts of Eu_2O_3 and Fe_2O_3 , was synthesized in a range of $f\text{O}_2$ values from air to IW-2. The XANES spectra of the glasses made in air show that the oxidation-reduction between Eu^{2+} and Fe^{3+} occurs both in a simple basaltic composition (DiAnFe), and in a Fe-Ti-rich basaltic composition (Fe-basalt). Moreover, in basaltic samples, made at IW buffer, the formation of metallic iron by direct reduction of Fe^{2+} by Eu^{2+} occurs.

The structural analyses have been carried out by EXAFS (Extended X-ray Absorption Fine Structure). A preliminar theoretical spectrum has been calculated from a model structure built according the few literature data available on crystalline compounds. The model has been iteratively modified both for bond distances and coordination numbers by a fitting procedure between the experimental and theoretical spectra. The use of a larger cluster, composed of not only by the first coordination shell (Eu plus oxygens) but also adding second and third contributions, allowed to build a satisfying representation of the glass structure around Eu, which has been used for the EXAFS refinement (Fig. 4).

EXAFS analyses confirm the different behaviour of Eu observed at variable $f\text{O}_2$ conditions. In air, Eu^{3+} , both for basaltic and haplogranitic composition, is bonded to six oxygens in a quite regular octahedron ($\text{CN} = [6 \pm 0.5]$) with distances $\langle \text{Eu}-\text{O} \rangle = 2.30 \pm 0.02 \text{ \AA}$. On the contrary, Eu^{2+} in the most reduced sample (HPG8An, $\text{Eu}^{2+}/(\text{Eu}^{2+} + \text{Eu}^{3+}) = 0.96$) has a higher coordination number and much longer $\langle \text{Eu}-\text{O} \rangle$ distances. The refined structure show a distorted polyhedron $[9 \pm 1]$ with an average distance $\langle \text{Eu}-\text{O} \rangle = 2.68 \pm 0.02 \text{ \AA}$. Then, EXAFS studies verify the different geometry of Eu for different oxygen fugacity conditions and also allowed to obtain the Eu-O distances both for the trivalent and divalent species. The data refined are coherent with those from literature; in fact the divalent europium is bonded to oxygens with longer distances respect to the trivalent Eu and also the number of first neighbors increase for the reduced species. From the data obtained in this study, is possible to found direct

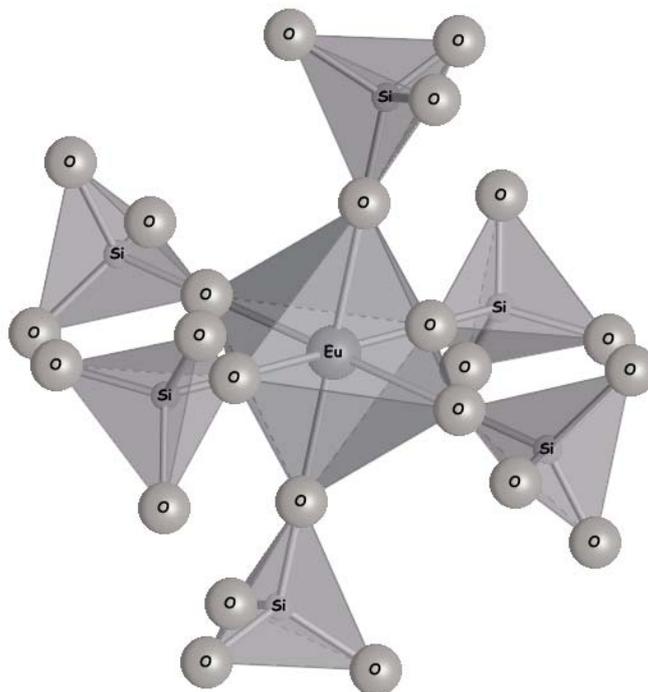


Fig. 4 - The 31-atoms refined model structure used to calculate all the contributions to the EXAFS signal arising from first, second and third coordination shells around Eu.

evidences to explain the anomalous Eu concentration in minerals and rocks. The local geometry around Eu^{2+} confirms the preference of Eu^{2+} to enter in the large site of plagioclase instead on the smaller one of pyroxene, which is enriched on the Eu^{3+} .

This work which presents the first structural data on Eu in silicate glasses, has demonstrated that for a better interpretation of the Eu anomalies observed in rocks and minerals, often used to constrain magmatic evolutions of igneous regions, the melt composition, the presence of Fe or other multivalent elements, and the redox conditions must be taken into consideration.

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