Europium structural role in silicate glasses: reduction kinetics at low oxygen fugacity.

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Abstract. This study is focused on the determination of the geochemical behaviour of europium (Eu) in a set of synthetic silicate glasses with composition relevant for the Earth Science and ranging from basaltic to granitic composition. The samples have been characterized through Eu LIII-edge by X-ray Absorption Spectroscopy (XAS) and the measurements have been performed in fluorescence mode at the ESRF (Grenoble, F). Eu LIII-edge XANES analysis allowed to obtain a semi-quantitative assessment of the Eu²⁺/(Eu²⁺ + Eu³⁺) redox ratio. Kinetics of europium reduction at low oxygen fugacity (IW buffer) has been studied on samples equilibrated at different times. Data obtained from kinetic experiments clearly show that glasses of basaltic composition reach equilibrium values of the Eu²⁺/(Eu²⁺ + Eu³⁺) ratio after 6 h at 1400 °C, whereas glasses of granitic composition reach equilibrium after 60 h at 1400 °C. Knowledge of Eu reduction kinetics is an absolute prerequisite for any study of Eu oxidation state at low oxygen fugacity.

1. Introduction
The chemical understanding of redox equilibria in glass forming melts has important practical applications to a numbers of scientific disciplines, which include glass technology, geology and metallurgy [1]. Rare Earth doped glasses have important technological applications for the production of optical devices, laser glasses and fibre amplifiers. In addition, lanthanides or Rare Earth Elements (REEs) are of great interest in geosciences: these elements, despite present in trace amounts, play an important role as indicators of magmatic processes that control the origin and evolution of igneous rocks. The distribution of REEs in igneous rocks are frequently used to constrain the mineralogy of the source materials, the degree to which magma composition has been modified by crystal fractionation, and to identify the mineral phases removed from the magma during differentiation [2, 3]. Moreover, the variation of the Eu²⁺/(Eu³⁺ + Eu⁵⁺) ratio can be used to determine the oxygen fugacity conditions prevailing during mineral formation. As the Eu²⁺/Eu⁵⁺ buffer is located at very low oxygen fugacity, the Eu²⁺/(Eu³⁺ + Eu⁵⁺) ratio can be used to constrain the formation conditions within a very large range of oxygen fugacity down to few log units below the Fe/FeO buffer. The Eu²⁺/(Eu³⁺ + Eu⁵⁺) ratio is therefore very useful in the study of meteoritic material [4] and, more generally, in studying planetary evolution.
Accurate knowledge of Eu structural role in silicate glasses/melts in a variety of melt compositions and \( f_0 \) conditions is of key importance for a better understanding of the parameters affecting its behaviour in nature as well as to rationalise its geochemical role during the crystallization from a magma.

Europium can play a variety of structural roles involving different oxidation states and coordination geometries in silicate melts. X-ray Absorption Spectroscopy (XAS) is an element selective technique allowing to get detailed information about oxidation state and bonding environment of an element even in highly diluted systems. It is therefore ideal to study REE in silicate glasses with composition chosen to represent terrestrial magmas.

As a preliminary step in the study of Eu behaviour at very low oxygen fugacity, we performed a series of experiments to investigate the kinetics of Eu reduction in silicate melts. This work is part of a larger project aimed at studying the Eu structural role and oxidation state in a set of glasses representative of silicate magmas from granitic to basaltic composition as a function of composition, temperature and oxygen fugacity.

2. Experimental Methods

Glasses with different composition, spanning from granitic to basaltic, were synthesised at high temperature and atmospheric pressure in a muffle furnace. The syntheses were carried out in two different steps. A blank oxide mixture was first mixed in stoichiometric proportions and melted in order to obtain a glass. The resulting glass was then finely ground and doped with different amount of \( \text{Eu}_2\text{O}_3 \) (from 0.1% to 5%wt. \( \text{Eu}_2\text{O}_3 \), Alfa Aesar 99.9%). This mixture was melted at high temperature in a platinum crucible and the produced melt cooled quickly in air. Other samples were synthesised in a gas-mixing furnace, at low and very low oxygen fugacity, corresponding, respectively to the FMQ and the IW buffer (Fayalite-Magnetite-Quartz and Iron-Wüstite, respectively). Usually, the IW indicates a highly reducing environment.

In order to know how much time is required to equilibrate a melt at low oxygen fugacity, a set of experiments were done on the kinetics of Eu reduction: two glasses (DiAn and HPG8An20) were melted at 1400 °C at low oxygen fugacity (IW buffer), and then left at the same conditions for several days. Splits of these melts were sampled at different times (from 6 to 72 hours), and rapidly quenched to get a glass, to study the degree of melt reduction as a function of time.

Eu L\(_{\text{III}}\)-edge EXAFS spectra were recorded at room temperature at the ESRF on the beamlines ID26 and BM08. A fixed-exit Si\(_{311}\) double-crystal monochromator was used, providing an energy resolution of ~0.3 eV at the Eu L\(_{\text{III}}\)-edge. However, the main limitation for energy resolution is the finite core-hole width of the absorbing element (~3.91 eV at the Eu L\(_{\text{III}}\)-edge [5]), resulting in a convoluted energy resolution (FWHM) of ~ 4 eV. The energy was calibrated by referring to the first derivative peak of a metallic Fe foil at 7112 eV. XANES spectra were recorded in step-scan mode with a typical energy step of 0.20 eV and counting 10 s per point and the average of four spectra was collected. The spectra were acquired in fluorescence mode, using a Ge multielements detector; the sample was positioned at 45° with respect to the beam and the detector at 45° with respect to the sample.

3. Results and discussion

Previous XAS studies on europium model compounds showed that a significant energy-shift (ca. 7-8 eV) occurs at the Eu absorption L\(_{\text{III}}\)-edge as a function of Eu oxidation state [6, 7, 8, 9, 10, 11,12]. This shift can be used to evaluate the valence of unknown europium compounds, as the shift in energy of the absorption edge can be related to the difference in the electron density between different oxidation states. In fact, when both oxidation states are present, the white line of the XANES spectra displays two components (labelled A and B in figure 1) relative to the Eu\(^{2+}\) and Eu\(^{3+}\) contributions respectively. The relative importance of these two components permits to qualitatively follow any variation in the
The relative amounts of the two Eu oxidation states, and is therefore useful in studying the kinetics of Eu oxidation or reduction.

The spectra of the glasses produced in air (at the most oxidising conditions) are shown on the top of figure 1; they show a prominent white line (B), whose energy is consistent with the presence of Eu$^{3+}$. However, also a shoulder is present at the low energy side (A), whose energy if consistent with the presence of a small amount of Eu$^{2+}$. The higher intensity of this shoulder (A) in the HPG8An20 spectrum can be interpreted as a higher Eu$^{2+}/(\text{Eu}^{3+} + \text{Eu}^{2+})$ ratio in this sample compared to the one with basaltic composition (DiAn). In figure 1 are also reported the spectra of glasses formed from melt splits sampled at different times from a melt kept at reducing conditions in CO/CO$_2$ atmosphere, and then subject to progressive Eu reduction.

**Figure 1.** XANES spectra related to the glasses of basaltic composition (1a) and to the granitic composition (1b). The data obtained from kinetic experiments clearly show that glasses of basaltic composition reach equilibrium values of the Eu$^{2+}/(\text{Eu}^{3+} + \text{Eu}^{2+})$ ratio after 6 h at 1400 °C, whereas glasses of granitic composition reach equilibrium after more than 48 h at the same temperature. A and B peaks have been assigned to Eu$^{2+}$ and Eu$^{3+}$, respectively.

As expected, the melt is subjected to a progressive reduction, resulting in an increasingly higher importance of the A peak in the white line which, in turn, corresponds to a higher contribution from Eu$^{2+}$ in the melt/glass. It can be clearly noted that the increase of the peak A intensity reaches a steady state very rapidly in the DiAn glass (6 hours), whereas it requires more than 48 hours for HPG8An20 (figure 2).

The different rate, at which equilibrium is reached in the melt, is consistent with the dissimilar interrelationship between the dissolved multivalent species and the gaseous redox components for the two compositions. The unlike behaviour of these two glasses depends on the diffusivity of oxygen within these melts, which, in turn, depends on the melt viscosity. The different values of melt viscosities at 1400 °C (~ 0.62 Pa*s for DiAn [13] and ~ 4 Pa*s for HPG8An20, [14]) can explain the very different Eu reduction kinetics at the studied conditions.

Despite some small change of the Eu oxidation state may occur during quenching of the melt, nevertheless these data are representative of the kinetics of Eu reduction in the melt. Both equilibrium and kinetic redox processes are essential to the development of desired glass/melt properties. Such processes have always played a key role in the production of glass, in particular in the manufacture of colored/decolored glass and in the synthesis of homogeneous bubble-free glass [1]. Knowledge of Eu reduction kinetics is an absolute prerequisite for any study of Eu oxidation state at low oxygen fugacity.
Figure 2. Intensity ratio of peaks A and B vs. equilibration time. The solid line indicates the basaltic composition, whereas, the dotted one indicates the granitic composition. The basaltic composition reaches steady values of A/B peak intensity (and, thus of the Eu$^{2+}$/(Eu$^{2+}$+Eu$^{3+}$) ratio) in a few hours, whereas the granitic one needs more than 2 days.

4. References

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