Structural behaviour of europium in silicate glasses

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Rare Earth Elements (REE) have demonstrated to be important geochemical indicators; in fact, the distribution of REE 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. Moreover, the variation of the Eu redox ratio can be used as oxygen fugacity indicators. As the Eu^{+2}/Eu^{+3} buffer is located at very low oxygen fugacity, the $Eu^{+2}/(Eu^{+2} + Eu^{+3})$ 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 $Eu^{+2}/(Eu^{+2} + Eu^{+3})$ ratio is therefore very useful in the study of meteoritic material and in studying planetary evolution and many authors had used the Eu partition coefficient vs. fO_2 to extrapolate redox conditions under which magmas have crystallized.

To this aim, synthetic silicate glasses have been used to study the dependence of the redox states of a Rare Earth Element (Eu) on the bulk melt composition and at different values of oxygen fugacity (from air to IW-2). The silicate glasses, doped with Eu, of composition spanning from basaltic to granitic, have been synthesized at high temperature and in controlled atmosphere in a range of oxygen fugacity values. The experiments allowed to produce a variety of glass samples used to investigate the structural and geochemical role of this element as a function of the physical and chemical conditions existing in a magma chamber (T, fO_2, viscosity).

The samples have been analyzed via Eu L_{III}-edge X-ray Absorption Spectroscopy (XAS) to obtain the Eu oxidation state and local geometry. Eu L_{III}-edge XANES peak analysis allowed also a quantitative assessment of Eu redox ratio and thus to determine, in all the glasses, the Eu oxidation state. XANES spectra vary systematically with composition and with fO_2 (log $fO_2 \sim 0$ to -11.6) indicating changes in the Eu oxidation state. The intensity of the shoulders on the absorption edges were quantified and used to determine $Eu^{+2}/(Eu^{+2} + Eu^{+3})$ ratio. Moreover, the local environment of Eu was determined by EXAFS (Extended X-ray Absorption Fine Structure). In fact, EXAFS data analyses allowed to determine the average Eu-O bond distances and coordinations around divalent or trivalent Eu in the studied glasses, highlighting the different Eu behaviour as function of the fO_2.

This work has clearly demonstrated that, besides oxygen fugacity, also melt composition plays a strong role in affecting Eu oxidation state and, for the first time, experimentally-derived structural data of Eu^{+2} in silicate glasses of geological interest are presented. Furthermore, this study has demonstrated that for a better interpretation of the Eu anomalies observed in rocks and minerals, which are often used to constrain magmatic evolutions of igneous regions, it is a determinant to assess the effect of bulk compositions since has been demonstrated the strong influence of this parameter on Eu oxidation state.