Europium oxidation state and local structure in silicate glasses

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ABSTRACT

Europium L\textsubscript{m}-edge XAS spectra were recorded for silicate glasses of different compositions, quenched from melts equilibrated at different oxygen fugacity (f\textsubscript{O\textsubscript{2}}). The Eu XANES spectra vary systematically with glass composition and with f\textsubscript{O\textsubscript{2}} (–log f\textsubscript{O\textsubscript{2}} ≈ 0 to –11.9) indicating changes in the Eu oxidation state. The intensity of the main peaks on the absorption edges were quantified and used to determine the Eu\textsuperscript{II}/(Eu\textsuperscript{II}+Eu\textsuperscript{III}) ratio. All the Eu-bearing glasses synthesized in air show the prevalent presence of Eu\textsuperscript{II} but also, unexpectedly, the presence of a small amount of Eu\textsuperscript{III} in the basaltic glasses and up to 20% of Eu\textsuperscript{III} in the haplogranitic sample. Moreover, XANES analyses of the samples synthesized at reducing conditions (from FMQ to IW-2) show that europium in haplogranitic glasses is always more reduced than in basaltic glasses. No relationship has been found between Eu valence and alkali content in the studied glasses. The structural environment of Eu in the glasses was determined by EXAFS analyses, demonstrating the different Eu behavior as function of the f\textsubscript{O\textsubscript{2}}. In fact, in air, Eu\textsuperscript{II} both for basaltic and haplogranitic compositions, is bonded to six O atoms in a regular octahedron (CN = [6 ± 0.5]) with similar <Eu-O> distances of about 2.30 ± 0.02 Å. On the other hand, the almost purely divalent samples have Eu\textsuperscript{II} in a higher coordination (CN = [9±1]) and longer <Eu-O> distances (2.68 ± 0.02 Å). This work clearly demonstrates that, in addition to oxygen fugacity, melt composition also plays a strong role in affecting Eu oxidation state. Moreover, for the first time, experimentally derived structural data of Eu\textsuperscript{II} in silicate glasses of geological interest are presented.

Keywords: Europium, oxidation state, silicate glasses structure, XAS

INTRODUCTION

The distribution of rare earth elements (REE) in igneous rocks is 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 (e.g., Schnetzler and Philpotts 1970; Henderson 1984; Blundy and Wood 2003). Among the 15 elements of the REE, we chose to study europium because, in comparison to the other REE whose behavior can be well predicted by their size and valence, Eu is present (like Ce) in natural systems with different valences that affect the partition coefficient and determine the crystal-chemistry behavior. Because a significant proportion of Eu in igneous systems is present in the divalent oxidation state, rather than the trivalent state typical of other REE in igneous systems, values for partition coefficients typically differ from those of the neighboring REE. This results in concentration anomalies that vary widely from mineral to mineral. The presence of positive or negative Eu anomalies can be strongly diagnostic for the involvement of certain minerals in petrogenetic processes (McKay 1989).

Furthermore, the variation of the europium oxidation state can be used as an indicator of oxygen fugacity. As the Eu\textsuperscript{II}/Eu\textsuperscript{III} buffer is located at very low oxygen fugacity, the Eu\textsuperscript{II}/(Eu\textsuperscript{II}+Eu\textsuperscript{III}) ratio can be used to constrain the formation conditions over a very large range of oxygen fugacity down to a few log units below the FeO buffer (Shearer et al. 2006). Therefore, the determination of the Eu\textsuperscript{II}/(Eu\textsuperscript{II}+Eu\textsuperscript{III}) ratio can very useful in the study of materials formed at highly reducing conditions such as meteoritic materials and thus, in studying planetary evolution (Wadhwa 2001; Karner et al. 2010). Many authors have used Eu valence as a quantitative oxybarometer (e.g., Philpotts 1970; Schnetzler and Philpotts 1970; Drake 1975; McKay 1989 and references therein) and more recently, Wadhwa (2001) examined the behavior of Eu in martian basalts to measure the f\textsubscript{O\textsubscript{2}} values. These works, however, are not based on direct measurements of the Eu oxidation state (i.e., the actual distribution of the two Eu redox species) but rather on values of Eu\textsuperscript{II} partition coefficients assumed from the partition coefficients of strontium. This lack of direct data may well impede the understanding of the behavior of Eu in magmatic systems.

The partition coefficient (D) is a very useful tool to describe magmatic processes (e.g., O’Hara 1995; Shaw 2000; Bédard 2006). The uncertainty with respect to D is a major source of error in modeling crystal/liquid fractionation or melting (Blundy and Wood 2003 and references therein). Most Eu partition coefficient data that are currently available are empirical,

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