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Europium oxidation state and local structure in silicate glasses

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Abstract

Europium L_{III}-edge XAS spectra were recorded for silicate glasses of different compositions, quenched from melts equilibrated at different oxygen fugacity (f_{O_2}). The Eu XANES spectra vary systematically with glass composition and with f_{O_2} ($-\log f_{O_2}$ ~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 $Eu^{2+}/(Eu^{2+}+Eu^{3+})$ ratio. All the Eu-bearing glasses synthesized in air show the prevalent presence of Eu^{3+} but also, unexpectedly, the presence of a small amount of Eu^{2+} in the basaltic glasses and up to 20% of Eu^{2+} 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_{O_2}. In fact, in air, Eu^{3+} 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^{2+} 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^{2+} in silicate glasses of geological interest are presented.

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