

Eu³⁺/Eu²⁺ ratios in glass equilibrated with plagioclase by micro XANES

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Rare earth element (REE) patterns of magmatic rocks provide useful information on the conditions during formation. One prominent feature is the Europium anomaly caused by fractionation of Eu²⁺ from other trivalent REEs due to preferential incorporation in feldspar. Former studies have shown that the distribution coefficient of Eu between melts and minerals is strongly correlated with oxygen fugacity (fO_2), and thus, it can be used as an oxygen barometer for magmatic processes (e.g., [1], [2]). This variation is based on the fact that the Eu³⁺/Eu²⁺ ratio shows a clear correlation to fO_2 for melts equilibrated at superliquidus conditions (e.g., [3]) which varies with melt composition [4]. The Eu partitioning between melt and plagioclase can be modeled by fitting a linear combination of two partition coefficients for Eu³⁺ and Eu²⁺ and the equilibrium constant of the Eu redox equilibrium in the melt [2]. This model implies that the Eu³⁺/Eu²⁺ ratio of the melt in equilibrium with plagioclase at a given fO_2 can be extracted from the Eu partitioning data. However, no independent proof of the Eu³⁺/Eu²⁺ ratio in melts equilibrated with solid phases has been provided. The scope of this study is to validate if the Eu³⁺/Eu²⁺ ratio in silicate melts in equilibrium with plagioclase is correlated to fO_2 in the assumed manner. Therefore, spatially resolved X-ray absorption near edge structure (XANES) measurements at the Eu-L₃ edge were performed on a series of Eu-doped plagioclase-saturated glasses in the haplotonalitic system, for which the Eu partition coefficient between plagioclase and melt is known [2]. Experiments are performed at beamline L at HASYLAB at Deutsches Elektronen-Synchrotron Hamburg (Germany). XANES spectra are measured on polished thin sections in fluorescence mode using a double crystal monochromator (Si111) and a focused beam of ~15 μm. The Eu³⁺/Eu²⁺ ratio in the glass can be determined from the ratio of the white line maxima for Eu³⁺ and Eu²⁺. The ratio of the two white lines provides a parameter proportional to the true Eu³⁺/Eu²⁺ ratio, which we call (Eu³⁺/Eu²⁺)^{*}. The spectra were fitted using Gaussian and Pseudo-Voigt functions (white lines) and two arctangent functions (background). All spectra are dominated by Eu³⁺ and show only a small contribution by Eu²⁺. Fitting results suggest no clear trend with fO_2 for Eu²⁺ and Eu³⁺. The latter remains nearly constant in the studied fO_2 range. Thus, the resulting (Eu³⁺/Eu²⁺)^{*} ratio is almost constant with oxygen fugacity. The data indicate that one cannot simply use the Eu³⁺/Eu²⁺ ratio of these melts to get information on the redox conditions, which strongly contrasts to previous studies on superliquidus melts (e.g., [3]) and augite-bearing basaltic melts [5]. This result may imply that the relationship of Eu³⁺/Eu²⁺ to fO_2 determined above the liquidus cannot be extrapolated to subliquidus conditions if plagioclase is present. It is possible that the presence of Eu-bearing plagioclase in our experiments buffers the Eu³⁺/Eu²⁺ ratio in the coexisting melt.

Reference:

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