Partitioning of Eu between augite and a highly spiked martian basalt composition as a function of oxygen fugacity (IW-1 to QFM): Determination of Eu\(^{2+}/\text{Eu}^{3+}\) ratios by XANES. J.M. Karner\(^1\), J.J. Papike\(^2\), S.R. Sutton\(^3\), P.V. Burger\(^4\), C.K. Shearer\(^2\), L. Le\(^5\), M. Newville\(^4\), and Y. Choi\(^4\). \(^1\)Dept. of Geological Sciences, Case Western Reserve Univ., Cleveland, OH 44106, \(^2\)Inst. of Meteoritics, Univ. of New Mexico, Albuquerque, NM 87131. \(^3\)Dept. of Geophysical Sciences, Univ. of Chicago, Chicago, IL 60637, \(^4\)Consortium for Advanced Radiation Sources, Univ. of Chicago, Chicago, IL 60637, \(^5\)ESC Group, JE23, Houston, TX, 77058.

Introduction: This study explores the partitioning of Eu between augite and melt under changing \(f\text{O}_2\) conditions in a highly-spiked (total REE, V, Sc = 5.5 oxide wt.\%) martian basalt composition. The high spike levels allowed us to 1) measure the REEs in pyroxene and glass by ion and electron probe, and 2) analyze both glass and pyroxene by X-ray absorption near edge spectroscopy (XANES). We report here on Eu partitioning between augite and melt in the samples and also present XANES data on the valence state of Eu in both glass and augite. Valence specific \(D\)-values are also calculated for Eu.

Results and discussion: Eu partitioning between augite/melt. Charges at four \(f\text{O}_2\) conditions (IW-1, IW, IW+1, QFM) produced pyroxenes ± rare olivine, spinel, in a matrix of glass (see Papike et al. [1], this volume, for experimental details and pyroxene stoichiometry). The pyroxene grains zoned from Mg-rich pigeonite (Wo\(_{18}\) mol\%) to Mg-rich augite (Wo\(_{33}\)). Our goal was to evaluate Eu and REE partitioning between the augite and melt, therefore analyses were taken on the augitic rims and adjacent glass. We also took great care in analyzing augite rims with similar Wo contents (Wo\(_{33}\)) from each sample; this is vital because REE partitioning can be greatly affected by the Ca (and Al) content of the pyroxene [2].

Figure 1a shows that Eu \(D\)-values for augite/melt increase steadily with \(f\text{O}_2\) from 0.09 at IW-1 to 0.27 at QFM. Over this range of \(f\text{O}_2\) conditions, Eu exists as Eu\(^{2+}\) and Eu\(^{3+}\), and increasing \(f\text{O}_2\) results in a higher Eu\(^{2+}/\text{Eu}^{3+}\) in the melt. The Eu\(^{3+}\) cation is much smaller and consequently fits better into the pyroxene M2 site than the Eu\(^{2+}\) cation, therefore \(D_{\text{Eu}}\) increases with \(f\text{O}_2\) because there is more Eu\(^{3+}\) in the melt available to partition into the crystallizing pyroxene. Our calculated \(D\)-values for Eu augite/melt are in good agreement with published values [3].

Figure 1b shows characteristic augite REE patterns that increase in \(D\) from La to Sm, a negative Eu-anomaly, and then a flattening from ~Gd to Lu [4]. All REEs substitute for Ca in the M2 site of augite, and thus the comparatively large LREE have lower \(D\)-values than the smaller HREE. The Eu-anomaly is due to the presence of some Eu\(^{2+}\) in the melt, which again is much less compatible in the M2 site than Eu\(^{3+}\). Augite REE patterns and \(D\)-values are in general agreement with those of other workers, which suggests Henry’s Law violation was not a significant issue despite the high doping levels of the starting composition.

Determination of Eu valence states by XANES. Figure 2a shows that XANES peaks from the Eu\(^{2+}\) and Eu\(^{3+}\) standards are separated by ~8 eV and that the peak area for Eu\(^{3+}\) is smaller than that for Eu\(^{2+}\). Figure 2b plots the XANES spectra for glass in the samples and shows the large variation in peak ratios with \(f\text{O}_2\), from almost pure Eu\(^{3+}\) at QFM, to almost pure Eu\(^{2+}\) at IW-1. Peak intensities for end-member (Eu\(^{2+}\), Eu\(^{3+}\)) glass spectra correspond well to those of the standards (Fig. 2a), indicating these standards are appropriate for these samples. Figure 2c shows representative pyroxene spectra from the samples.

Figure 2d shows XANES Eu valence state data in sample pyroxene and glass. A clear correlation of increasing Eu valence with \(f\text{O}_2\) is apparent in both glass and pyroxene. For example, at IW-1 the Eu valence in the glass (black circles) is ~2.16, or in other words 84% Eu\(^{2+}\), 16% Eu\(^{3+}\). The Eu\(^{2+}/\text{Eu}^{3+}\) ratio decreases with increasing \(f\text{O}_2\) and at QFM the glass contains 6% Eu\(^{2+}\), 94% Eu\(^{3+}\). Pyroxene shows the same systematics as the co-existing glass where open circles represent the average and black bars denote the range of XANES analyses. In all samples the Eu valence is higher in the pyroxene relative to the glass, and this difference decreases steadily with increasing \(f\text{O}_2\). This observation confirms the idea that Eu\(^{3+}\) is more compatible within the pyroxene structure. Lastly, the grey circles represent XANES analyses from two samples that were quenched above the liquidus, i.e., before crystallization of any phases. The determined Eu\(^{2+}/\text{Eu}^{3+}\) in the “quench glass” is nearly identical to that of the glass that exists in the samples that crystallized pyroxene. The observation confirms that the samples were effectively buffered by a specific gas mixture at a specific \(f\text{O}_2\) throughout crystallization. A best-fit curve to our glass data predicts that Eu\(^{2+}/\text{Eu}^{3+}\) (in a melt of this composition) should be equal at ~IW-0.5, which is a close match to the calculated value of [5] for a basaltic composition.

Determination of valence specific \(D\)-values. XANES data and partitioning data allow for the calculation of \(D_{\text{Eu}^{2+}}\) and \(D_{\text{Eu}^{3+}}\). For example, ion probe data shows that at QFM the concentration of Eu in augite and glass is 1862 and 6808 ppm, respectively. XANES data show 94% of the Eu in the augite is Eu\(^{3+}\), while 93% of the Eu in the glass is Eu\(^{2+}\). Multiplying the Eu concentrations in the two
phases by the percentage of Eu$^{3+}$ in each phase, and then dividing Eu$^{3+}$ (augite)/Eu$^{3+}$ (glass) yields a $D_{\text{Eu}^{3+}}$ of 0.276. Previous experiments have shown that $D_{\text{Eu}^{3+}}$ should be analogous to $D_{\text{Sm}^{3+}}$, as the two elements have the same charge and are roughly the same size [4]. At similar Wo contents, $D_{\text{Sm}}$ augite/melt is $\approx 0.2$ [4], which is in agreement with our estimate. Using the same procedure as above our best estimate for $D_{\text{Eu}^{2+}}$ augite/melt (at IW-1) is 0.07.

Several workers have modeled the behavior of Eu$^{2+}$ as being similar to that of Sr$^{2+}$ in pyroxene [6]. Again our calculated $D$-value of 0.07 is in the range of published values for $D_{\text{Sr}}$ in pyroxene [7]. The agreement of our $D$-value estimates with those from experiments and natural systems demonstrates the usefulness of combining traditional partitioning data with direct valence determination by XANES.


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