

EU²⁺ AND REE³⁺ DIFFUSION IN ENSTATITE, DIOPSIDE, ANORTHITE, AND A SILICATE MELT: A DATABASE FOR UNDERSTANDING KINETIC FRACTIONATION OF REE IN THE LUNAR MANTLE AND CRUST. Y. Liang¹, D. J. Cherniak², Z. T. Morgan¹, and P. C. Hess¹, ¹Department of Geological Sciences, Brown University, Providence, RI, 02912, ²Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY 12180. (Yan_Liang@Brown.edu).

Introduction: The abundance and distribution of REE in various lunar samples have played a crucial role in understanding the origin and evolution of the Moon. Due to the relatively reducing environment a large fraction of Eu is in 2+ state during lunar magmatic and metamorphic processes [1]. Due to their differences in size and charge (hence differences in partition and diffusion coefficients), Eu²⁺ can be fractionated from REE³⁺ during lunar magmatic processes. The extent of fractionation depends on crystal-melt partition coefficients and REE diffusion coefficients in the crystals and the melt. REE partition coefficients for a number of minerals important to lunar magma genesis have been reported in the literature (e.g., anorthite and pyroxene [2]), whilst REE³⁺ diffusion coefficients in anorthite and diopside have recently been measured at conditions relevant to terrestrial magmatic and metamorphic processes [3-5]. In an effort to compile a set of REE diffusion data relevant to our on-going studies of magma transport and melt-rock reaction in the lunar mantle and crust, we have measured the rate of Eu²⁺ and REE³⁺ diffusion in enstatite and silicate melts. Based on published Sr²⁺, Pb²⁺, and REE³⁺ diffusion data and ionic size considerations we also estimated the Eu²⁺ diffusion coefficients in diopside and anorthite. Preliminary results from these studies are summarized below.

Silicate melt: As a first step towards an understanding of Eu²⁺ and REE³⁺ diffusion in lunar magmas we measured the diffusion coefficients of Eu²⁺, Sm³⁺, and Gd³⁺ in a CMAS melt (10%CaO-7%MgO-21%Al₂O₃-62%SiO₂) at 1420-1600°C and 1 GPa. The CMAS melt was chosen because self diffusion coefficients of Ca, Mg, and Si have been measured for the same melt composition and at the same *P* & *T* [unpublished]. Diffusion couples were formed from pre-synthesized glass cylinders in Mo capsules (to ensure reducing condition) following the procedure described in [6]. REE abundance in quenched charges was measured by electron microprobe. Figure 1 presents our measured REE and Ca, Mg, and Si diffusion data as a function of temperature. The solid lines are calculated from the expression $D = D_0 \cdot \exp(-E_a/RT)$, where the pre-exponential factor (D_0 in m²/s) and activation energy (E_a , in kJ/mol) for the elements of interests are as follows (log₁₀ D_0 , $E_a \pm 1\sigma$): Sm (-1.87, 311±28), Eu (-2.59, 277±13), Gd (-1.75, 315±25), Ca (-2.74, 264±75), Mg (-2.52, 269±78), and Si (-1.60, 349±104). Systematic variations in the diffusivities and activation energies among the elements shown in Fig. 1 are consistent with the general effects of ionic size and charge on the rate of cation diffusion in molten silicates. The fact

that the activation energy of Eu is very similar to those of Ca²⁺ and Mg²⁺ suggests that the valence of Eu is most likely 2+ in this melt. Overall we found that the diffusivities of REE³⁺ are independent of their ionic radius (to within experimental resolution) and the diffusivity of Eu²⁺ is about a factor of two larger than the diffusivities of REE³⁺ in this melt. This is consistent with the study of [7] who found a factor of 1.3 to 10 increases in Eu²⁺ diffusivity relative to REE³⁺ diffusivities between jadeite and diopside melts. Given the relatively depolymerized nature of the mare and picritic magmas, we expect the relative differences in cation diffusivity between Eu²⁺ and REE³⁺ in these melts to be similar to the CMAS melt shown in Fig. 1.

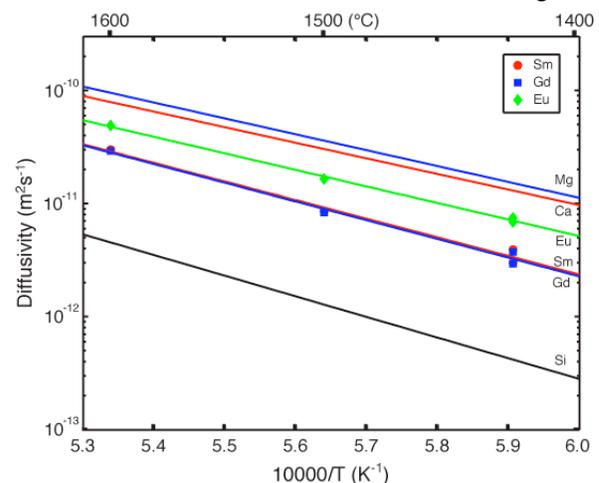


Figure 1. Tracer and self diffusion in a CMAS melt.

Enstatite: There is only one preliminary measurement of Nd diffusion in orthopyroxene reported in the literature (1.1×10^{-21} m²/s, 827°C, 1 bar, IW buffer, [8]). Given the important role of orthopyroxene (and low Ca-pyroxene) in lunar petrogenesis, we have undertaken an experimental study of REE diffusion in enstatite. The experiments were run with a source consisting of a Eu aluminate powder and MgSiO₃ powder, mixed in proportions of 1:7 (by weight). The mixture was then heated at 1100C for 1 day in air, followed by an anneal at 1100C for 1 day, buffered at IW. The prepared source was placed in a Pt capsule with a specimen of natural enstatite, and sealed under vacuum in a silica glass capsule with an IW buffer. Experiments were run in vertical 1-atm tube furnaces. Following completion of anneals, Eu profiles in enstatite were measured with Rutherford Backscattering Spectrometry. From a series of Eu diffusion runs conducted at 950-1150°C, 1 bar and IW buffer an Arrhenius relationship for Eu²⁺ diffusion in enstatite was obtained,

$$D_{\text{Eu}^{2+}} = 1.4 \times 10^{-3} \exp(-445 \text{ kJ mol}^{-1}/RT) \text{ m}^2/\text{s}$$

Figure 2 shows that our measured Eu^{2+} diffusion data overlaps the Pb diffusion data in enstatite [9]. The activation energy for Eu^{2+} diffusion in enstatite is similar to the activation energy for Sr^{2+} diffusion in a synthetic diopside (456 kJ mol^{-1} , [10]). Interestingly, the diffusivity of Eu^{2+} in enstatite is only slightly larger than the diffusivity of Sr^{2+} in diopside (Fig. 2). However, when extrapolated to 827°C , the calculated diffusivity of Eu^{2+} in enstatite ($10^{-24} \text{ m}^2/\text{s}$) is significantly smaller than the Nd data reported in [8].

Our preliminary measurement of Eu diffusion in enstatite in air (using a source of similar composition to that described above for the IW experiments, but heated in air only prior to diffusion anneals) where the valence of Eu is likely $3+$, indicates that the diffusion rate of Eu^{3+} is more than an order of magnitude slower than the rate of Eu^{2+} diffusion in enstatite at IW buffer. This is in good agreement with observed trends of Sr^{2+} and REE^{3+} diffusion in pyroxene and plagioclase (see below) as well as our CMAS data shown in Fig. 1. Since the ionic sizes of Eu^{2+} and Sr^{2+} are nearly identical we expect that the differences in cation diffusivity between Eu^{2+} and REE^{3+} in enstatite are similar to those of Sr^{2+} and REE^{3+} in diopside.

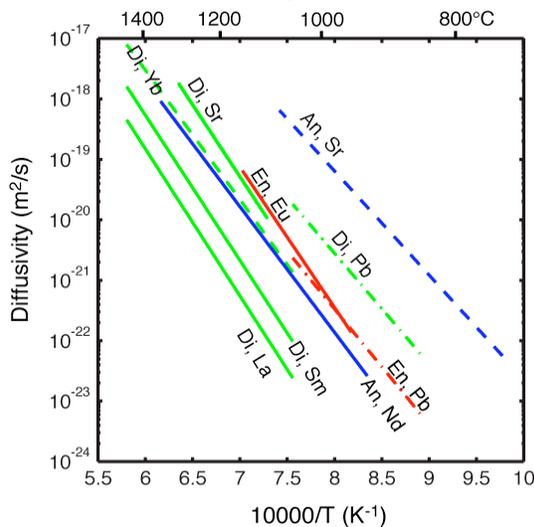


Figure 2. Diffusion of Eu^{2+} , Sr^{2+} , Pb^{2+} , and REE^{3+} in enstatite (En), diopside (Di), and anorthite (An).

Anorthite and diopside: Diffusivities of Eu^{2+} in these two minerals have not been measured. Since the ionic radius of Eu^{2+} (1.25\AA , 8-fold coordination) is very similar to the ionic radii of Sr^{2+} (1.26\AA) and Pb^{2+} (1.29\AA), we can make estimates of Eu^{2+} diffusivities in anorthite and diopside, under reducing conditions, based on the diffusivities of Sr^{2+} and Pb^{2+} in these minerals.

According to [3,13,14] diffusivities of REE^{3+} are not sensitive to their ionic size in plagioclase and diffusivities of Sr^{2+} and Pb^{2+} in an anorthite (An_{93}) are practically identical [$700\text{--}1100^\circ\text{C}$, 1 atm, QFM buffer]. Hence to a good approximation, we can use the diffu-

sivity of Sr^{2+} in anorthite as a proxy for the diffusivity of Eu^{2+} in anorthite, normal to (010) direction we have

$$D_{\text{Eu}^{2+}} = 3.85 \times 10^{-6} \exp(-330 \text{ kJ mol}^{-1}/RT) \text{ m}^2/\text{s}$$

Figure 2 shows that the diffusivity of Eu^{2+} is 2-4 orders of magnitude larger than the diffusivity of Nd^{3+} in the anorthite.

Temperature and pressure dependence of REE^{3+} diffusion in diopside were reported in [4,5]. According to these studies the diffusion rate of HREE^{3+} is about 2-10 times faster than the diffusion rate of La^{3+} (also see Fig. 2). Cherniak [14] showed that Pb diffusion rates in diopside are positively correlated with oxygen fugacity. The large difference in Sr diffusion data between natural and synthetic diopside in [10] can be explained by differences in oxygen fugacity [14]. To a crude approximation, we use the Sr diffusion in the synthetic diopside data of [10] as a proxy for Eu^{2+} in diopside, parallel to c axis, we have

$$D_{\text{Eu}^{2+}} = 2.4 \times 10^{-3} \exp(-456 \text{ kJ mol}^{-1}/RT) \text{ m}^2/\text{s}$$

Figure 2 shows that the diffusivity of Eu^{2+} is about factors of 2-100 faster than the diffusivities of REE^{3+} in diopside.

Discussions and future works: A database for cation diffusion is crucial to our understandings of the cooling history of lunar and planetary samples, as well as magma transport and melt-rock reaction processes in the lunar mantle and crust [15-17]. The large differences in diffusivities between Eu^{2+} and REE^{3+} in the minerals suggest that significant kinetic fractionation of REE can take place during high temperature processes on the Moon. For example, Morgan et al. [15] showed that Eu can be enriched in the lunar mantle relative to other REE during melt transport processes, even in the absence of plagioclase. The much smaller difference in REE diffusion in anorthite and enstatite suggests the extent of kinetic fractionation of Nd and Sm between these two minerals are likely smaller than we expected earlier [16]. Clearly additional studies are needed to further characterize REE^{3+} diffusion in enstatite and low Ca-pyroxene.

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