

REE DISTRIBUTION COEFFICIENTS FOR PIGEONITE: CONSTRAINTS ON THE ORIGIN OF THE MARE BASALT EUROPIUM ANOMALY. G. McKay (SN4, NASA-JSC, Houston, TX, 77058) J. Wagstaff, and L. Le (Lockheed ESCO, 2400 NASA Rd. 1, Houston, TX 77058)

Introduction. A long-held paradigm of lunar science is that the complementary REE patterns and Eu anomalies of the lunar crust and mare basalt source regions reflect an early differentiation event of global scale resulting from the crystallization of a lunar magma ocean (MO) [e.g. 1,2,3]. The positive Eu anomaly of the crust is generally thought to result from plagioclase enrichment, while the negative Eu anomaly in mare basalts is thought to be inherited by the source region from an evolved MO in which prior plagioclase removal had produced a negative Eu anomaly [e.g. 2].

The need for plagioclase removal has recently been reexamined [4,5]. These authors explicitly addressed the question of whether prior plagioclase removal is required to produce Eu anomalies of the magnitude observed in mare basalts, and arrived at opposite conclusions.

Part of the uncertainty in this issue is a result of inadequate mineral/melt partition coefficient data, especially for Eu at lunar oxygen fugacities. The situation is most critical for low-Ca pyroxene (a major carrier of REE among MO crystallization products throughout much of the MO crystallization sequence), but less so for olivine and high-Ca pyroxene. Olivine distribution coefficients are so low [6] that even a small proportion of pyroxene in the source region will dominate REE abundances in both cumulates and their partial melts. High-Ca pyroxene distribution coefficients have been studied by several workers [e.g. 7,8,9] under near-lunar oxygen fugacities, and indicate a significant Eu anomaly (Fig. 1).

The magnitude of the Eu anomaly for Low-Ca PX is less well constrained. OPX distribution coefficients [10] indicate only a very minor anomaly (Fig. 1). However, those results were obtained before the difficulty of measuring very low distribution coefficients on small crystals was appreciated [6], so the magnitude of the anomaly is likely to be unreliable. The goal of our current study is to provide reliable values for the partitioning of REE and Sr between low-Ca pyroxene and melt at near-lunar fO_2 , so that the origin of the mare basalt Eu anomaly can be better constrained. This abstract reports additional results obtained since our initial progress report on this topic [11].

Experiments. McKay [12] reported distribution coefficients for trivalent REE between pigeonite and a melt produced by 15-20% crystallization of a synthetic basalt resembling 12015, but did not study partitioning of Eu. For the present study, we prepared a similar starting composition containing about 1 wt% each of Gd, Eu, and Sr. Pellets (125mg) of this starting material were suspended on wire loops in a controlled atmosphere (CO/CO_2) furnace at oxygen fugacities near IW, held at 1300°C for four hours, cooled to 1200° in 2 hours, then to 1175° at 0.3°/hr, held for 24 hours, and then air quenched. This multi-stage cooling history permitted growth of large (>200 μm wide) pigeonite crystals for which even very low partition coefficients could be measured without interference from adjacent glass [6]. Resulting charges were sectioned, polished and analyzed with the JSC Cameca microprobe, with no analyzed spot being closer than 100 μm from the nearest glass, to ensure absence of analytical interference.

Results. Our goal is to combine $D(Eu)$ and $D(Sr)$ values from our current study with $D(REE)$ values from our 1981 study [12] to provide constraints on the origin of the mare basalt Eu anomaly. However, the average $D(Gd)$ value from the current series of experiments [11] is only about 60% as large as that from our 1981 study [12], making direct comparison of current average Eu values with earlier results suspect. We recently speculated [11] that the discrepancy with our 1981 values might be the result of differences in average WO content ($Ca/Ca+Fe+Mg$) between the two series of experiments, assuming that the variation of REE distribution coefficients with pyroxene WO content noted by McKay *et al.* [13] for synthetic shergottite pyroxenes is also present in the less WO-rich pyroxenes of this study. Our latest results confirm this hypothesis. Pigeonite/melt REE partition coefficients are clearly correlated with the WO content of the crystal (Fig. 1). Samples from our 1981 study (filled triangles in Fig. 1) have higher WO contents than most of the samples from our recent experiments (open circles, Fig. 1), and hence higher values for $D(Gd)$. When the correlation with WO is considered, agreement between the 1981 experiments and the current ones is much better than a simple comparison of averages would suggest.

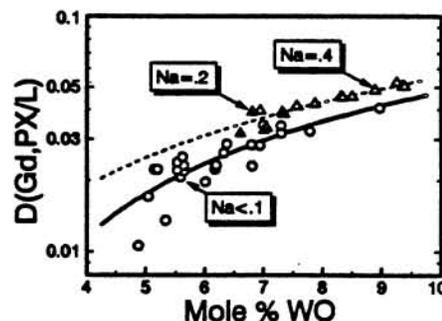


Figure 1. Variation of $D(Gd)$ with WO content of pigeonite.

Nevertheless, differences in WO do not completely explain the discrepancy. The older samples (filled triangles) still fall slightly above the correlation line for the new samples (solid line, Fig. 1). One major difference, in addition to WO content, is that the earlier samples contained ~0.2 wt% Na₂O in their melts, whereas the new samples contain <0.1 wt%. To see if the difference in Na was responsible for the older samples falling above the correlation line, we ran additional experiments with melts containing ~0.4 wt% Na₂O. The resulting D(Gd) values (open triangles in Fig 1.) clearly plot along a correlation line above that for the low-Na samples, indicating a clear influence of Na on Gd partitioning. It thus appears that discrepancy between our old and new values for D(Gd) is the combined result of differences in melt Na and pyroxene WO content, and comparison of new Eu and Sr partition coefficients with old values for the other REE will have to take these differences into account.

Figure 2 compares WO-correlated variations of D(Eu) and D(Sr) with those of D(Gd) for samples with low Na and oxygen fugacities on the IW buffer. Values for both Eu and Sr fall along correlation lines parallel to that for Gd. Thus, despite variations in partition coefficient values, D(Eu)/D(Gd) and D(Sr)/D(Gd) ratios remain constant over the range of WO contents in Fig 2. Thus comparison of results from our present and earlier study may be safely made in terms of distribution coefficient ratios.

To investigate the expected variation of D(Eu) with oxygen fugacity we performed experiments at IW, one log unit below IW, and 3.7 log units above IW, the latter corresponding to QFM. To compensate for the variation of D values due to differences in pyroxene WO content, we focus on the ratio D(Eu)/D(Gd). Observed values are shown in Fig. 3. Individual points are shown as open circles and averages for each oxygen fugacity as filled circles. There is nearly a 4-fold variation in D(Eu) from IW/10 to QFM. The curve shows the variation expected assuming that Eu²⁺/Eu³⁺ varies as fO₂^{-1/4}, D(Eu) approaches D(Sr) at very low fO₂, and 0.9*D(Gd) at high fO₂. For all reasonable lunar oxygen fugacities, D(Eu)/D(Gd) < 0.4, thus providing a significant negative Eu anomaly in the pigeonite distribution coefficient pattern.

Discussion. As discussed above, because of differences in D(Gd) between our 1981 results and those of our present study, we rely on the current experiments only to define the magnitude of the Eu and Sr anomalies in the pigeonite partition coefficient pattern. We take the absolute values for the trivalent REE from our earlier study, and use D_{Eu/Gd} and D_{Sr/Gd} ratios from the current study to compute values for D_{Eu} and D_{Sr} which are consistent with the earlier trivalent values. We assume the appropriate oxygen fugacity for lunar petrogenesis is IW. The resulting distribution coefficient pattern is shown in Figure 4, along with the OPX values of [10] for comparison. It is clear from these results that low-Ca pyroxene has a much larger capacity to develop Eu and Sr anomalies than the earlier data suggest. These results are in qualitative agreement with partition coefficients derived by [14] from ion probe analyses of Wo₁₂ pyroxenes from lunar mare basalt, but suggest an even larger Eu anomaly for pyroxenes with lower Ca content, in agreement with arguments based on crystal chemistry [5]. Whether the Eu and Sr anomalies in low-Ca pyroxene partition coefficients are large enough to explain the Eu anomaly in mare basalt without prior plagioclase crystallization awaits detailed modelling studies (in progress).

References: [1] Walker *et al.* (1975) PLSC 6th, 1103. [2] Taylor (1982) *Planetary Science: A Lunar Perspective*. [3] Wood (1975) PLSC 6th, 1087. [4] Brophy and Basu (1990) PLPSC 20th, in press. [5] Shearer and Papike (1989) GCA 53, 3331. [6] McKay (1986) GCA 50, 69. [7] Grutzeck *et al.* (1974) *Geophys. Res. Lett.* 1, 273. [8] McKay *et al.* (1988) *Meteoritics* 23, 289. [9] McKay *et al.* (1989) LPSC XX, 677. [10] Weill and McKay (1975) PLSC 6th, 1143. [11] McKay *et al.* (1989) Workshop on Lunar and Volcanic Glasses, LPI. [12] McKay (1981) EOS, Trans. AGU 62, 1070. [13] McKay *et al.* (1986) GCA 50, 927. [14] Shearer *et al.* (1989) GCA 53, 1041.

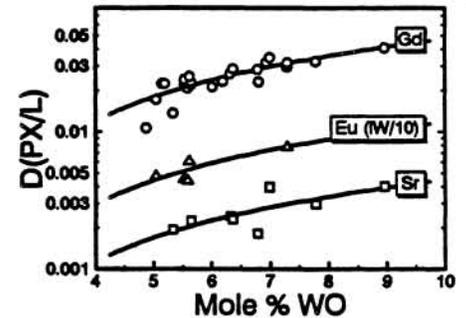


Figure 2. Variation of PX/L distribution coefficients with WO for Gd, Eu, and Sr.

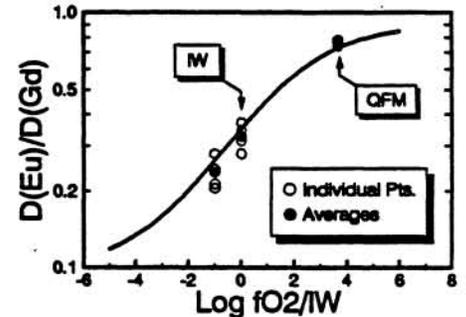


Figure 3. Variations of D(Eu)/D(Gd) with oxygen fugacity.

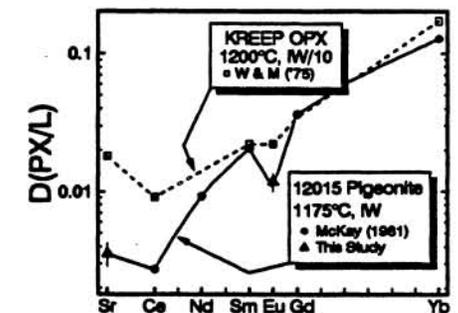


Figure 4. Distribution coefficient patterns for orthopyroxene [10] and pigeonite.