CONSTRAINTS ON THE ORIGIN OF THE MARE BASALT EUROPIUM ANOMALY: REE PARTITION COEFFICIENTS FOR PIGEONITE.

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Introduction. A much-cherished notion among lunar scientists is that the 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 (LMO) [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 LMO in which prior plagioclase removal had produced a negative Eu anomaly [e.g. 2].

The need for plagioclase removal has recently been a topic of lively debate [4,5]. Two groups explicitly considered whether prior plagioclase removal is required to produce Eu anomalies of the magnitude observed in mare basalts, and arrived at opposite conclusions, leaving the issue unsettled.

Part of the uncertainty in this issue resulted from inadequate partition coefficient data, especially for Eu at lunar oxygen fugacities. The situation was most critical for low-Ca pyroxene, a major carrier of REE among LMO crystallization products throughout much of the LMO crystallization sequence. Experimental OPX distribution coefficients [6] suggest only a very minor Eu anomaly, and are not compatible with the anomaly observed in mare basalts without prior plagioclase removal. However, the OPX results of [6] were obtained before the difficulty of measuring very low distribution coefficients on small crystals was appreciated [7], and are therefore suspect. It is conceivable that pyroxene distribution coefficients with a larger Eu anomaly might be consistent with no prior plagioclase removal. 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 (and Sr) anomaly can be better constrained.

This abstract continues our series of reports on pigeonite/melt REE partition coefficients and their implications for LMO evolution and the origin of the mare basalt Eu anomaly. Some years ago [8] we measured Ds for several trivalent REE, but did not study Eu. More recently [9,10,11], we showed that the partition coefficient pattern for pigeonite has a larger Eu anomaly than suggested by earlier data for OPX [6], but we had not yet assessed the significance of this fact for LMO evolution. In this abstract, we report additional partitioning data extending our earlier results to pyroxenes of lower Ca content. Moreover, we report modeling results that make it clear that even though the Eu anomaly in the pigeonite D_{REE} pattern is larger than formerly believed, it is still insufficient to permit formation of even the most primitive mare basalts, e.g. Apollo 15 green glass (A15 GG), by *simple* cumulate remelting without prior plagioclase crystallization or assimilation of a Eu-depleted component.

Experimental Results. Experimental procedures were described in [10]. Our most recent results are shown in Fig. 1, together with earlier results from this study [9,10], and our 1981 results for trivalent REE [8]. Our latest results confirm that the correlation of D_{Gd} with WO we reported in [10] also holds for Sm, Nd, and Yb. We have not investigated the effect of Na for Sm, Nd, and Yb, but there is no reason to expect that it would differ significantly from the effect we reported for Gd [10]. Because of these correlations, differences in WO and Na can result in significant differences in D values over the range of pyroxene compositions observed in our experiments. Hence, the correlations with WO and Na must be taken into account when computing the magnitude of Eu and Sr anomalies in the D pattern from experimental datasets.
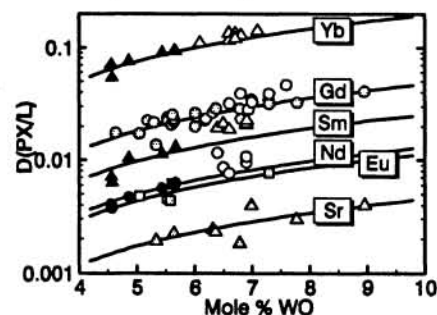

Figure 1. Variation of D with WO content of pigeonite. Shaded symbols are from [9,10]. Open symbols are Na-bearing experiments from [8]. Filled symbols are new data. Eu data are for fO_2 = IW/10.

Table 1 gives REE and Sr partition coefficients interpolated to WO_5, the average composition of liquidus pyroxenes in multiply-saturated high pressure experiments on VLT ultramafic glasses [12]. Most of our models use D_{Eu} for fO_2 = IW, but some use lower values (see below). The resulting distribution coefficient pattern is shown in Figure 2, along with the OPX values of [6] for comparison. Even at IW, 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 [13] from ion probe analyses of WO_{12} lunar mare basalt pyrox-

Table 1. Pigeonite/liquid distribution coefficients for REE and Sr. Values are interpolated to pigeonite with 5 mole % Wollastonite.							
Ce	Nd	Sm	Eu(IW)	Eu(IW/10)	Gd	Yb	Sr
.00172	.0058	.011	.0068	.0050	.021	.087	.0020

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enes, but suggest an even larger Eu anomaly for pyroxenes with lower Ca content, in agreement with crystal chemical arguments [5].

LMO Evolution and Mare Basalt Generation Models. It is clear that the new partition coefficients will permit generation of mare basalts with larger Eu and Sr anomalies than those produced using older values. Do they make *enough* of a difference to permit generation of basalts with REE patterns matching those observed, without requiring prior plagioclase removal?

We have studied this question using petrogenetic models similar to those of [4], [5], and [14] but including a trapped liquid component in the mafic cumulates. We assumed that the LMO had an initially flat REE+Sr pattern, but allowed its level to float. Mare

Figure 2. Distribution coefficient patterns for orthopyroxene [6] and WO$_5$ pigeonite.

basalt was formed by remelting an instantaneous LMO cumulate consisting of OL, PX, and trapped liquid (TL). REE and Sr abundances were computed for the evolving LMO, the instantaneous cumulate, and the mare basalt, using D_{OL} from [7] and D_{PX} from Table 2 . Abundances in the resulting basalt were compared with those in A15 GG to judge the success of the model. We used various ratios of OL/OPX crystallizing prior to cumulate formation, degrees of LMO crystallization at cumulate formation, and proportions of OL, OPX, and TL in the cumulate, and adjusted the degree of partial melting to provide an optimum match in REE and Sr abundances between the model basalt and A15 GG.

TL content is the only variable with a significant effect on the quality of match between the model basalt and A15 GG. Optimized REE+Sr patterns (normalized to A15 GG) are shown in Fig. 3 for TL contents of 0 and 3%. Shaffer *et al.* [14] found that remelting of mafic LMO cumulates could not simultaneously match Eu/Sm and Sm/Ce ratios in primitive ultramafic glasses. As shown in Fig. 3, a TL component improves the fit considerably for Ce, but makes it slightly worse for Yb and Sr. None of our simple cumulate remelting models could produce better than about 10% agreement in relative Sr and Eu abundances between model basalt and A15 GG. Although this might be considered a good fit in more complex petrogenetic models, in this case it is not, because the best model basalt reproduces only about half of the Eu anomaly observed in A15 GG.

Figure 3. GG-normalized REE+Sr patterns for model basalts. Two patterns are for models with no prior plagioclase removal, for no TL and 3% TL. One pattern is for model with prior plagioclase removal.

We tried decreasing the pyroxene D_{Eu} and D_{Sr} values, in case our experimental values are still overestimates. For TL=0, we obtained good matches (better than 10% for all elements) with Ds about 10x lower than in Table 2. However, a 10x discrepancy is unlikely, considering that we are obtaining seemingly reliable values for D_{Ce} of more than 3x lower than D_{Eu}. The discrepancy becomes worse with increasing TL, so that for TL contents of more than about 1%, required Ds become negative. In case Ds are enhanced at mantle P,T, we tried increasing Ds for all elements uniformly, but this made little difference in the quality of the matches. Increasing D_{REE+3} fivefold without changing D_{Eu} or D_{Sr} permitted good matches, although we regard such shifts with P,T as unlikely, but possible.

We also tried removing plagioclase before forming the mafic cumulate, and were able to produce a variety of models with near-perfect matches (Fig. 3). Finally, to simulate KREEP assimilation during magma ascent, we tried models which added a small amount of KREEP to the model partial melts, and were able to produce melts with matches within 5% for all elements.

Conclusion. We have been unsuccessful in matching REE and Sr in A15 GG using experimental D_{Px} values, without resorting to either prior plagioclase removal or assimilation of a Eu-depleted component. Less primitive basalts or glasses are even more difficult to match with simple models. Enhancement of D_{REE+3}, but not D_{Eu} and D_{Sr}, under increased P and T, is the only way we see to avoid prior plagioclase removal or complex petrogenesis, but we consider such differential shifts in Ds unlikely.

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, 25. [5] Shearer and Papike (1989) GCA 53, 3331. [6] Weill and McKay (1975) PLSC 6th, 1143. [7] McKay (1986) GCA 50, 69. [8] McKay (1981) EOS, Trans. AGU 62, 1070. [9] McKay *et al.* (1989) Workshop on Lunar and Volcanic Glasses, LPI Tech. Rept. 90-02, 48. [10] McKay *et al.* (1990) LPS XXI, 773. [11] McKay *et al.* (1990) LAPST-LPI Workshop on Mare Volcanism, 19. [12] Chen *et al.* (1981) PLPSC 13th, A171. [13] Shearer *et al.* (1989) GCA 53, 1041. [14] Shaffer *et al.* (1990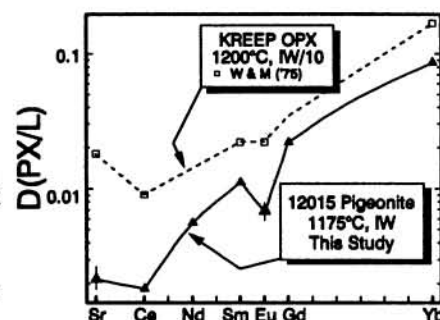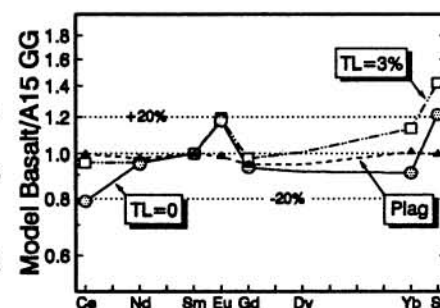) Lunar Planet. Sci. XXI, 1130.