RARE EARTH ELEMENT PARTITIONING IN LUNAR MINERALS: AN EXPERIMENTAL STUDY.

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Introduction: The partitioning behavior of rare earth elements (REE) between minerals and melts is widely used to interpret the petrogenesis and geologic context of terrestrial and extra-terrestrial samples. REE are important tools for modelling the evolution of the lunar interior. The ubiquitous negative Eu anomaly in lunar basalts is one of the main lines of evidence to support the lunar magma ocean (LMO) hypothesis, by which the plagioclase-rich lunar highlands were formed as a flotation crust during differentiation of a global-scale magma ocean [1]. The separation of plagioclase from the mafic cumulates is thought to be the source of the Eu depletion, as Eu is very compatible in plagioclase. Lunar basalts and volcanic glasses are commonly depleted in light REEs (LREE), and more enriched in heavy REEs (HREE) [1]. However, there is very little experimental data available on REE partitioning between lunar minerals and melts. In order to interpret the source of these distinctive REE patterns, and to model lunar petrogenetic processes, REE partition coefficients (D) between lunar minerals and melts are needed at conditions relevant to lunar processes. New data on D_{REE} for plagioclase [2], and pyroxenes [3,4] are now available, but there is limited available data for olivine/melt D_{REE} [5-12], particularly at pressures higher than 1 bar, and in Fe-rich and reduced compositions – all conditions relevant to the lunar mantle.

Based on terrestrial data, REE are highly incompatible in olivine (i.e. D << 1), however olivine is the predominant mineral in the lunar interior, so it is important to understand whether it is capable of storing even small amounts of REE, and how the REEs might be fractionatied, in order to understand the trace element budget of the lunar interior.

This abstract presents results from high-pressure and temperature experiments investigating REE partitioning between olivine and melt in a composition relevant to lunar magmatism.

Methods: The starting composition for this study was based on A14b, a composition used by [13] based on lunar picritic glass sample 14307. Currently no lunar samples have been identified as mantle rocks, but A14B is based on the most ultramafic green glass sample, and has therefore likely undergone the least modification from its initial primary mantle melt. The starting composition was synthesized from mechanical mixtures of anhydrous oxides and carbonates, with 200ppm of each trace element added using ICP-MS standard solutions. The mixture was then melted at 1600°C and re-ground, before conditioning at 1 log

unit below the iron-wüstite (IW-1) buffer. This additional melting step ensures complete homogenization of the trace elements, and removes all water from the composition.

Experiments from 0.5 GPa to 1.5 GPa were performed in a 13mm QuickPress piston cylinder using $BaCO_3$ as a pressure medium, graphite sample capsules and heaters. Experiments at 3.5 GPa to 4.0 GPa were performed in a multi-anvil press using graphite sample capsules and rhenium heaters. All experiments were quenched isobarically.

Experimental run products were analyzed for major and minor elements using the JEOL 8530F electron microprobe at NASA Johnson Space Center, and for trace elements, using Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) at the University of Houston using USGS glasses BHVO and BIR as standards.

Results: 16 successful experiments are discussed here, although not all had a grainsize large enough for LA-ICP-MS analysis. At 0.5 – 1.5 GPa, olivine is the liquidus phase, with orthopyroxene (opx) co-crystallizing with olivine at temperatures below 1550°C. The liquidus at 0.5 GPa is approximately 1600°C, rising to 1650 °C by 1.8 GPa. At 3.5 GPa, however, it appears to be depressed, although there is some uncertainty in the temperatures. Thermal modeling of the experimental assembly shows that the hotspot in the capsule could be more than 100°C hotter than the temperature measured by the thermocouple at the top of the capsule.

The forsterite content of experimental olivines ranged from Fo_{81} in near-liquidus experiments down to Fo_{76} in equilibrium with opx. Orthopyroxene compositions show a similar trend, ranging from enstatite-rich ($En_{81}Fs_{15}Wo_4$) in near liquidus experiments at high pressure to more pigeonitic ($En_{68}Fs_{19}Wo_{12}$) at low pressure co-crystallizing with olivine.

Runs CM-8, CM-10, CM-12, and CM-16 contained crystals that were suitable to analyze using LA-ICP-MS to determine partition coefficients.

Olivine/melt partition coefficients increase from the LREE (La – Gd) to HREE (Y – Lu) with Lu being the most compatible (Fig. 1), although all REE can still be considered very incompatible in olivine. The concentration of LREE such as La and Ce is so low in olivine that it is close to the detection limit of the instrument. Therefore the uncertainty on these measurements is much larger, and the resultant partition coeffi-

cients must be considered with some caution. The incorporation of a very small melt inclusion will proportionally change the measured LREE much more than the measured HREE.

Discussion:

Trace Element Partitioning: Our experimentally determined partition coefficient fall within the range of previously published $D_{REE}^{olivine/melt}$[5-12]. However, the variation in published data is very large, particularly for LREE. [7] reported D_{La} and D_{Sm} in a lunar composition which are very high compared to terrestrial data (fig. 1). These experiments contained up to 5 wt% of the element of interest in order to reach concentrations in the olivine crystal high enough for analysis by electron microprobe. This method has been shown to produce anomalously high Ds, as at high concentrations departures from Henry's Law are possible [16]. Our experimentally determined $D_{REE}^{olivine/melt}$ are similar to those from studies on terrestrial basalts, indicating there may not be as much of a difference between lunar and terrestrial olivne D_{REE} values as [7] previously thought.

Our new D_{REE} can be used in a variety of petrologic calculations, including calculating the REE composition of mare basalt source regions, and tracking the trace element budget of LMO crystallization. For example we can calculate the abundance of REEs in the lunar interior at increasing degrees of fractional crystallization using the Rayleigh fractionation equation (after [14]). When beginning from a chondritic source composition [15], our new partition coefficients suggest that olivine has the potential to fractionate LREE from HREE. Sm/Yb increases from chondritic 0.905 to 0.959 after 50% olivine crystallization, as HREE such as Yb are slightly more compatible in olivine than LREE such as Sm, leading to an enrichment of LREE relative to HREE in the melt. This distribution is opposite to that observed in lunar basalts, which are enriched in HREE relative to LREE [2].

We can also model crystal compositions in lunar cumulates. Our experimentally derived D_{REE} suggest that olivine crystallizing from a chondritic source will have a negative Eu anomaly (Fig. 2). Negative Eu anomalies in lunar basalts are generally assumed to be the result of plagioclase extraction from the mantle during LMO crystallization (e.g. [2]), however this modelling suggests that there is the potential for the lunar mantle to have an inherent negative Eu anomaly that is not related to formation of a plagioclase-rich flotation crust. However, this inference requires further examination, as REE abundances in olivine are very low, and at the low fO_2 conditions of lunar basalts the majority of Eu should be in the reduced Eu^{2+} form, which could more readily take part in substitutions

with Fe^{2+} and Mg^{2+} in the olivine structure over other REE^{3+} cations. The cause of this apparent small negative Eu anomaly in our experimental data is not yet clear, but if it is a real effect it could have wider implications for the composition of the LMO cumulates and lunar basalt sources.

Conclusions: Using the new experimentally determined olivine/melt D_{REE} we can begin to understand the trace element composition of the lunar mantle, and the petrogenesis of lunar magmas. Our new D_{REE} allow LREE to be enriched in the residual melt during olivine crystallization, and crystallizing olivine to have inherent negative Eu anomalies, adding further to the debate on LMO crystallization processes.
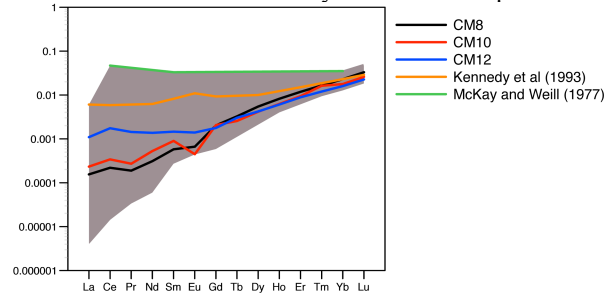
Figure 1: REE partition coefficients for experimentally grown olivine in lunar composition 14307 compared to literature data [8-13]
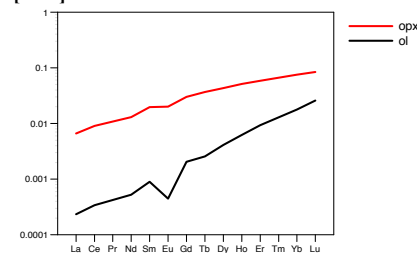
Figure 2: Chondrite normalized REE abundances in modeled olivine (blue) and opx (orange). Experimental D_{REE} produce olivine with a marked negative Eu anomaly.

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