INTERNALLY CONSISTENT REE PARTITIONING MODELS FOR ANORTHITE AND LOW-CALCIUM PYROXENE: A REAPPRAISAL OF SUBSOLIDUS REEQUILIBRATION WITH APPLICATIONS TO PARENT MAGMA COMPOSITIONS OF LUNAR FERROAN ANORTHOSITES

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Introduction: The canonical lunar formation and evolution model involves giant impact, a magma ocean, and cumulate overturn. According to the lunar magma ocean (LMO) model, ferroan anorthosites (FANs) are part of the lunar anorthositic crust formed via plagioclase flotation in a globally distributed LMO [1-3]. Plagioclase in FANs is high in anorthite content. Mafic minerals in FANs are predominately low-Ca pyroxenes (opx and pigeonite) plus smaller amounts of olivine, augite, and traces of ilmenite, chromite, and Fe-Ni metal. Low-Ca pyroxenes in polymict samples tend to be more heterogeneous with compositions varying from grain to grain. Whole rock as well as mineral compositions suggest that FANs crystallized from parent magmas with close to chondritic refractory incompatible trace element ratios and nearly flat REE patterns (10-30x chondritic) [3-8]. This is consistent with a crystallization model whereby plagioclase was on the liquidus after 75-80% crystallization of LMO [9].

In detail, however, it is evident that complicated magmatic and subsolidus processes were involved in the petrogenesis of FANs. For example, REE abundances in melts derived from ion probe analysis of coexisting plagioclase and low-Ca pyroxene in FANs (and Mg-suite rocks) often do not agree with each other [3, 5, 7-8, 10]. This discrepancy may result from (1) inconsistent crystal/melt partition coefficients; (2) processes involving subsolidus redistribution of REE between anorthite and low-Ca pyroxene; and (3) inaccurate trace element analyses [5, 7-8]. In general, LREE abundances in low-Ca pyroxene are lower than those in plagioclase and augite in FANs, hence (3) is possible at least for some of the low-Ca pyroxene data. However, HREE abundances in low-Ca pyroxene derived melts are still not consistent with those derived from plagioclase and augite, suggesting hypotheses (1) and/or (2) are viable.

We have recently developed a parameterized lattice strain model for REE partitioning between low-Ca pyroxene and basaltic melts relevant to lunar magma genesis [11-12]. In this study, we present new experimental results for REE partitioning between anorthitic plagioclase and lunar basaltic melts (K_D). Utilizing these new K_D's and published trace element data for lunar samples [7-8, 10] we reassess hypotheses (1) and (2) above and parent melt compositions of FANs.

Methods: Partitioning experiments were carried out at 1300-1400°C and 0.6-0.8 GPa for 24-96 hours using a 19.1 mm piston cylinder apparatus and graphite-lined molybdenum capsules following the procedures described in [11]. Starting compositions for the experiments were mixtures of anorthite glass and synthetic Apollo 15 red glass (compositions given in [11]). Partitioning experiments were first brought to a higher temperature (1425-1475°C) to melt and homogenize the starting mixture and then slowly cooled to run conditions at 0.2 or 1°C/min. Quenched charges were analyzed for major elements using a Cameca SX100 electron microprobe at Brown University and for trace elements using a LA-ICP-MS at the Graduate School of Oceanography at the University of Rhode Island.

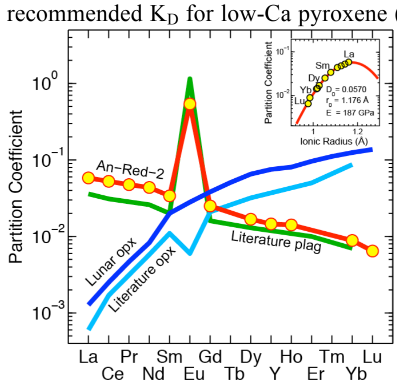

Fig 1. Diagram showing measured REE K_D for anorthite (red) from one of the partitioning experiments in this study and our recommended K_D for low-Ca pyroxene (blue) from [11]. For comparison, the widely used REE K_D for lunar plagioclase and low-Ca pyroxene from refs. [13-15] are also shown. Inset is the Onuma diagram showing excellent fit of the lattice strain model to our measured REE K_D.

Results: Three partitioning experiments have been conducted so far. The run products consist of anorthite crystals ($An_{97.9-98.2}$) and quenched melts. The melts have 6-12wt% TiO_2, ~40% SiO_2, ~20% Al_2O_3, and Mg# [100×Mg/(Mg+Fe), in molar] of 43-49. In general, our measured K_D's for trace elements vary systematically as a function of ionic radius, ionic charge, and melt composition, with K_D for trivalent REE ~1.5-2.5 orders of magnitude larger than those of the high field strength elements. Figure 1 compares REE K_D's for one representative run with the widely used partition coefficients in the lunar literature [13-15]. The characteristic postive Eu anomaly in anorthite is due to the substitution of Eu^{2+} for Ca^{2+}.

Partition coefficients obtained in this study and those reported in the literature for plagioclase (An# > 53) allow us to develop a parameterized lattice strain model for the trivalent REE + Y partitioning between anorthitic plagioclase and lunar basaltic melts ([16], see also inset to Fig. 1). Together with a recent model for REE partitioning between low-Ca pyroxene and basaltic melts [11-12], we will be able to quantify the effect of subsolidus reequilibration on REE redistribution between anorthite and low-Ca pyroxene in lunar samples.

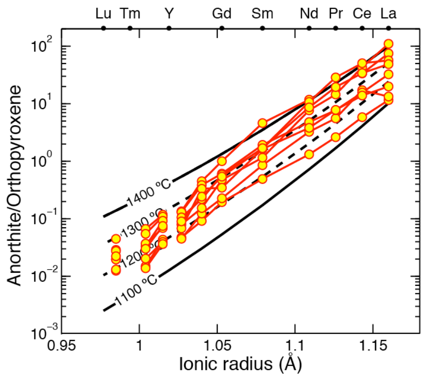

Fig 2. Onuma diagram showing $K_{An/opx}$ for REE in lunar FANs calculated using ion probe data reported in ref. [7]. For comparison, our model-derived $K_{An/opx}$ are also shown for four choices of temperatures (solid and dashed lines).

Subsolidus reequilibration of REE in FANs: To assess the effect of subsolidus reequilibration on REE redistribution between anorthite and low-Ca pyroxene, we combine the two parameterized lattice strain models and obtain a temperature- and composition-dependent model for REE partitioning between anorthite and low-Ca pyroxene ($K_{An/opx}$). Figure 2 compares the calculated $K_{An/opx}$ for REE in FANs using ion probe data reported in ref. [7] and our model-derived $K_{An/opx}$ for temperatures of 1100-1400°C. The salient features of our new model are that (a) LREE are preferentially partitioned into anorthite, whereas HREE are preferentially partitioned into low-Ca pyroxene; (b) $K_{An/opx}$ decreases with the decrease of temperature. Consequently, LREE in low-Ca pyroxene and HREE in anorthite in FANs are more strongly affected by subsolidus reequilibration due to their lower abundances in the respective minerals. Because abundances of LREE in anorthite and HREE in low-Ca pyroxene are considerably less susceptible to subsolidus redistribution, they may be used to estimate compositions of the melt from which FANs were crystallized, assuming a magmatic temperature of 1200-1300°C.

FAN-derived melt compositions: Figure 3 displays REE abundances in melts calculated using REE concentrations in anorthite and low-Ca pyroxene in FANs from refs. [7-8] and the new REE K_D's for anorthite (this study) and low-Ca pyroxene [11]. The grey field in Fig. 3, which is defined by melts derived from LREE in anorthite and HREE in low-Ca pyroxene in FANs, may be taken as one possible candidate for the end-stage composition of LMO. Interestingly, LREE in this model LMO is slightly depleted, in contrast to earlier results [7-10]. Hence LREE in the bulk Moon may be more depleted than previously believed.

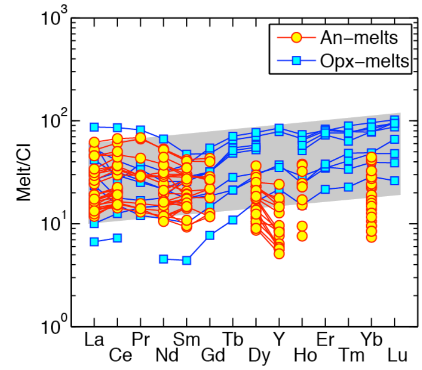

Fig 3. Composition of LMO based on REE abundances in anorthite and low-Ca pyroxene in FANs. The grey field represents one possible interpretation of the end-stage LMO composition.

Discussion: Although subsolidus reequilibration is likely to play an important role in controlling the abundances of REE in anorthite and low-Ca pyroxene in FANs, other processes may also contribute to the discrepancy in anorthite- and low-Ca pyroxene-derived melt compositions for the HREE. Because of the characteristic REE K_D for anorthite and low-Ca pyroxene (red and blue lines in Fig. 1), crystallization of anorthite from LMO preferentially enriches residual melts in HREE relative to LREE. Thus, if low-Ca pyroxenes in FANs were formed from interstitial melts in an anorthositic mush, they would be progressively enriched in HREE. This would result in a calculated melt composition with higher HREE abundances than those calculated from plagioclase K_D. We will further explore this and other scenarios in the future as well as applications to lunar Mg-suite rocks.

References: [1] Warren (1985) *Annu. Rev. Earth Planet. Sci.* 13, 201-240. [2] Warren (1990) *Am. Mineral.* 75, 46-58. [3] Papike et al. (1998) *Rev. Mineral.* 36, E1-E234. [4] James et al (1989) *Proc. Lunar Planet. Sci. Conf.*, 19th, 219-243. [5] James et al (2002) *GCA* 66, 1269-1284. [6] Phinney (1991) *Proc. Lunar Planet. Sci.* 21, 29-49. [7] Floss et al. (1998) *GCA* 62, 1255-1283. [8] Papike et al. (1997) *GCA* 61, 2343-2350. [9] Synder et al (1992) *GCA* 56, 3809-3823. [10] Papike et al (1996) *GCA* 60, 3967-3978. [11] Sun and Liang (2013) *GCA* in review. [12] Yao et al (2012). *Contrib. Mineral. Petrol.* 164, 261-280. [13] McKay et al (1982). *Lunar Planet. Sci.* XIII, 493-494. [14] Phinney and Morrison (1990) *GCA* 54, 1639-1654. [15] Jones (1995) *Rock Physics and Phase Relations: A Handbook of Physical Constants* 3, 73-104. [16] Sun and Liang (2013), submitted to LPSC.