

PARTITIONING OF HYDROGEN AND FLUORINE BETWEEN FELDSPAR AND MELT UNDER THE CONDITIONS OF LUNAR CRUST FORMATION. J. R. Caseres¹, J. L. Mosenfelder¹, and M. M. Hirschmann¹,

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Introduction: The volatile inventory of the modern Moon gives hints to the early volatile history of the nascent Earth-Moon system. The initial water content of the Moon may reflect the initial water content of Earth [1], or it may reflect delivery in a late veneer [2]. The Moon was previously thought to be dry owing to high temperature formation processes, but documentation of appreciable H₂O in lunar glass beads proved otherwise [3]. Subsequently, hydrogen in melt inclusions, apatite, the regolith, and ferroan anorthosite feldspar has also been documented [4]. Diversity of results from these different records suggests either that H₂O is heterogeneously distributed in the lunar interior or that the fidelity of different recording phases varies.

Documentation of up to 3.3 ppm H₂O in plagioclase from ferroan anorthosite (FAN) by Hui et al. [5] (with a revised FTIR absorption coefficient from [6]) potentially provides crucial information about H₂O in the source of the lunar highlands, which are a direct product of the primitive lunar magma ocean (LMO). Translation of the feldspar H content to the magma H content requires an accurate plagioclase/melt partition coefficient, $D_H^{plag-melt}$, which remains poorly constrained. Johnson [7] found a value of 0.004 from natural plag/glass pairs from Mt. St. Helens (MSH) dacite, whereas Hamada et al. [7] found $D_H^{plag-melt} = 0.01 \pm 0.005$ and 0.005 ± 0.001 from experimental basalt-anorthite pairs with water-poor and water-rich compositions, respectively. Recalibration of FTIR absorption coefficients for feldspar [9] results in recalculated values of 0.002 from MSH [7], and 0.005 and 0.003 from basalt/anorthite experiments [8].

In this study we measure experimentally the partition coefficient of hydrogen and fluorine between plagioclase and melt for conditions appropriate to lunar highland crust formation and present preliminary values. Combination with previous [5, 9] and new measurements of lunar anorthosite plagioclase [10] allows revised constraints on H in the source regions of the lunar highlands and therefore possibly in the lunar magma ocean.

Experimental: We used an approach similar to that of Longhi [11], but with added water. The experiments consisted of a model melt composition, constructed to be similar to glass analyzed in Longhi's [11] experiment FP0701-3, and 250-300 μm grains of natural anorthite (An₉₅, 90 ppm H₂O [12]) from Great Sitkin Island, AK. The feldspar grains were added be-

cause crystals of sufficient size for SIMS do not grow from the melt on tractable experimental time scales. The model melt was synthesized from reagent grade oxides and carbonates. In preliminary experiments, 2 wt% H₂O was added to the model melt composition by substituting Al(OH)₃ for a portion of Al₂O₃. However, these experiments did not produce quenched melt pools large enough for analysis, so additional liquid H₂O was added in subsequent experiments.

In successful experiments additional water was added by syringe to the iron capsule, prior to welding it shut. Different amounts of water were added, seeking experiments that resulted in melt pools large enough for analysis. If too much water was added, all of the plagioclase seeds melted. Successful experiments contained ~77 wt% model melt (with ~2 wt% H₂O), ~20 wt% anorthite grains, and ~3 wt% liquid water (Fig. 1). Experiments were held at 1150°C and 0.8 GPa in a piston cylinder for 24 hours.

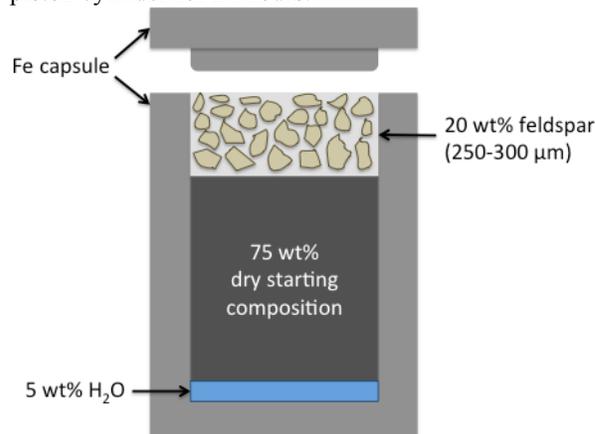


Figure 1: Iron capsule design, with proportions of materials needed to generate an analyzable melt pool. Water shown is the total added from Al(OH)₃ and liquid water.

Experimental charges were stratified by density (Fig. 2). Feldspars floated in a layer on top of the melt pool. In the successful experiments feldspar grains were partially melted, but were still large enough to be analyzed by SIMS. A mush of olivine and orthopyroxene crystals lay beneath the melt pool at the bottom of the capsule. Two types of iron are seen in the quenched products. One is irregularly shaped and forms interstitially with the crystals, as also observed in Longhi's anhydrous experiments [11]. The second type is present as spheres throughout the experiment and is in-

ferred to have been molten iron hydride during the experiment.

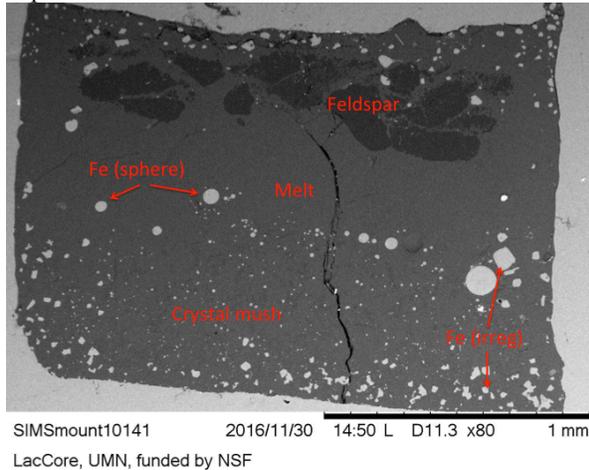


Figure 2: A successful experiment with a large melt pool that retains its seeded feldspar grains.

Analytical: Capsules were cut in half and mounted to brass stubs using ethyl cyanoacrylate for polishing. The polished sample was then removed from the stub and cleaned in acetone and isopropanol before mounting in indium.

SIMS measurements were performed at Caltech on the Cameca 7f-GEO using previously described methods [6, 13]. The samples were assessed for hydrocarbon contamination by monitoring $^{12}\text{C}/^{30}\text{Si}$, and analyses with ratios > 0.001 were discarded. Contamination was observed on feldspars but not on glass, likely owing to material trapped in cleavage planes. Only two experiments yielded usable partition coefficients because of this problem. Cleaning procedures will be revised in future studies to account for this issue.

Results and discussion: For the two uncontaminated experiments, the glasses had 0.36 ± 0.003 wt% H_2O and 0.65 ± 0.008 wt% H_2O and coexisting feldspar had 82 ± 11 ppm H_2O and 118 ± 6 ppm H_2O , respectively. This results in partition coefficients of 0.023 ± 0.003 and 0.018 ± 0.001 , respectively, which are much higher than [7, 8] but not outside the range of what is known for nominally anhydrous minerals [14].

Hui et al. [5] report up to 3.3 ppm H_2O in feldspar from FAN 60015, 2.6 ppm in FAN 15415, and 1.4 ppm in Mg-suite troctolite 76535, taking into account the revised absorption coefficient [6]. Our recent analyses challenge such high concentrations in the feldspar [10], but we will consider 3.3 ppm as an upper limit. At this limit, the melt in equilibrium with FAN contained no more than 160 ppm H_2O . FAN was formed from plagioclase floatation after $\sim 70\%$ crystallization of the LMO [4]. If we assume a bulk value for

$D_H^{\text{peridotite-melt}}$ of 0.006 to 0.01 [14] and a simple Rayleigh fractional crystallization model, we estimate that the initial lunar magma ocean contained at most 50 ppm H_2O .

Fluorine partitioning. Owing to contamination from the mortar and pestle used to homogenize the starting materials, low levels of F were measured in the melt (12.4 ± 0.2 ppm and 11.0 ± 0.2 ppm) and feldspar. The feldspar contains up to 0.2 ppm F, but is very close to the detection limit. From these preliminary data, we constrain an upper limit of $D_F^{\text{plag-melt}} \leq 0.02$. More precise constraints on F partitioning will be obtained in future experiments by intentionally adding F.

Mosenfelder et al. [10] report up to 1.1 ppm F in anorthites from 10 different FAN samples. Combined with the partition coefficient, we estimate the FAN magma had up to 50 ppm F. Using the same simple model of Rayleigh fractional crystallization in our H_2O calculation with a bulk partition coefficient from [15], we estimate an upper limit of 15 ppm F in the LMO.

Comparison to other measurements and models. The estimated upper limit of 160 ppm H_2O for melts in equilibrium with the anorthositic crust and 50 ppm in the LMO are much lower than Hui et al.'s [5] estimates of 1600 ppm H_2O and 330 ppm H_2O , respectively. Our estimate for H_2O in the LMO is also lower than Hauri et al.'s [1] lower estimate of 133 ppm H_2O .

Our initial LMO estimates overlap with McCubbin et al.'s [4] estimates for H_2O and F in the bulk silicate moon (BSM). McCubbin et al. [4] did not estimate volatile contents of the FAN magma, but gave estimates of 300 to 1250 ppm H_2O and 660 ppm F in urKREEP. Our estimated ratio of $\text{H}_2\text{O}/\text{F}$ in FAN magma is 3.2, which is higher than the range of 0.5–1.9 estimated for urKREEP [4] but subject to large uncertainties bearing further investigation

References: [1] Hauri E. H. et al. (2015) *EPSL*, 409, 252-264. [2] Albarède F. (2009) *Nature*, 461, 1227-1233. [3] Saal A. E. et al. (2008) *Nature*, 454, 192-195. [4] McCubbin F. M. et al. (2015) *Am. Min.*, 100, 1668-1707. [5] Hui H. et al. (2013) *Nat. Geosci.*, 6, 177-180. [6] Mosenfelder et al. (2015) *Am. Min.*, 100, 1209-1221. [7] Johnson E. A. (2005) *Goldschmidt Conf. Abs.*, A743. [8] Hamada, M. (2013) *EPSL*, 365, 253-262. [9] Mosenfelder J. L. and Hirschmann M. M. (2016) *LPSC XLVII*, Abstract #1716. [10] Mosenfelder et al. (2017) *LPSC XLVIII*, this conference. [11] Longhi J. (2003) *JGR*, 108(E8), 5083. [12] Johnson E. A. and Rossman G. R. (2004) *Am. Min.*, 89, 586-600. [13] Mosenfelder J. L. et al. (2011) *Am. Min.*, 96, 1725-1741. [14] Tenner T. J. et al. (2009) *Chem. Geol.*, 262, 42-56. [15] Rosenthal A. et al. (2015) *EPSL*, 412, 77-87.