WATER IN THE MOON: THE PERSPECTIVE FROM NOMINALLY ANHYDROUS MINERALS. J. L. Mosenfelder[1], J. L. Andrys[2], J. R. Caseres[1], and M. M. Hirschmann[1]. [1]Department of Earth Sciences, University of Minnesota, 310 Pillsbury Dr. SE, Minneapolis, MN, 55455 (jmosenfe@umn.edu). [2]Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA

Introduction: Support for the revolutionary hypothesis of a "wet" lunar magma ocean (LMO) [1] in part hinges on volatile measurements in lunar materials using modern analytical techniques with low detection limits. Hydrogen has been found using SIMS and FTIR in lunar glass beads, apatites, olivine-hosted melt inclusions, and nominally anhydrous minerals (NAMs). With respect to NAMs in particular, low (< 10 μg/g) but detectable H concentrations have been reported for plagioclase (Pl) from ferroan anorthosites (FAN) and an Mg-suite rock [2,3] and Pl, K-feldspar, and pyroxenes from basaltic and granitic clasts in polymict breccias [4].

We previously reported [5] new SIMS data from FAN (15415 and 60015) and troctolite 76535 that call into question the original finding [2] of up to 6.4 μg/g H_2O in Pl in these three samples. Here we offer possible explanations for discrepancies between our studies. Moreover, we present experimental constraints on volatile incorporation in Pl that have implications for the wet LMO hypothesis.

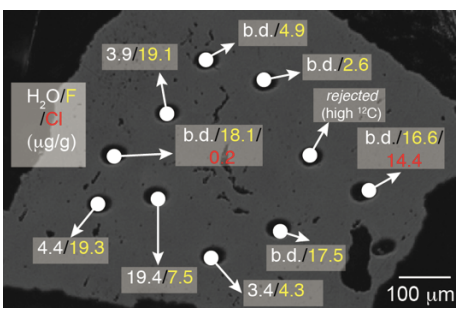

Figure 1. SIMS analyses of a chip of 60015, 819, showing highly variable H_2O, F, and Cl.

Measurements of natural samples: We conducted an extensive SIMS investigation [5] and found no H or F above detection limit in 76535. Preservation of H in this Mg-suite sample is unlikely based on diffusion kinetics for H in Pl [6] and quantitative estimates from P zoning in olivine [7] of the slow magmatic cooling rate of this rock. We also could not verify the H concentrations found by [2,3] in 15415, although it contains up to 0.6 μg/g F, consistent with other FAN that we studied (13 FAN samples in total).

Our most striking results are on 60015. Analyses of multiple chips from this highly shocked sample (e.g. Fig. 1) yield highly variable concentrations of H_2O (up to 28 μg/g), F (up to 45 μg/g), and Cl (up to 20 μg/g), in all cases with low ^{12}C (indicating no contamination from organic material). The high variability and presence of Cl – which is insoluble in Pl – suggest that the volatiles reside in melt inclusions, previously identified in 60015 [8]. We hypothesize that volatiles were remobilized from lunar soil during the shock event that produced the splash melt rind on 60015. This may explain why our results on split 819 (from the outer portion of 60015) differ from those of Hui et al. [2,3] on split 787 (from the inner portion of the rock). On the other hand, original FTIR spectra of 60015 [2] (Fig. 2) bear a strong resemblance to liquid H_2O (and not to OH in anorthite [9]), which may reflect an artifact from sample preparation. Further work to verify the distribution of volatiles in this sample is clearly warranted.

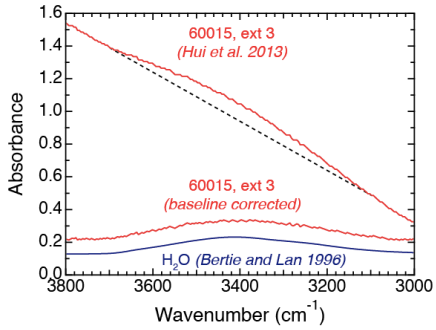

Figure 2. Comparison of FTIR spectra of 60015, 787 (ext3) and liquid H_2O. The published spectrum of 60015 [2], scaled to 1 cm thickness, was baseline corrected using a simple linear fit between 3700 and 3100 cm^{-1}. The spectrum of liquid H_2O from [10] was scaled to 0.001 cm.

Experimental studies: Experimental constraints on H incorporation in Pl come from solubility and Pl-melt partitioning measurements [11,12,13]. Fig. 3 demonstrates a strong effect of oxygen fugacity on subsolidus H incorporation in Pl. Our new results (with H measured by SIMS) on compositions between An45 and An95 (annealed at 800-850 °C and 0.5 GPa at fO_2 fixed by either the IW or NNO buffers) are in excellent agreement with previous data on An58 [11]. These experiments confirm that solubility increases by a factor of 2-3 for compositions and oxygen fugacities relevant to the Moon. Importantly, partitioning data also show an enhancement of H incorporation in Pl, with significantly higher $D_H^{Pl\text{-}melt}$ at low fO_2 conditions [12,13] compared to $D_H^{Pl\text{-}melt}$ inferred for samples from terrestrial settings [14,15,16]. We suggest that reduction of Fe^{3+} to Fe^{2+} plays a key role in H incorporation, based on the fact that our natural Pl starting materials contain up to 0.5

wt% FeO_{tot} (likely incorporated as both Fe^{3+} and Fe^{2+} in tetrahedral and A-sites, respectively [17]).

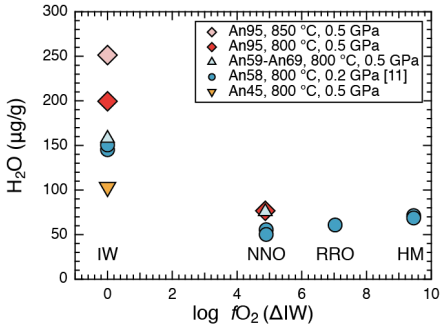

Figure 3. Effect of fO_2 (O_2 buffers listed below data) on H solubility in Pl. Data from this study collected by SIMS; data from [11] corrected for more recent FTIR calibration [18].

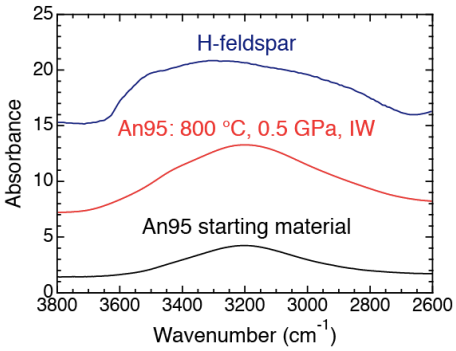

Figure 4. Comparison of unpolarized FTIR spectra of $HAlSi_3O_8$ [19] with natural anorthite (An95) before and after annealing at 800 °C, 0.5 GPa at fO_2 controlled by the IW buffer. Polarized spectra show highest absorption when the E-vector is close to the a-axis [9]. Spectra normalized to 1 cm except for $HAlSi_3O_8$, arbitrarily scaled for comparison.

FTIR spectra (Fig. 4) show no obvious changes in speciation mechanism after annealing in our solubility experiments. Furthermore, there is a broad similarity between O-H absorption bands in natural Pl and synthetic H-feldspar [19] ($HAlSi_3O_8$, where Na is completely replaced by H). Based on these considerations, we suggest the following model (Fig. 5) for H incorporation in Pl: 1) at higher fO_2, Ca and/or Na cation vacancies are predominantly responsible for H incorporation, with the broad band explained by disorder and/or H-bonding; 2) at fO_2 near ΔIW, Fe^{3+} in tetrahedral sites reduced to Fe^{2+} is charge compensated by an additional H^+ in an adjacent vacant A-site, enhancing overall uptake of H (i.e. ${}^{IV}Fe^{3+} + O^{2-} = {}^{IV}Fe^{2+} + OH^-$). In principle, the same model and fO_2 dependence could apply to F, which readily substitutes for O^{2-} in NAM lattices including Pl [18] and requires the same charge balance. We are currently testing this hypothesis by doping our partitioning experiments with F.

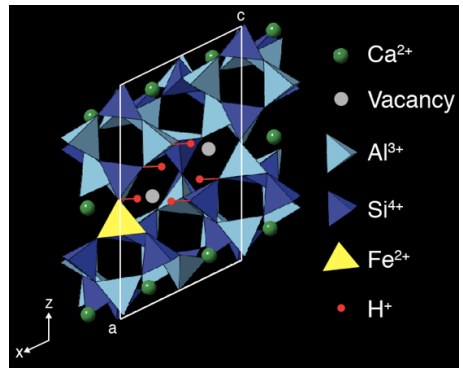

Figure 5. Structure of anorthite projected on (010) showing some possible OH^- sites. For clarity, Ca3 atoms normally visible in this projection are not shown. One ${}^{IV}Al^{3+}$ is replaced by ${}^{IV}Fe^{2+}$, balanced by a third H^+ in the adjacent vacant A-site that otherwise only accomodates two H^+. OH^- bonds are shown schematically in an orientation approximately consistent with the known polarization from FTIR spectra [9].

Conclusions: Given the evidence for endogenous lunar volatiles from other materials, it is important to understand how H and F are partitioned into and incorporated in NAMs at *P-T-*fO_2 conditions relevant to the Moon, regardless of whether these elements were actually preserved through a ~4.4 billion history including cooling of the LMO and surface reworking after emplacement. Our work highlights the importance of distinguishing primary from secondary H and F in lunar samples and taking into account the key role of fO_2 in estimating volatile concentrations of the LMO.

References: [1] Saal A. E. et al. (2008) *Nature* 454, 192–196. [2] Hui H. et al. (2013) *Nat. Geosci.* 6, 177–180. [3] Hui H. et al. (2017) *EPSL* 473, 14-23. [4] Simon J.I. et al. (2017) *LPS XXXXVIII,* Abstract #1248. [5] Mosenfelder J.L. et al. (2017) *LPS XXXXVIII,* Abstract # 2473. [6] Johnson E.A. and Rossman G.R. (2013) *Am. Min.* 98, 1779-1787. [7] Hammer J.E. et al. (2017) *LPS XXXXVIII,* Abstract # 1274. [8] Sclar, C.B. and Bauer J.F. (1974) *Proc. 5th Lunar Sci. Conf.*, 319-336. [9] Johnson E.A. and Rossman G.R. (2003) *Am. Min.* 88, 901-911. [10] Bertie J.E. and Lan, Z. (1996) *Appl. Spectros.* 50, 1047-1057. [11] Yang, X. (2012) *GCA* 97, 46-57. [12] Caseres J.R. et al. (2017) *LPS XXXXVIII.* Abstract #2303. [13] Lin Y.H. et al. (2017) *LPS XXXXVIII.* Abstract #1286. [14] Hamada et al. (2013) *EPSL* 365, 253-262. [15] Caseres J.R. et al. (2018) *AGU 2018*, VI43I-0249. [16] Mosenfelder J.L. et al. (2018) *AGU 2018*, MR23B-0085. [17] Hofmeister A.M. and Rossman G.R. (1984) *Am Min.* 11, 213-224. [18] Mosenfelder J.L. et al. (2015) *Am Min.* 100, 1209-1221. [19] Behrens, H. and Müller, G. (1995) *Mineral Mag.* 59, 15-24.