

**LOW TO EXTREMELY LOW WATER ABUNDANCES MEASURED IN NOMINALLY ANHYDROUS MINERALS IN MAFIC TO GRANITIC APOLLO ROCK CLASTS.** J. I. Simon<sup>1</sup>, R. Christoffersen<sup>1,2</sup>, J. Wang<sup>3</sup>, C. M. O'D. Alexander<sup>3</sup>, R. D. Mills<sup>4</sup>, and E. H. Hauri<sup>3</sup>, <sup>1</sup>Center for Isotope Cosmochemistry and Geochronology, Astromaterials Research & Exploration Science, NASA Johnson Space Center, Houston, TX 77058, USA (Justin.i.simon@NASA.gov), <sup>2</sup>Jacobs-JETS contract, Houston, TX 770058, USA, <sup>3</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd, Washington, DC 20015, USA, <sup>4</sup>Department of Geological Sciences, University of North Carolina, Chapel Hill, NC 27599, USA.

**Introduction:** Lunar sample-based volatile studies have focused on assessing the inventory and distribution of water in the Moon. Some have focused on the relatively young mare basalts [1] and pyroclastic glasses [2], which result from partial melting of the relatively young lunar mantle. Less certain is the water inventory for the oldest materials available, which have the greater potential to record the earliest history of volatiles in the Moon (and thus provide evidence for the “wet” vs. “dry” accretion hypotheses of the Earth-Moon system, e.g., [3-5]).

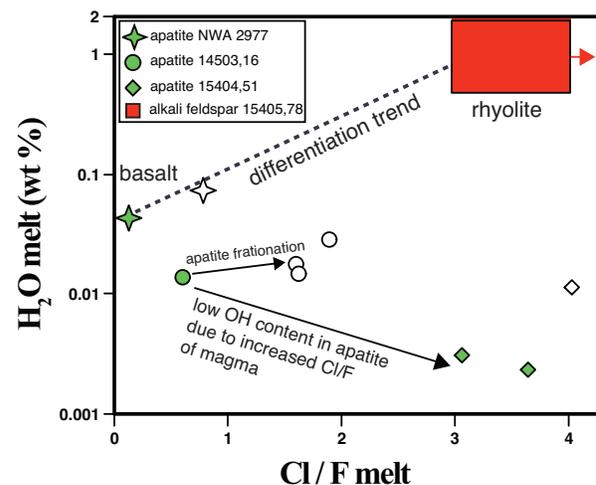
Studies of volatiles in ancient lunar rocks have largely focused on apatite. One recent FTIR study of plagioclase reported a relatively “wet” (~320 ppm) magma for primordial ferroan anorthosites (FANs) [6]. Another, a NanoSIMS study of alkali feldspar [7], reported a “wet” (~1 wt. %) felsic magma, but due to the differentiation processes required for silicic magmatism in the lunar crust, predicted an essentially “dry” (<100 ppm) bulk Moon.

Thus, despite evidence that appears to complicate the early “dry” Moon paradigm, there is no apparent unanimity among the measurements, even those on apatite (e.g., [8] vs. [9]). This disparity is clearly seen by the order of magnitude different water estimates for lunar “alkali-rich suite rocks” (Fig. 1). Some of the apparent differences may be explained by recent improvements in the apatite-based water estimates that better account for relative compatibilities of OH<sup>-</sup>, Cl, and F [10].

In the present work, we seek to expand our understanding of the volatile abundances in early formed lunar magmas, their source reservoirs, and to address the potential role that felsic magmas play on the lunar hydrogen budget over time by employing NanoSIMS analysis of nominally anhydrous minerals.

**Apollo Igneous Clast Samples:** Here we report analyses of nominally anhydrous minerals contained in: (1) the >3.9 Ga, coarse-grained mafic clast 14303, 363 (plag and opx) extracted from the Fra Mauro Formation crystalline-matrix breccia that is likely part of Imbrium basin ejecta [11]; (2) the well-known relatively young (~4.03 Ga), granitic clast 14321, 1062 (alkali feldspar and SiO<sub>2</sub>) [12-14] also from the Fra Mauro Formation crystalline matrix breccia; (3) the ≥4.2 Ga, granitoid clast 12013, 141 (plag) from a complicated polymict

breccia [15]; and (4) the potentially ~4.3 Ga, med. coarse-grained clast 15405, 255 (plag, opx, and cpx) representing or co-genetic to quartz monzodiorite [16] from KREEP-rich breccia.



**Figure 1.** Plot shows estimated water content of lunar magmas after [7]. Apatite data from [17]. Schematic differentiation trend is shown between basalt and rhyolite.

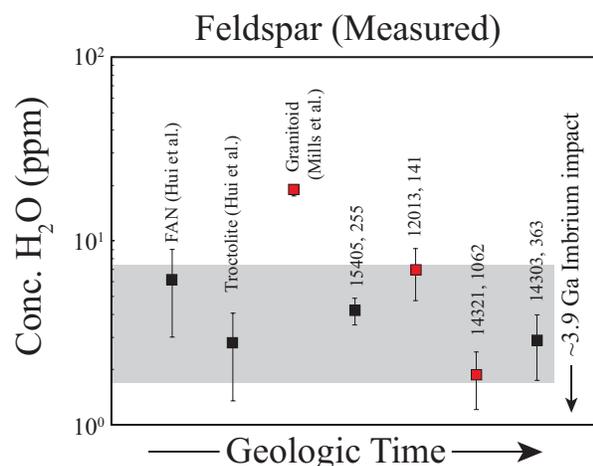
**Analytical Methods:** The abundance of H<sub>2</sub>O was measured in feldspar, pyroxene, and a SiO<sub>2</sub>-phase using the Cameca NanoSIMS 50L in the Dept. of Terrestrial Magnetism at the Carnegie Institution of Washington, following the techniques of [1,18]. Nine internal standard materials (ranging from ~0 to ~1.58 wt. % H<sub>2</sub>O) were used to establish a calibration curve and three external standards, including two well-studied natural feldspars (sanidine from the Bishop Tuff, California [19] and adularia from Val Kristallina, Switzerland [20]), and an anhydrous synthetic SiO<sub>2</sub>-material (Suprasil) were used to monitor instrumental relative sensitivity factors and detection limits, respectively. An electron gun was used for charge compensation, the instrumental mass resolving power was set at ~8000 in order to separate <sup>16</sup>OH<sup>-</sup> from <sup>17</sup>O, and the sample analysis chamber remained at low pressure (≤4.5×10<sup>-10</sup> Torr).

Every analysis location included pre-sputtering where the primary ion beam of Cs was rastered over a 15×15 μm area for ~3 minutes. Data was then collected while the ~2 nA primary ion beam was rastered over an

area of  $7 \times 7 \mu\text{m}$ . Negatively charged ions of  $^{12}\text{C}$ ,  $^{16}\text{OH}$ ,  $^{19}\text{F}$ ,  $^{30}\text{Si}$ ,  $^{32}\text{S}$  and  $^{35}\text{Cl}$  were measured simultaneously for  $\sim 5$  minutes from the central  $\sim 3 \times 3 \mu\text{m}$  of the rastered area on six electron multipliers using ion counting.

Measurements of the external standards afford several useful constraints: (1) consistency with results of [20] demonstrates the veracity of both groups' analytical methods and data handling, (2) comparison to the water estimate in coeval quartz-bearing melt inclusions [19] provides an empirical estimate of OH<sup>-</sup> partitioning ( $D_{\text{feld/melt}} \sim 0.0001$ ) between feldspar and melt, and (3) the lower OH<sup>-</sup> content in the lunar SiO<sub>2</sub> (described below) indicates a resolvable amount of water in the Suprasil standard. Although this  $\sim 1$ -2 ppm apparent excess is essentially negligible for many studies, it is significant for low abundance work, such as this study, and therefore the lower water content of the lunar SiO<sub>2</sub> phase is subtracted from the other measured concentrations.

**Results:** In general, the measured water contents in all of the nominally anhydrous phases are lower than in their potential terrestrial equivalents (cf. the 10's to  $\leq 200$  ppm measured in feldspar by [20] and in this study). In detail, plag =  $2.9 \pm 1.1$  ppm (2SD) and opx =  $5.8 \pm 0.6$  ppm (2SD) in the  $> 3.9$  Ga mafic clast 14303, 363; Alkali feldspar =  $1.9 \pm 0.6$  ppm (2SD) and SiO<sub>2</sub>-phase =  $0.0 \pm 0.4$  ppm (2SD) in the  $\sim 4.03$  Ga granitic clast 14321, 1062; plag =  $6.9 \pm 2.2$  ppm (2SD) in the  $\geq 4.2$  Ga granitoid clast 12013, 141; and plag =  $4.2 \pm 0.7$  ppm (2SD) and opx+cpx =  $3.6 \pm 1.0$  ppm (2SD) in the  $\sim 4.3$  Ga evolved clast 15405, 255 (Fig. 2).



**Figure 2.** Water content in lunar feldspar plotted in approximate chronological order. Red squares indicate felsic clasts that exhibit decreased abundance with time.

**Discussion and Preliminary Conclusions:** Although this work expands the range of compositions investigated, all of the new measurements indicate drier

melts than those reported by [6,7] (cf. [8]). This observation is exemplified by the extremely low water contents measured in the youngest felsic sample studied, granite clast 14321, 1062. At face value, this granite is more than an order of magnitude drier than the lunar granitoid ( $\sim 1.0$  wt. %) studied by [7] and the terrestrial Bishop Tuff rhyolite ( $\sim 2.9$  wt.%) [19].

The difference between estimates for low water content in mafic melt based on plag measured in 14303, 363, and possibly the more evolved melt based on plag measured in 15405, 255, as compared to the higher values of granitoids also based on feldspar (15405, 78, [7] and 15405, 255, this study) can be reconciled by reasonable petrogenetic models for differentiation, e.g., Fig. 1.

It is noteworthy that in general the new data are similar to the measured values for feldspar in the FANs ( $\sim 6$  ppm) and troctolites (2.7 ppm) of [6]. No standard lunar magma ocean differentiation scenario can reconcile the differences implied between the low and homogeneous values measured in this study (and [6]) for the range of rock compositions and the 2-3 orders of magnitude higher values inferred for the 'primordial'  $\geq 4.3$  Ga FANs [6].

Based on the available data it appears that: (1) the felsic rocks (or their sources) have lost water over time, (2) the studied FANs, and possibly other primitive rocks, had their water contents affected by some petrogenetic processes other than those described by the standard lunar magma ocean model, and (3) the bulk Moon was rather dry ( $\leq 10$ 's ppm), but not anhydrous and thus may not have required late volatile addition to explain the range of water contents reported in the differentiated lunar magmas.

**References:** [1] Hauri, E. H. et al. (2011) *Science* 333, 213-215, [2] Saal, A. E. et al. (2008) *Nature* 454, 192-195, [3] Drake, M. J. and Richter, K. (2002) *Nature* 416, 39-44, [4] Albarède, F. (2009) *Nature* 461, 1227-1233, [5] Paniello, R. C. et al. (2012) *Nature* 490, 376-379, [6] Hui, H. et al., (2013) *Nature Geoscience* 6, 177-180, [7] Mills, R. D. et al. (2017) *Geochem. Persp. Lett.* 3, 115-123, [8] Robinson, K. L. et al. (2014) 45<sup>th</sup> LPSC, Abst. #1777, [9] Barnes, J. J. et al. (2014) *EPSL* 390, 244-252. [10] Boyce, J. W. et al. (2014) *Science* 344, 400-402, [11] Swann, G. A. et al. (1971) *Science* 173, 716-719, [12] Warren, P. H. et al., (1983) *EPSL* 64, 175-185, [13] Shih, C.-Y. et al. (1993) *EPSL* 57, 4827-4841, [14] Simon, J. I. et al. (2011) 42<sup>nd</sup> LPSC Abst. # 2754, [15] Quick, J. E. et al. (1981) *Proc. 12<sup>th</sup> Lunar Planet. Sci. Conf.* 117-172, [16] Ryder, G. (1976) *EPSL* 29, 255-268. [17] McCubbin, F. M. et al. (2010) *PNAS* 107, 11223-11228, [18] Hauri, E. H. et al. (2006) *Chemical Geology* 235, 353-365, [19] Schmitt, A. K. and Simon, J. I. (2004) *CMP* 454, 192-325, [20] Mosenfelder, J. L. et al. (2015) *Am. Min.* 100, 1209-1221.