**ORIGIN OF LUNAR WATER AND EVIDENCE FOR A WET MOON FROM D/H AND WATER IN LUNAR APATITES.**
J. P. Greenwood[1], S. Itoh[2], N. Sakamoto[2], P. H. Warren[3], M. D. Dyar[4] and H. Yurimoto[2], [1]Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 USA, [2]Natural History Sciences, Hokkaido University, Sapporo 060-0810 Japan, [3]Dept. of Earth & Space Sciences, UCLA, Los Angeles, CA 90095 USA, [4]Dept. of Astronomy, Mount Holyoke College, S. Hadley MA 01075 USA.

**Introduction:** Since the discovery of trace amounts of water in lunar fire-fountain glasses in 2008 [1], several groups have more recently reported on the existence of copious amounts of water in lunar apatite [2-5], with maximum values of 6050 ppm determined from mare basalt 12039 apatite [5]. Modeling of these results to determine the original content of water in the lunar mantle is fraught with difficulties and unknowns in key parameters [2,3]. We have recently reported the first D/H measurements of lunar water from ion microprobe measurements of D/H in apatite from Apollo rock samples [5]. A recent study of Cl isotopes in lunar materials has cast doubt on the estimates of lunar mantle water derived from apatite OH contents, and has called for a dry Moon during lunar petrogenesis [6]. Here we report new measurements of water and D/H in lunar apatite from 12039,43 measured using the Hokudai ion microscope. Sample 12039 is notable for having the highest water content measured for a lunar apatite, but also a large range in water content (960-6050 ppm $H_2O$) of individual apatite grains. Of equal importance, apatite from 12039 has a large range in δD (+391 to +1010‰), indicating that lunar water is distinctly different than terrestrial water.

**Methods:** A 1” round epoxy-impregnated lunar thin-section of 12039 (,43) made by NASA for this study, was carbon-coated and was pumped at $10^{-8}$ torr for 4 days prior to ion microprobe spot analyses and SCAPS imaging (see [5] for detailed methods).

**Results:** In this study, we have measured D/H and $^{1}H/^{18}O$ in eight apatite grains from 12039,43 (Fig. 1), bringing our total to thirteen apatite grains in 12039 [5]. The combination of plentiful and large apatite grains in coarse-grained pigeonite basalt 12039 have allowed us to make multiple measurements of D/H and $H_2O$ (presumably OH) in individual apatite grains from multiple thin-sections. We find that the water contents of individual apatite grains are homogeneous, but vary among different grains (as found in our previous work[5]). Only one grain in 12039,43 was large enough for multiple spots, and δD values for those two spots were identical (δD=+765±42‰ and +765±34‰).

**Discussion:**

*D/H of the Moon.* The mean and standard deviation of δD analyses of mare basalts 10044, 12039, and 75055 are +681±132‰ (n=27) (Fig. 2). The mean and standard deviation of δD of 12039,43 are +698±61‰ (n=9). This is almost identical to the mean δD of 12039,42 (mean δD=+689±180‰ (n=13) [5]), but with much less variability. Clearly the data are dominated by 12039, but the mean δD of 10044 is similarly elevated relative to Earth (10044: mean δD=+606±30‰ (n=4)), as is the lone analysis of 75055 (δD=+735±36‰). That the D/H of these 3 mare basalts from different landing sites should be so similar argues that the mare source region is also similarly elevated in D/H. Other possibilities to explain the similarity in D/H of these 3 samples are likely untenable, but are considered below.

The δD of two analyses of an intrusive highlands alkali anorthosite clast (14305,303) are also elevated relative to Earth (δD=+238±72‰; +341±53‰) (Figs. 1 and 2), but less so than those of mare basalts 10044, 12039, and 75055. An important point of an elevated D/H for this intrusive sample is that it would seem to argue against late-stage assimilation of regolith material (derived from comets or asteroids) by the extrusive mare lavas to explain the elevated D/H of the Moon.

*Degassing and D/H fractionation.* Several processes that can lead to an elevated D/H of lunar samples or the bulk Moon include degassing of $H_2$ or $H_2O$ during a giant impact event or lava extrusion, subsolidus diffusion of hydrogen in apatite, or dehydration of apatite. Degassing of $H_2$ with Rayleigh distillation of the total hydrogen reservoir ($H_2$ + $H_2O$) has been invoked to explain the elevated D/H of fire-fountain mare glass beads [7]. The elevated δD of lunar basalts 10044, 12039, and 75055 is difficult to explain via this mechanism, because we see no correlation between δD and $H_2O$ of apatite grains (Fig. 1). Also, the Cl contents of apatite grains are increasing during crystallization, which is not to be expected if Cl is degassing during apatite crystallization [5]. Outgassing from the Moon following a giant impact could have led to an elevated D/H via outgassing of hydrogen [5]. This would likely have led to a globally elevated D/H for the Moon. The current dichotomy in D/H of apatite between the mare and highlands (Figs. 1 and 2) is difficult to reconcile with a giant impact origin for elevated D/H of *both* mare and highlands rocks.

*Origin of lunar water.* If the D/H of water in lunar apatite is not formed by the processes of degassing, diffusion, or dehydration (due to the lack of correlation in D/H and $H_2O$ expected for these processes [5]; Fig.

1), then the D/H of lunar apatite may serve as a constraint for the nature of the late-accretionary population of material. If so, the only solar-system materials with D/H similar to that of mare basalt apatite would be bulk carbonaceous chondrites or comets [8]. D/H of water from carbonaceous chondrites is similar to the D/H of water in the Earth's mantle [8], suggesting cometary material as a source of water to the Moon [5].

*Is the Moon wet or dry?* Recent work on Cl isotopes of lunar samples suggests that the Moon is anhydrous as previously believed [6]. Olivine basalt 12040 is the only sample to be analyzed for both $\delta^{37}$Cl [6], δD and $H_2O$ [5]. A SIMS analysis of $\delta^{37}$Cl in apatite suggests that it grew in a dry environment. A leachate analysis of $\delta^{37}$Cl of 12040 suggests a wet environment for this rock, pointing to extreme heterogeneity in 12040. Our analyses of water and δD in apatite of 12040 are in agreement with the SIMS $\delta^{37}$Cl measurement, because we find apatite in 12040 to be the only dry apatite we have analysed from a mare basalt [5].

Thus, a number of samples appear to have formed in a wet environment [2-5], and a number appear to have formed under anhydrous conditions [6]. The majority of samples that we have studied probably formed under relatively wet conditions [5]. For example, it is expected that OH will favor the melt rather than apatite [3]. For a reasonable partition coefficient, this means that the very late stage lunar mare magmas had ~1 to 6 wt.% $H_2O$ (albeit after ~95-99% crystallization of anhydrous minerals). If assimilation of volatile-enriched materials did not occur (?), then the source region should have >ppm levels of water. Until more samples have been investigated from a variety of lunar lithologies, the answer to the question "How wet is the Moon?" cannot yet be fully addressed.

**References:** [1] Saal A. E. et al. (2008) *Nature 454,* 192-196. [2] McCubbin F. et al. (2010) *PNAS 107,* 11223 [3] Boyce J. et al. (2010) *Nature 466*, 466. [4] McCubbin F. et al. (2010) *Am. Min. 95* 1141 [5] Greenwood J. P. et al. (2011) *Nature Geosci.* doi:10.1038/NGEO1050. [6] Sharp Z. et al. (2010) *Science 329,* 1050 [7] Hauri E. et al. (2010) *Fall AGU* abst. [8] Robert F. *Meteorites and the Early Solar System II,* (eds. D. Lauretta & H. Y. McSween, Jr.) 341.

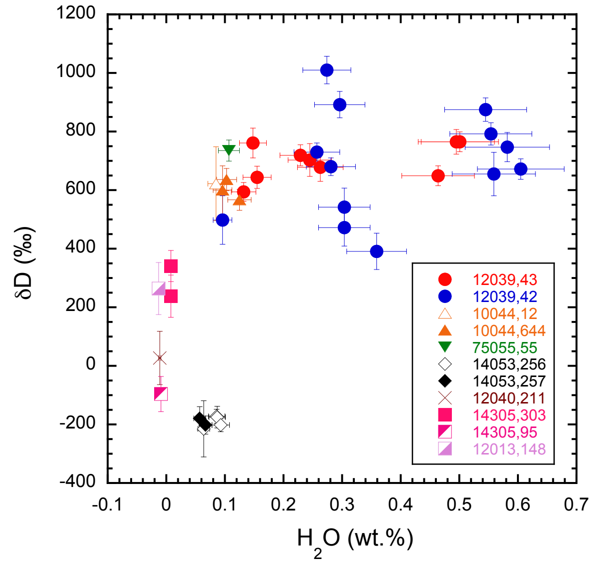


Figure 1. δD vs. $H_2O$ (wt.%) plot of apatite from lunar samples collected during the Apollo programme. Samples with low water (12040 and 14305,94) may be reflecting terrestrial adsorbed water.

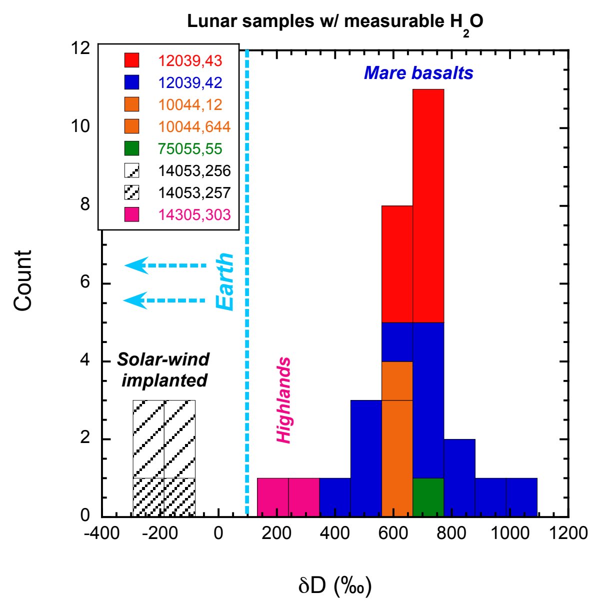


Figure 2. Histogram of δD analyses of lunar samples with measurable water. The upper range of Earth water is denoted by the blue dashed line. The clear dichotomy between the highlands and mare basalt D/H can be seen here.