WATER IN APOLLO ROCK SAMPLES AND THE D/H OF LUNAR APATITE. J. P. Greenwood<sup>1</sup>, S. Itoh<sup>2</sup>, N. Sakamoto<sup>3</sup>, L. A. Taylor<sup>4</sup>, P. H. Warren<sup>5</sup> and H. Yurimoto<sup>2,3</sup> <sup>1</sup>Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 (jgreenwood@wesleyan.edu), <sup>2</sup>Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan, <sup>3</sup>Creative Research Initiative "Sousei", Hokkaido University, Sapporo 060-0810, Japan, <sup>4</sup>Dept. of Earth & Planetary Sciences, University of Tennessee, Knoxville, TN 37996-1410, <sup>5</sup>Institute of Geophysics & Planetary Physics, University of California, Los Angeles, CA 90095.

**Introduction:** A major finding of the Apollo program was the complete lack of bona fide lunar water in lunar soil and rock samples [1]. In the last year, trace levels of water (at the ppm levels) were found in the primitive lunar mare glasses [2], but a D/H measurement was not reported. Here we report the first hydrogen isotope measurements of lunar water in the hydrous mineral apatite  $[Ca_5(PO_4)_3(F,Cl,OH)]$  from Apollo rock samples.

**Methods:** Lunar thin-sections were studied by a combination of light, electron and ion-beam microscopy. Apatite in a range of crystalline mare basalt samples (10044, 12039, 12040, 14053, and 75055), two highlands breccias (12013 and 14305), and a phosphate-bearing anorthositic clast (14305, 303) were analyzed for water content and D/H using terrestrial apatite standards [3]. We had two detection methods for water in ion-beam analyses-1) quantitative spot analysis and 2) semi-quantitative SCAPS imaging (Fig. 2). Due to the high levels of water in many lunar mare apatite grains, we did not need to significantly modify our published method for analysis of water in Martian apatite with the Hokudai Cameca ims 1270, with SCAPS 2-D ion detector [3]. Two major differences: 1) plagioclase was analyzed for water as a background determination in all thin-sections, and 2) all samples and standards were kept under vacuum of 1.0 E-8 Torr for more than 3 days in a new 20 sample airlock system to remove terrestrial adsorbed water.

**Results:** The results of our ion microprobe spot analyses are shown in Fig. 1 and discussed below.

12039: 12039 has the highest water content and D/H of samples analyzed in this study, as well as a very large range in D/H and water content, and has significant variation in water content between apatite grains.

10044: We studied two thin-sections of 10044 (10044, 12 and 10044, 644). 10044, 12 is an original Apollo thin-section (made in 1969-1970) and has likely been studied by many groups for the last 40 years. 10044, 644 is a new thin-section cut for this study, that arrived at Wesleyan University days before SIMS analyses. We see no significant difference in  $\delta D$  and  $H_2O$  of apatite between these thin-sections.

75055: Only one apatite grain was large enough for our analytical technique in the PM assigned to us and the water and D/H results are very similar to 10044. Petrologically, 75055 has been compared to 10044, and suggested to be very similar in petrogenesis (albeit from different landing sites).

12040: Apatite in this sample is dry. This olivine basalt has been suggested to have undergone olivine accumulation and cooled slowly in the lunar subsurface [4]. Therefore, this basalt likely had time to efficiently degas its water before apatite crystallization; alternatively, the lack of water reflects genetic differences between samples of the Apollo 12 basalt suite [5].

14053: This sample is anomalous in that the water content is similar to 10044 and 75055, but D/H has a terrestrial signature. The two thin-sections studied here were made at a different time than other sections in this study, and may have suffered terrestrial contamination. Alternatively, 14053 has been considered the most reduced rock from the Moon. Its proposed origin, which involved 1) emplacement on the lunar surface, 2) followed by solar-wind implantation of hydrogen, and 3) reheating in an impact event to produce intense reduction features [6], is consistent with the low D/H found here. Future work on other PMs of this rock are needed to resolve this issue.

12013 and 14305, 94 (Highlands breccias): Apatite grains embedded in brecciated regions were analyzed. Apatite in both samples are dry, which can be understood from the expected impact metamorphism that accompanied brecciation.

14305, 303 (Highlands anorthositic clast): Apatite grains from a phosphate-bearing alkali anorthosite clast [7] were analyzed. These water analyses are suspect, as they require extrapolation of our apatite standard curve to lower values. However, the highlands apatite is drier than mare apatite, but we are not certain as to the exact amount.

Discussion-Water content of the lunar mantle: The water content of the lunar mantle can be estimated from the data presented here with some assumptions: 1) water measured in 12039 represents mantle-derived water, and not water derived from assimilated material, such as cometary-derived regolith on the lunar surface; 2) apatite is the only water-bearing mineral in the lunar

basalts, and 3) water behaves as a perfectly incompatible element during mantle melting. With these assumptions, and using a batch melting model, we estimate the water content of the lunar mare basalt source region. For small degrees of partial melting (3-5%), we estimate 2-12 ppm H<sub>2</sub>O in the 12039 source region.

**Discussion-Origin of lunar water:** The  $\delta D$  values measured here for 12039, 10044, and 75055 range from  $\sim$ 400 to  $\sim$ 1000‰. These values of D/H are unique among natural materials in terrestrial collections and argue against contamination. Potential contaminants such as carbon coat and epoxy were measured and had low  $\delta D$ , as expected. Two possibilities present themselves to explain the elevated D/H relative to Earth. One possibility involves a cometary input to the mare basalt source region, or that the lunar magmas were able to assimilate cometary material upon emplacement onto or near the lunar surface. Spectro-

scopic measurements of D/H in comets are in the appropriate range of  $\delta D$  [8]. A second possibility is that the Earth-Moon system was able to diffusively equilibrate its volatiles shortly after the giant impact [9], and that the original D/H of the Moon was similar to that of the Earth's. The D/H of water was then fractionated to its present value during hydrodynamic escape of hydrogen during the Moon's formation.

**References:** [1] Epstein S. and Taylor H. P. (1973) *GCA*, 2, 1559-1575. [2] Saal A. E. et al. (2008) *Nature 454*, 192-196. [3] Greenwood J. P. et al. (2008) *GRL*, 35, L05203, doi:10.1029/2007GL032721. [4] Walker D. et al., (1976) *Proc. Lunar Sci. Conf.* 7<sup>th</sup>, 1365-1389. [5] Neal C. R. et al. (1994) *Meteoritics*, 29, 334-348. [6] Taylor L. A. et al. (2004) *Am. Min.* 89, 1617-1624. [7] Warren P. H. et al. (1983) *JGR*, 88, B151-B164. [8] McKeegan K. D. and Leshin L. A. (2001) *RIMG*, 43, 279-318. [9] Pahlevan K. and Stevenson D. J. (2007) *EPSL*, 262, 438-449.

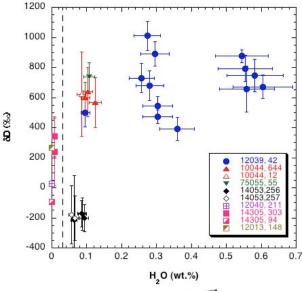


Figure 1.  $\delta D$  vs.  $H_2O$  (wt.%) for lunar mare and highlands rocks. The black dashed line represents our confidence limit for low  $H_2O$  materials. Error bars are  $2\sigma$ .

Figure 2 (Bottom left and Bottom right). Bottom Left: BSE image of late-stage crystallization area in 12039. Bottom Right: SCAPS image of apatite area overlain on BSE image. Red circle indicates location of spot analysis. High hydrogen appears bright in this image. The euhedral portion of the apatite grain appears brighter than surrounding water-poor phases. Cracks are very high in terrestrial water contamination.

