**PRIMITIVE LUNAR WATER IN EVOLVED ROCKS?** K.L. Robinson[1,2], J.J. Barnes[3,4], R. Tartèse[3], K. Nagashima[1,] L.J. Hallis[2], I.A. Franchi[3] , M. Anand[3,4], , and G.J. Taylor[1,2] [1]Hawaii Institute of Geophysics and Planetology, 1680 East-West Rd., Honolulu, HI 96822. [2]UHNAI ,[3]Planetary and Space Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK. [4]Department of Earth Sciences, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK. krobinson@higp.hawaii.edu

**Introduction:** Since the identification of water in lunar pyroclastic glasses [1], and apatite [2], the idea of the Moon as an anhydrous body has been completely revised. Hydrogen isotope measurements are a potential way to determine the source of the Moon's water through the D/H ratio, which varies depending on solar system source [3 and references therein], although fractionation during lunar formation, magmatic processing inside the Moon, and loss from magma and lava bodies complicate the picture. The study of apatite has allowed water to be measured in several lunar rock types, including mare basalts [3-6], more evolved lithologies such as the felsites and quartz monzodiorites [7], and deep intrusives [7,8]. Typically, apatites in mare basalts contain more water than apatites in KREEP-rich lithologies. Also, many lunar samples have elevated δD values with respect to typical terrestrial values [3,5-7], while other samples have lower, more Earth-like δD values [8,9]. However, several processes such as magma crystallization, volatile degassing, transport of metasomatic fluids, or spallogenic production can modify initial water characteristics, and it is not yet clear if all the existing data indicate diverse water reservoirs or could be reconciled with a single, homogeneous, water reservoir in the lunar interior. Here we present new data providing evidence for a low-D reservoir in the lunar interior with some of the lowest δD values yet reported in lunar apatite (Fig. 1).

**Samples:** The water content and δD measurements were made for apatites in alkali-suite (felsites 14321,1047 and 77538,16; quartz monzodiorites 14161,7069 and -,7373; alkali anorthosite in 14305,656) and magnesian suite (troctolite 76535,52,-,56) rocks. All of these rocks are rich in KREEP, and some were formed through fractional crystallization of a KREEP basaltic parent magma (felsites, QMDs) [7, 10,11]. Sample 15404,55 is a thin section of a clast from the 4-10 mm sieve fraction of soil sample 15400 (Fig.2). It was selected for its similarity to alkali-suite rock 15404,51, which contains apatite measured for $H_2O$ abundance (but not δD) by McCubbin et al. [2].

15404,55 has a subophitic texture with nearly equal proportions of exsolved pyroxenes and plagioclase feldspar, with silica, K-feldspar (often intergrown with silica), merrillite, apatite, and ilmenite.

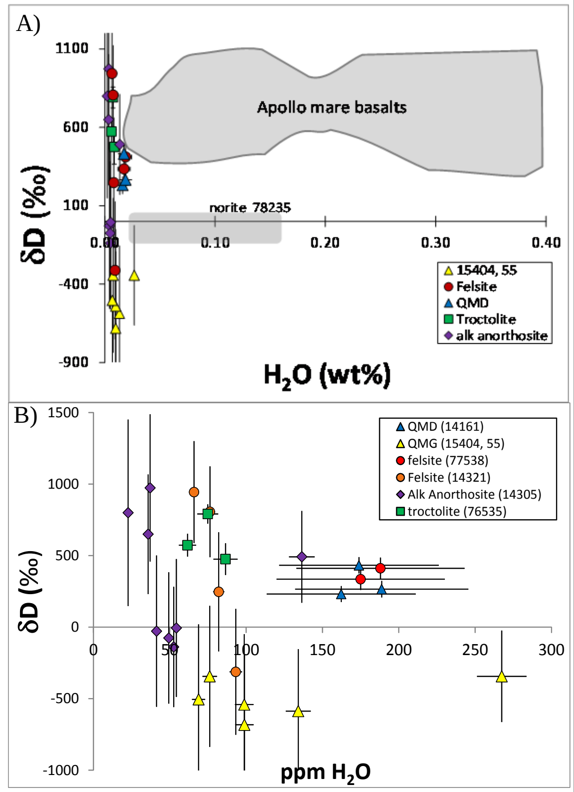


Fig. 1. A) Plot of measured δD vs. wt. % $H_2O$ in lunar apatites from various rock types [3,5-8]. The evolved rocks [this abstract, 7] are much drier than the mare basalts [3,5,6]. Note the distinctive low δD of 15404,55. Earth's mantle δD is -140 to +60 [12]. B) Enlarged version of plot (A) showing spread among low-water samples. X-axis is changed to ppm $H_2O$.

Using the modal abundances of these minerals, we have classified sample 15404,55 as a quartz monzogabbro (QMG). Based on the very elevated REE and FeO contents [pers. com., D. Mittlefehdt], 15405,55 and its sister section -,53 are similar to other Apollo 15 QMDs [11]. All contain exsolved pyroxene, indicating a hypabyssal magmatic setting.

**Methods and Results:** H isotope and water content measurements were performed using the Cameca ims 1280 ion microprobe at the University of Hawaii and the Cameca NanoSIMS 50L at the Open University. NanoSIMS protocol is detailed in [5,6] and ims 1280 protocol is detailed in [12].

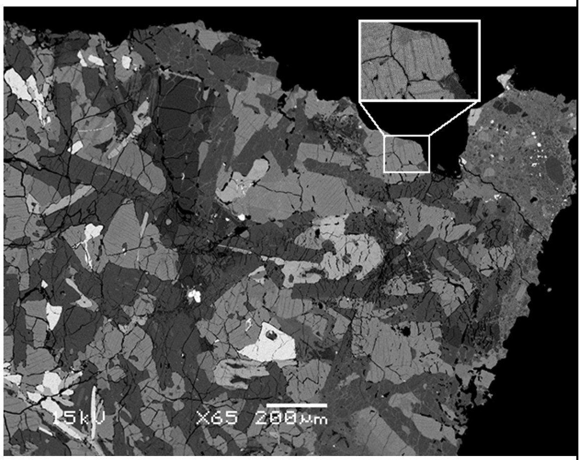


Fig. 2. Backscattered electron image of a representative area of 15404,55. Darkest gray is silica, medium gray is plagioclase, light gray is exsolved pyroxene, and white is ilmenite.

Both protocols use a wt. % $H_2O$ vs. $^1H/^{18}O$ calibration curve e.g., [3] to calculate water content of apatite grains, and the same standards characterized by [13] for water content and δD. Small apatite grain size necessitated the use of the NanoSIMS to measure 15404,55, 14305,656, and 14321,1047. Apatites in 77538,16, 76535,52 and -,56, 14161,7069 and -,7373 and one grain in 14321,1047 were measured on the UH SIMS [7]. Data presented here are not corrected for spallogenic production of H and D. This correction is < 10‰ for 15404,55, because of its very young exposure age [15].

Apatite has a maximum water content of only 267± 9 ppm $H_2O$ in 15404,55. This water content is consistent with measurements presented in [2]. Most apatite contained less than 200 ppm $H_2O$. Compared to mare basalt apatite in which water contents are often > 1000 ppm, apatite in the KREEP-rich, intrusive rocks analyzed in this study are all very dry.

The δD results are more intriguing. While NanoSIMS D/H measurements of low-water content samples have large uncertainties, the range in measured δD values from 14305,656 and 14321,1047 are broadly consistent with the ims 1280 measurements made in other evolved lithologies. In contrast, apatite δD in 15404,55 ranges from about -338 to -683 ‰. This δD range is lower than any previously measured lunar apatite, and plots well below the known terrestrial range (Fig. 1).

**Discussion:** Low δD values (< -200 ‰) have also been observed in pyroclastic glasses after correction for spallogenic production of D [9], as well as in the apatite of sample 14053 [3]. The low δD of apatite in 14053 was attributed to solar wind implantation and later metamorphism [3]. However, we do not believe a similar process could have affected 15404,55. Soil sample 15400 was classified as very immature [14] and there is no evidence that the sample was metamorphosed, such as the abundant metallic iron in its groundmass as is present in 14053. It was collected from on top of a boulder (impact melt breccia 15405), which has an exposure age of only 11 My [15].

*Primitive δD?:* The QMDs/QMG were produced through extensive fractional crystallization of a KREEP-basaltic parent magma [10,11]. The presence of finely-exsolved pyroxenes (Fig. 2) indicates that they formed in a shallow intrusive environment (hypabyssal), in relatively small magma bodies [11]. Based on calculations performed with VolatileCalc [16] up to 0.8 wt. % $H_2O$ is soluble in rhyolitic melt at 100 bars pressure, which is equivalent to 2 km depth on the Moon. Solubility increases with pressure, so 0.8 wt% is likely a minimum value. Water was thus likely soluble in the QMD magma.. Water solubility in the melt is important because degassing can fractionate H isotopes. It is unlikely that the A15 QMD/QMG magma degassed, as it formed at depth and pressure where water would have been soluble.

Where did this low δD water come from? Many previously measured apatites and glasses seem to indicate a general enrichment in D in lunar samples compared to terrestrial samples. Even low δDs from lunar samples are still in the typical terrestrial mantle range (-140 to +60 ‰ [12]). However, recent data from terrestrial deep mantle samples suggests the primordial δD of Earth may be lower than current surface and upper mantle reservoirs (as low as -220 ‰, [17], this meeting). Therefore, our measured low δD lunar reservoir could represent the primordial δD of primitive Earth at the time of the Moon-forming impact.

**Acknowledgements:** This research was supported by the NASA Astrobiology Institute CAN NNA09DA77A and LASER NNX11AE85G.

**References:** [1] Saal, A. E. et al. (2008) *Nature, 454*, 192-195. [2] McCubbin, F. M. et al. (2010) *PNAS, 107*, 11223-11228. [3] Greenwood, J. P. et al. (2011) *Nature Geosci., 4*, 79-82. [4] Boyce J. W. et al. (2010) *Nature*, *466*, 466-469. [5] Barnes, J. J. et al. (2013) *Chem. Geo., 337-338*, 48-55 [6] Tartèse R. et al. (2013) *GCA, 122*, 58-74. [7] Robinson K. L. et al. (2013) *44th LPSC* Abst.#1327. [8] Barnes J. J. et al. (2013), *EPSC* Abst.#105. [9] Saal A. E. et al (2013) *Science*, *340*, 1317-1320. [10] Taylor, G. J. et al. (2012) *Meteoritics & Planet. Sci., 47*, 861-879. [11] Ryder, G. & Martinez, R. R. (1991) *Proc. Lunar Planet. Sci*., *21*, 127-50. [12] Hallis L. J. et al. (2012) *EPSL*, *359-360*, 84-92. [13] McCubbin F. M. et al. (2012), *Geology*, *40*, 683–686. [14] Morris R. V. (1978) *Proc. Lunar Sci. 7*,. 2287-2298. [15] Drozd R. J. et al. (1976) *Proc. Lunar Sci. 7*, 599-623. [16] Newman S. and Lowenstern J. B. (2002) *Comp. & Geosci., 28*, 597-604. [17] Hallis L.J et al. (2014) *45th LPSC* Abst.#1283.