TOWARDS A WETTER MOON: IMPLICATIONS OF HIGH VOLATILE ABUNDANCES IN LUNAR APATITE.

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Introduction: The Moon was considered a dry planetary body until the discovery of trace amounts of water in fire-fountain glasses in 2008 [1]. Since this important discovery, several groups have found large amounts of water (i.e non-trace levels) in lunar apatite [2,3,4,5] and in olivine-hosted melt inclusions in lunar glass beads [6]. A general consensus on what this means for the lunar volatile budget has not been reached, with several groups continuing to argue for a dry lunar interior [7,8]. Here we present new results on hydroxyl abundances and D/H of apatite in four lunar samples not previously reported on. We also examine the implications of our results for the water contents of a low-Ti mare basalt magma, with consideration for degassing of H_2 and high H_2/H_2O in reduced lunar magmas.

New Results: We were able to analyze hydroxyl contents and D/H in four samples not previously investigated.

10047,228. This coarse-grained low-K ilmenite basalt had two apatite grains large enough for our analytical technique [e.g. 4]. Water contents of apatite in this mare basalt (1094 and 1538 ppmw OH) were lower than other Apollo 11 and 17 samples (>2000 ppmw OH; see Fig. 1; also [4]). D/H of hydroxyl in these apatite grains is elevated (δD=+767±80‰ and +730±48‰; 2σ) and similar to the range of D/H seen in other mare basalt apatite grains (Fig. 1). These data continue to suggest a global mechanism to explain elevated D/H in mare basalt apatite grains [4].

12064,8. This coarse-grained low-Ti ilmenite basalt had only one apatite grain large enough for our analytical technique. This is the 2nd lowest water content for a mare basalt that we have measured (only 12040 olivine basalt, which was dry, is lower in our work). While the water content of this apatite grain is low (330 ppmw), the δD continues to be high and similar to other mare basalts (δD=+707±74‰; 2σ).

72395,6. This impact melt breccia had one apatite grain located in a brecciated region (non-clast) of the sample. The apatite grain was essentially dry, as we have found for other apatite grains located in brecciated regions of lunar samples [4].

79215,74. This holocrystalline feldspathic impact rock has a granoblastic texture, and the largest apatite grains described from the Moon [9]. The mm-sized apatite megacrysts in this sample were previously described as having formed in an impact annealing process [9]. Rim and core analyses of apatite grains were dry in this sample (Fig. 1).

Water content of a Low-Ti mare basalt magma:
Apatite grains from low-Ti mare basalt 12039 have the highest water contents measured in a lunar material [4,10,11]. We measure 1920-12,100 ppmw OH in 13 apatite grains from basalt 12039 (Fig. 1). Apatite crystallizes after ~95% crystallization in lunar basalts [12], and is petrographically associated with the latest crystallizing phases in basalt 12039, such as fayalite, K-,Ba-rich feldspar, fayalite, FeS, and mesostasis. If we assume the highest OH content apatite represents the most crystallized area, and assume a partition coefficient of 0.4 for OH between apatite and late-stage lunar melt (as done by [3]), this suggests a melt with ~1.5 wt.% H_2O in equilibrium with late-stage apatite in 12039. Assuming 99% crystallization yields a parent melt for 12039 of ~150 ppm H_2O. With consideration of the above assumptions, this can be viewed as a *minimum amount of water in the parent melt of 12039,* as we have assumed no degassing, nor that these melts may have a significant fraction of their hydrogen in the form of H_2 [13].

Degassing of H_2 and its effect on lunar water contents. Lunar apatites have been found to have very high D/H, up to 2x terrestrial [4]. It has been suggested that volatile element depletion patterns of lunar glass beads are most consistent with lunar melts having undergone significant degassing upon eruption [1,6]. Cl isotopes of lunar apatites also suggest significant degassing of hydrogen prior to apatite crystallization [7]. Degassing of H_2 from lunar magmas should leave residual H_2O enriched in δD due to the large isotopic fractionation between these species (~150‰ at 900˚C [14]). If the high D/H of lunar apatites is due to degassing of H_2, then >90% of total hydrogen would need to be lost via Rayleigh distillation from a magma with terrestrial D/H to produce the D/H values we measure in lunar apatites. If we assume 90% degassing of total hydrogen from mare magmas, this would suggest that the parent magma (prior to degassing and crystallization of anhydrous phases) of 12039 had ~1300 ppm H_2O+H_2+OH, an extraordinary amount of hydrogen for a lunar melt.

*f*O$_2$ *of lunar magmas and its effect on lunar water contents.* Lunar magmas are more reduced than terrestrial magmas [e.g. 11]. A recent study suggested that dissolved H$_2$/H$_2$O of high silica melt varies between ~0.2 for IW and ~2 for IW-2 at 1000˚C [13]. If this type of behavior is analogous to that of lunar melts, this would suggest that a significant portion of lunar dissolved hydrogen could exist as H$_2$. It is possible that apatite is insensitive to melt H$_2$ contents, and only reflects melt OH and H$_2$O content, due to the unreactivity of molecular H$_2$. If apatite in lunar melts is only able to react with water species, then apatite OH contents reflect melt OH (and/or H$_2$O), and not total dissolved hydrogen. This would suggest that total H contents of lunar melts would likely need to be even higher than we have estimated above for a degassed and undegassed parent melt of basalt 12039.

D/H of the Moon. The mean and standard deviation of δD analyses of mare basalts 10044, 10047, 12039, 12064, and 75055 is +687±126‰ (n=30). That the D/H of these five mare basalts from three different landing sites should be so similar argues that the mare source region is also similarly elevated in D/H.

The δD of apatite from an intrusive highlands alkali anorthosite clast (14305,303) is also elevated relative to the Earth (δD=+238±72‰; +341±53‰; 2σ), but less so than mare basalts 10044, 10047, 12039, 12064, and 75055. The elevated D/H of this intrusive sample seems to rule out assimilation of regolith material (derived from comets or asteroids) by the extrusive mare lavas to explain the elevated D/H of the Moon. The elevated D/H of this intrusive sample also calls into question a degassing mechanism to explain elevated D/H of mare basalts.

Degassing of H$_2$. The mean and standard deviation of apatite from pigeonite basalt thin-section 12039,43 is +698±61‰ (n=9). This is almost identical to that of thin-section 12039,42 (δD=+689±180‰ (n=13)), but with much less variability. We have analyzed 13 apatite grains in 12039, and these grains exhibit a 6-fold change in water content with almost no change in D/H (Fig. 1). This argues strongly against a model of degassing of H$_2$ *during apatite crystallization* to explain elevated D/H of mare basalt apatite. Our results on D/H of lunar apatite do not rule out degassing of lunar magmas *before or after* apatite crystallization.

If degassing of H$_2$ from lunar mare magmas is the main factor in creating elevated D/H of lunar mare apatite, then this process acted on a global scale, and would suggest that lunar magmas lost almost identical amounts of hydrogen and that they also started with nearly identical total hydrogen contents to explain the similarity in D/H of lunar mare apatite grains.

Conclusions. The high hydroxyl contents of some apatite grains in low-Ti pigeonite basalt 12039 suggests lunar melt water contents of ~1.5 wt.% in the latest stages of lunar basalt crystallization. A starting water content of 150 ppm is suggested for the parent melt of 12039. If this water was derived from the source region (and is not introduced to the magma during transport or eruption), we can estimate the water content of the source region assuming apatite is the only hydrous mineral and water behaves as a perfectly incompatible species. For 3-5% partial melting of the 12039 mare basalt source region, we estimate 5 to 8 ppm H$_2$O. This can be viewed as a minimum, as we assume no degassing prior to apatite crystallization, and that the majority of H$_2$O is present as OH and/or H$_2$O in lunar melt. Large-scale degassing of H$_2$ from lunar melts would suggest a significantly higher hydrogen component in the lunar mantle.

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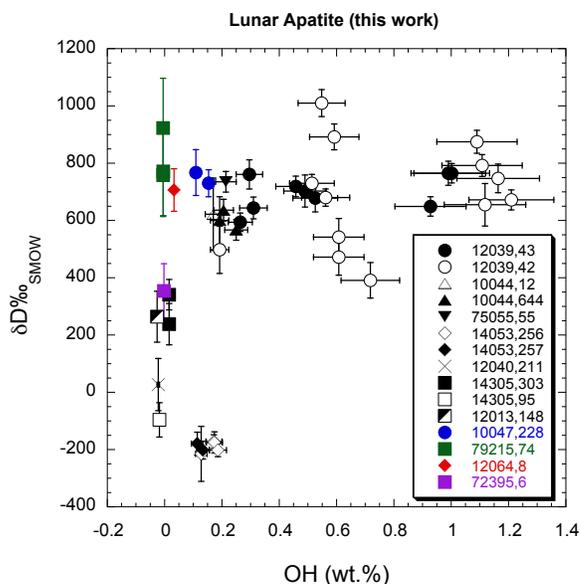

Figure 1. δD vs. OH of lunar apatite grains. Error bars are 2σ.