WATER IN EVOLVED LUNAR ROCKS: IMPLICATIONS FOR WATER DISTRIBUTION IN THE LUNAR MANTLE.

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Introduction: With the recent detection of water in lunar pyroclastic glasses [1], apatites [2], and melt inclusions [3] the question of water in the lunar mantle has become an important issue. The abundance of water in the lunar mantle is not known, although some workers are attempting to constrain the amount based on sample measurements and computer modeling [1-4]. The source of the Moon's interior water is also not known, although this may be elucidated through study of the D/H ratio of water in lunar apatites [5,6]. As the abundance and source of the Moon's interior water have important implications for the formation and thermal evolution of the Moon, understanding the formation of these "hydrous" phases is essential.

Apatite $[Ca_5(PO_4)_3(F,Cl,OH)]$ is a useful phase in which to search for lunar water because it incorporates water as OH into its crystal structure. Greenwood et al. [5] note that there was no difference between apatite measured in fresh thin sections versus Apollo-era thin sections, which implies that the OH in apatite is resistant to exchanging O or H with terrestrial water. Interestingly, the H_2O abundance of apatite in various lunar rocks ranges significantly. Apatite in mare basalts seem to have the highest H_2O content (0.7wt% in Northwest Africa 2977, [2]), while apatites in the more evolved, KREEP-related rocks have very little H_2O (<0.03wt% [2,5,6]). H_2O abundances in apatite in various lunar rocks are plotted on Fig. 1.
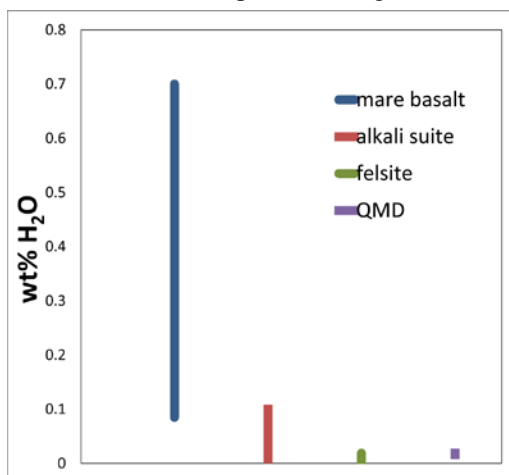

Fig.1 H_2O of lunar apatites by rock type. Note the variability in water content of the mare basalts. Mare basalt, alkali suite, and felsite data from [2,5], additional felsite data from [6], quartz monzodiorite (QMD) data from this work.

Felsites and evolved lunar volcanism. The felsite suite consists of evolved Si-rich (~70wt% SiO_2) rocks with graphic intergrowth of quartz and K-feldspar [7].

Based on felsite texture and the presence of quartz rather than another silica polymorph, Robinson and Taylor [7] argue that the felsites and their corresponding Fe-rich phase are formed in small intrusive bodies through silicate liquid immiscibility of an evolving magma of KREEP-basalt composition. The quartz monzodiorites (QMDs) are also evolved lunar rocks. They exhibit a cumulate texture and are probably fractional crystallization products of KREEP basalts [8].

Both the felsites and the QMDs formed at depth. The fact that they formed intrusively suggests that they may have been able to escape degassing of any water that was present in their various source magmas. Up to 1% water is soluble in basalt and rhyolite melts even at modest pressures on the Moon (100MPa or 2km depth; calculated with VolatileCalc [9]). This makes the evolved rocks ideal for preserving H_2O of their parent magmas and interior source region(s).

As observed by Elkins-Tanton and Grove [4], this lack of water in apatite in the KREEP-related rocks is unexpected (Fig.1). Water acts like an incompatible element at low abundances, and will become enriched in a crystallizing melt. Apatite comes out relatively late during the crystallization process. Thus, KREEP-rich magmas should be enriched in water by the time apatite begins to crystallize. However, the few measurements for evolved rocks [2,5] indicated that they contained very little water, which would imply that their source regions also contained very little water [4]. Robinson et al. [6] recently reported small concentrations of H_2O (~180ppm) in apatite in the felsite/ferrobasalt pair 77538,16. We report additional analyses here.

Methods: Apatites were identified using optical and electron microscopy, and EDS element mapping in felsites in thin sections 14321,1047 and 77538,16, and in QMDs 14161, 7069 and -,7373 [8]. All apatites were analyzed for P, Ca, Si, Na, Fe, Ce, F, Cl, Y, and La with the UH JXA-8500F electron microprobe. Apatites were then selected for SIMS analysis based on their estimated OH contents, which were calculated by difference in the halogen site after [2]. Hydrogen isotopic composition and water content of selected apatites were analyzed in situ with the UH ims 1280 ion microprobe with a Cs^+ primary beam in two separate rounds of measurements in May and November 2011. H_2O content of apatite samples was estimated from a calibration curve on H_2O (wt.%) vs. $^1H/^{18}O$ determined using 3 terrestrial apatite standards with different H_2O contents after [5,6]. These standards were also used for instrumental fractionation correction of measured

D/H ratios. The detection limit for water content was estimated by measuring anhydrous minerals present in the same sections. The May detection limit was ~100ppm, with δD and water content uncertainties of 74 ‰ and 30%. The November detection limit was ~110ppm, with δD and water content uncertainties of ~60‰ and 30%. The uncertainties include reproducibility of standard measurements.

Results: We measured a total of 9 points on 7 apatite grains in 4 samples. Apatite in felsite 14321,1047 and two apatites in 14161,7373 had H_2O content below our detection limits. One apatite in QMD 14161,7069 and one in -,7373 had H_2O content slightly below our detection limits. Apatite in 77538,16 contained ~180ppm H_2O, with δD of ~+300-+400‰ [6]. Fig. 2 shows these data compared with literature apatite data.
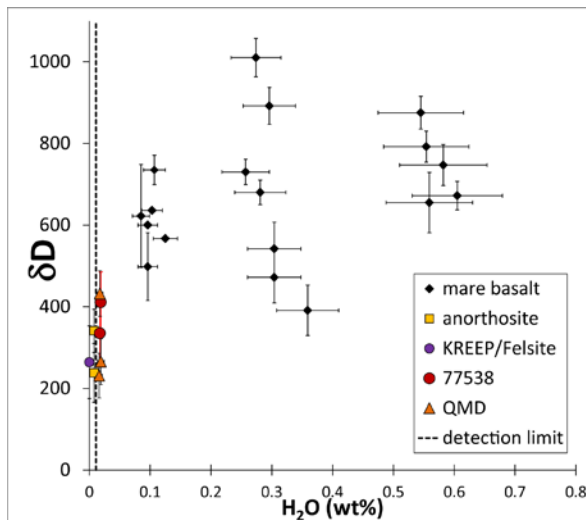

Fig. 2. δD vs. H_2O plot of lunar apatites by rock type. Note the spread and high H_2O abundances in the mare basalts, while the evolved, KREEP-related rocks cluster at very low H_2O abundance and lower δD. Data from [5]; 77538 data from [6]; QMD data this work. Dashed line shows Nov. detection limit of 110ppm.

Discussion: We found very little or no detectable water in the apatites measured. Apatites in all the samples contain significant (wt% level) amounts of rare-earth elements. Since H_2O follows REEs during magmatic fractionation, this indicates that these highly evolved, KREEP-rich magmas contained little water to begin with. KREEP formed as the late-stage product of the crystallizing lunar magma ocean, and was enriched in incompatible elements, including H_2O. This supports the hypothesis that that the lunar magma ocean had a low initial water content, as argued by [4]. By the time apatite crystallized in a KREEP-rich rock, H_2O would have also been concentrated in the melt. Since the apatites contain very little water, the source magma must have contained even less water. This also supports the idea that the mare basalt source regions were

distinctly richer in H_2O, perhaps due to incorporation from external sources [4,5,10].

The δD values in apatite in 77538 with detectable water are elevated, which agrees with findings in [5]. Since the measured H_2O is barely above detection limit, we cannot say with total certainty that the δD of lunar water in 77538 is elevated with respect to Earth. However, this conclusion may be supported by our measurements of the QMDs. H_2O was at detection limit in two apatites in the QMDs. We do not claim to have definitively detected water in these samples, but their δD numbers are intriguing. Fig. 3 shows δD of apatite in lunar rocks compared with terrestrial water. The δD in the felsites and the QMDs appears to be lower than the mare basalts, but still elevated with respect to Earth. This supports the conclusion in [5] that the Moon is elevated in D compared to Earth.
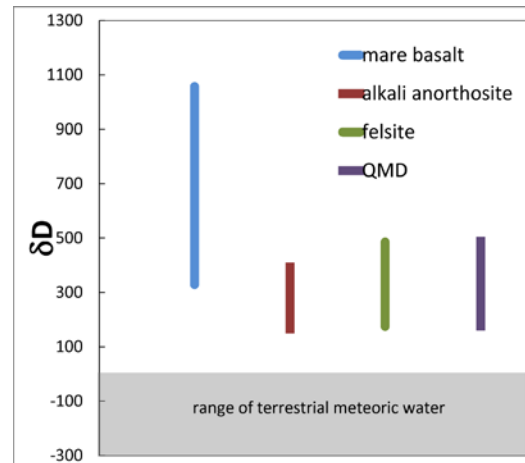

Fig. 3. Range of δD of apatite in lunar rocks. The evolved rocks have low δD in comparison to the mare basalts, but are enriched in D compared to Earth. Mare basalt, alkali anorthosite, and felsite data from [5,6]; QMD data from this work. Terrestrial δD from [11]. Lines include 2σ uncertainties.

Conclusions: 1. Mare basalts and pyroclastic glasses [1] are significantly higher in H_2O than the evolved rocks. 2. Lunar water appears to be enriched in D.

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