

## THE WATER BUDGET OF THE MOON: ESSENTIAL CONSIDERATIONS

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**Introduction:** Water (OH and H<sub>2</sub>O) occurring both ON and IN the Moon can be divided into Endogenic (present within the Moon since its formation) and Exogenic (added to the Moon, post-formation and from multiple sources).

The present study reviews the various sources that contribute to the overall lunar water budget. It also refines and expands upon previous work on lunar water, notably the relationship between apatite water versus mesostasis volume and the Fe-content versus water in NAMS.

**Exogenic Water:** An early explanation for the formation of nanophase, single-domain metallic Fe in lunar glass [1], involved the extreme reducing environment imparted by solar-wind hydrogen upon impact-produced melting of lunar regolith. This hydrogen broke Fe-O bonds to produce Fe. That this should have involved the formation of water was largely overlooked. In fact, water occurring in “rust” in lunar rocks was largely “disproven” by Taylor et al [2] as due to oxyhydration by terrestrial water. Later in 1995, Taylor et al [3] searched, with FTIR, for water in the impact-produced glass in agglutinates – but found little to none. It was only in 2012 that Liu et al. [4], was able to determine that, indeed, there is abundant water from several sources in agglutinates.

Remote-sensing of the Moon discovered the presence of water ON the lunar regolith, so-called “space dew” [5-8]. This water was reasoned to form by solar-wind proton bombardment [9], and demonstrated to be experimentally feasible [10]. In addition, water-ice in permanently shadowed craters at the poles has been reported to be mainly of cometary input [11, 12]; this ice has been the subject of much concern due to its huge quantities.

Most of the water in lunar regolith is of extra-lunar origin from three sources: a) cometary and carbonaceous chondrite input; b) hydrogen reduction of FeO [1]; and c) solar-wind proton formation [9, 10]. The water in the indigenous minerals makes a significant contribution, the fourth source.

**Endogenous Water – New Instrumentation:** Using SIMS, up to 46 ppm H<sub>2</sub>O was determined in lunar volcanic glass beads, and modeled to be after much more water lost by diffusion [13].

Starting back in Apollo time, only Cl and F were determined by EMP in lunar apatite, and OH was suspected but could not be confirmed. McCubbin et al speculated upon abundant OH in lunar apatite, but still only with EMP data [14]. At LPSC 2010, SIMS data on lunar apatites, reported values up to 7000

H<sub>2</sub>O [15-17]. This was followed by the reports of even higher quantities, up to 12,000 ppm, as well as large D/H values suggesting cometary water as the ultimate source of endogenic water, the source of much controversy [18-21]. Others have added even more apatite data [22]. To add more evidence, SIMS data measured water in melt inclusions in olivine in lunar volcanic glasses [23].

From Earth, we know that nominally anhydrous minerals (NAMs) contain significant amounts of OH [24], and although the abundances are small, NAMs are a major reservoir. This is possibly so for the Moon, as well. The most abundant water-bearing NAMs are reasoned to occur particularly in the vicinity of late-stage mesostasis [25], in which apatite grains also occur. Liu et al [25] conducted exploratory SIMS analyses for water abundances on NAMs in 3 lunar basalts (12056, 12063, 74255) and determined observable water in fayalitic olivine and Fe-rich pyroxenes. But exact contents await more rigorous study. Despite small OH contents, pyroxene, plagioclase, and olivine makes up >90 % in the majority of all lunar rocks. Small amounts of water have been shown in ferroan anorthosites [26].

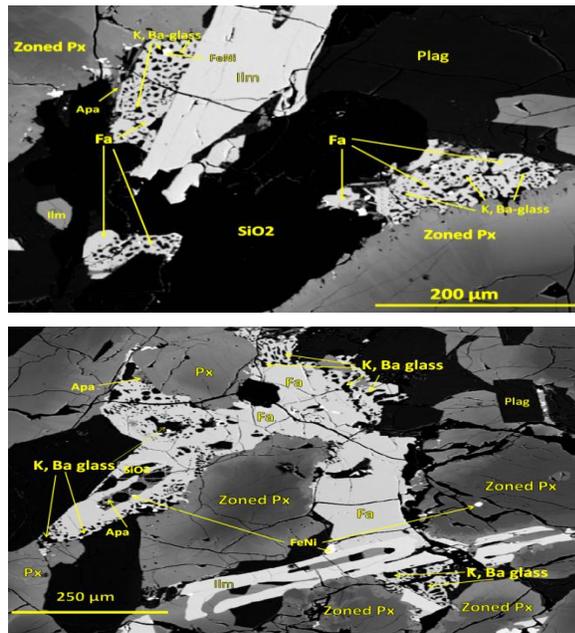
These discoveries have led to speculation of water IN the Moon up to hundreds of ppm. However, work based upon chlorine and zinc isotopes of lunar magmatic samples [27, 28] indicates the requirement of water-poor magmas and thus a “dry” Moon. This controversy is far from resolved. It is with the determination of the water content in the primary magmas that complications emerge. Adding to the controversy is that the models of lunar formation and magma-ocean solidification indicate that the final few % of the Lunar Magma Ocean (LMO), known as the urKREEP, might have had between 10 to 1000 ppm of water [29]. Apatite in KREEP-rich rock, however, is not enriched in water [20].

**Lunar Basalt Mesostasis:** The late-stage melts of the mare basalts can be used as process analogs to the KREEP portion of the LMO [30]. Lunar basalts, due to their relatively large contents of FeO (12-25 wt%) and low oxygen fugacity (IW-1) have all undergone “Fenner Trend” iron-enrichment leading to formation of mesostasis, rich in incompatible elements (REEs, LIL, H<sub>2</sub>O), and many of these mesostasis have undergone silicate-liquid immiscibility (SLI; [31]). It is the KREEPy mesostasis in mare basalts that is the focus a part of this research.

**Methods:** The method of preparation for samples 12056, 12063, and 74255 is adapted from Liu et al

[21]; chips were crushed, to reveal fresh surfaces and reduce the number of cracks and contamination; smaller grains were hand-picked. Selected grains included olivine and pyroxene mineral separates, to represent NAMs, and mixed grains that contain mesostasis. Samples 14053, 70035, 10017 and 12051, were prepared using the technique of Usui et al [32], which used rock chips mounted in indium.

Major-element characterization of the NAMs and mesostasis was completed using a Cameca SX100 EMP at the University of Tennessee. SIMS analysis was carried out at Caltech using a Cameca ims-7f GEO ion probe, with the same analytical conditions as those reported in Liu et al [21].



**Fig 1.** BSE images of two mesostases from sample 12063 illustrating variability in size and proportions of mesostases. Adjacent pyroxenes show Fe-zoning with enrichment towards mesostasis. Abbreviations: Fa, fayalite; Px, pyroxene; Plag, plagioclase; Ilm, ilmenite; K-Ba-glass, K-rich glass; Si, tridymite

**Results:** The proportion of mesostasis (Fig 1) for each sample within this study is highly variable with sample 10017 showing the highest proportion of mesostasis at nearly 8 vol% and samples 74255 and 14053 containing ~1 vol% [23].

Major-element compositions of mesostasis and NAMs are also extremely variable, not only between samples but also within one sample. Fayalite within the mesostasis of sample 12063 varies between  $Fo_{10}$  to  $Fo_4$ . Sample 12056 shows the most Fe-rich fayalite mesostasis with  $Fo_{1-2}$ . Pyroxenes which crystallized in contact with mesostasis show zoning between Fe-rich rims to more Mg-rich cores (Fig 1). For example, in sample 12056, pyroxene in contact with mesostasis exhibits  $En_{0.5-3}Wo_{3-36}$  at the rim and  $En_{41-44}Wo_{18-34}$

within the core. Pyroxene within sample 74255 is primarily enstatite-rich ( $En_{38-74}Wo_{14-41}$ ).

Preliminary results suggest a poor correlation between Fe-content of NAMs and water content. Although the most Fe-rich, late-stage minerals are water-bearing, the abundance does not directly correspond to Fe-enrichment. However, water content is thought to show variation with the size of mesostasis pocket; smaller pockets containing lower abundances as a result of the rapid diffusion of H.

**Discussion:** In the haste to infer mantle water content, the heterogeneous nature of mesostasis within a single sample has largely been overlooked. The heterogeneity has been shown in reported apatite  $H_2O$  data. For example, the OH contents in several apatites in basalt 12039 varied by a factor of 6, and the  $\delta D$  values varied by a factor up to 3 [17]. Thus, to accurately document the water content of a given sample, it is crucial to study the heterogeneity of mesostasis. The OH compositions of apatite should be weighed with respect of the individual mesostasis in which they occur, in order to determine an average OH content for a rock – and its magma.

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