

# THE SEARCH FOR WATER IN IGNEOUS LUNAR MATERIALS: A RE-ASSESSMENT OF THE LUNAR MAGMATIC VOLATILE BUDGET

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**Introduction:** Magmatic volatiles such as  $H_2O$ , F, Cl,  $CO_2$ , and S play a critical role in physiochemical processes that control thermal stabilities of minerals and melts, magma eruptive processes, and transport of economically important metals. Of these volatiles, water is the dominant magmatic volatile in terrestrial magmas both because of its abundance and its strong effect on physical properties. From samples collected thus far, it has become widely accepted that lunar magmas were depleted in magmatic volatiles, particularly dissolved water. There are two primary lines of reasoning behind the general acceptance of lunar magmas as nominally anhydrous. One is based upon micro-FTIR analyses of lunar volcanic glasses. These yielded  $H_2O$  and  $OH^-$  species concentrations below detection limits [1]. The other is linked to the currently accepted model for lunar formation, which is that of a giant impact [2]. The high-temperatures associated with this event are theorized to cause depletion in volatile elements and compounds (including  $H_2O$ ) [3, 4]. This is consistent with analysis of lunar materials for relatively volatile elements such as Na and K, which are both depleted [3, 4]. However, neither the direct evidence for dry glasses nor giant-impact volatile depletion can completely rule out the possibility that lunar magmas did contain dissolved water.

**Lunar Volcanic Glasses:** Low abundances of measured  $OH^-$  and  $H_2O$  were obtained for lunar fire-fountain glasses. This, however, does not necessarily constitute proof that the magmas from which these glasses quenched did not contain magmatic water at any stage of their evolutionary history. Volatile contents of quenched glasses only reflect magmatic volatile budgets if quenching is rapid enough to minimize degassing effects. However, most models of lunar fire-fountain eruptions predict a fumarolic gas cloud that allows sufficient time for degassing and volatile diffusion [1, 5]. It has been suggested by [5] that the fumarolic gas cloud associated with lunar fire-fountain eruptions contained at least some water, possibly in the same abundance as  $Cl^-$ , in order to facilitate precipitation of the observed Zn-sulfides on the glass surfaces. However, degassing likely begins upon ascent through the lunar crust at more elevated pressure. By the time that the very low pressure of the surface is reached, most magmas should be nearly anhydrous because water is nearly insoluble in silicate liquids at lunar surface pressures [6], and any direct information on the water contents at the higher pressure stages would be lost

from the glasses. Shock-induced devolatilization during post-eruptive meteorite and comet impacts has further potential for obscuring this information.

**Volatile Element Depletion:** The volatile element depletion prevalent in all lunar rocks makes it difficult to argue against volatile depletion during the Moon-forming impact, however this volatile depletion *does not* require that  $H_2O$  was completely absent in lunar magmas. Because the Moon-forming event occurred early on, ~10-30 Myr after the formation of the solar system [7, 8], there was still heavy bombardment of meteoritic and cometary material [9, 10]. The addition of cometary material would not likely enrich the lunar lithosphere in highly volatile elements like Pb or moderately volatile elements like Na or K (as they would likely occur in ~C1 proportions in such materials); however, enrichment in  $H_2O$  is reasonable because meteoritic and cometary bodies commonly contain significant amounts of  $H_2O$ -ice [4]. Upon impact, cometary  $H_2O$  could have been incorporated into the lunar lithosphere (particularly during the time of the magma ocean [11, 4]), which could then have been stored in magmatic minerals that crystallized from the magma ocean. Secondary melting of these minerals to form post magma-ocean lunar magmas [12-20]) would then involve incorporation of some water into the magmas through the breakdown of hydrous minerals at temperatures significantly below that needed to melt the equivalent dry assemblage. This would supersede the requirement of an enriched KREEP component to produce the extra heat needed for melting and would allow for an additional mechanism upon which post magma-ocean magmas could have been generated.

**Evidence for Dissolved Water:** Some permissive evidence does exist within lunar magmatic minerals that is permissive for the presence of more magmatic  $H_2O$  in lunar magmas than is currently accepted. Although amphiboles are rare in lunar samples collected to date, six different grains have been identified in both Apollo and Luna mission samples [21-23]. Such amphiboles require a significant amount of dissolved water at depth for stability. Apatite, a volatile-bearing phosphate, is found in a great number of lunar samples. Although this mineral has not been analyzed directly for its water content, crystal chemical considerations of its compositions show a significant amount of "missing" component in its monovalent anion site that would normally been attributed to  $OH^-$  [24] in terrestrial materials.

**Other Magmatic Volatiles:** In addition to water, CO<sub>2</sub>, halogens, and S play important and diverse roles in silicate melts. Carbon dioxide can dissolve to a significant extent in mafic silicate melts and plays an important role in eruptive processes. Fluorine is similar to water in that it enhances melt stability due to depolymerization [25]. Chlorine, on the other hand, enhances the formation of a volatile phase (i.e., vapor, fluid, brine, halide melt) even at low water contents. In an open magmatic system, this can lead to early dehydration of the residual magma. Sulfur is of particular interest because of its affinity for complexing with transition metals. These volatiles in combination with water are primarily responsible for magmatic economic deposits that may be important for long-term presence of humans on the Moon. Although extensive work has been done on the role of CO<sub>2</sub> in lunar magmas, much less is known regarding the other geologically important volatiles.

**Sample Collection:** Defining the lunar magmatic volatile budget requires a combined effort of both manned and robotic sample collection for gathering of an extensive and diverse set of lunar rock samples. Samples most needed are bedrock samples, that is, samples from below the lunar regolith. This requires (i) identification of regions excavated sufficiently by meteorite impact to expose possible bedrock and (ii) selective sampling of promising material for return. Such efforts would be greatly enhanced if some *in situ* microscopic imaging and preliminary chemical analysis were conducted of potential bedrock material in order to be more selective about choice of material for sample return and to provide additional information about material not returned. Sampling of more than one locality is important to establish the extent of compositional diversity of igneous material and provide for the development of more accurate models of lunar evolution. This may require Robotic missions similar to MER, particularly in areas with poor accessibility for manned exploration.

**Concluding Remarks:** If lunar magmas had more dissolved water than currently considered, the ramifications for our understanding of the physical and compositional evolution of the Moon would be enormous. The implications would affect our understanding of lunar mantle and crust compositional evolution, the thermal evolution of the lunar mantle, and the potential for usable natural resources. Such natural resources may include subsurface cold-traps of water-ice-rich material produced by cooling of degassed magmatic fluids. Such material would be protected from the sublimation-loss processes that dictate surface ice storage potential. This, coupled with the potential importance in understanding the other magmatic volatiles justifies expanding the collection of geologically significant

lunar samples in a concerted effort for defining the lunar magmatic volatile budget.

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