VOLATILE CONTENT OF LUNAR VOLCANIC GLASSES AND THE VOLATILE DEPLETION OF THE MOON. E. H. Hauri[1], A. E. Saal[2], Malcom J. Rutherford[2] and Diane T. Wetzel[2] [1]DTM Carnegie Institute of Washington, DC 20015 (ehauri@ciw.edu), [2]Dept. of Geological Sciences, Brown University, Providence RI 02912 (asaal@brown.edu).

Introduction: The detection of magmatic water in lunar volcanic glasses, and the high pre-eruptive abundance of water in melt inclusions from one of these samples, has provided the first definitive evidence for the accretion and retention in the Moon's interior of one of the most volatile elements in the solar system [1-3]. This surprising result, the culmination of over four decades of intensive geochemical investigation, provides a severe constraint on high-temperature models that seek to explain the formation and evolution of the Moon. With increasing consideration of the orbital dynamics of the Earth-Moon-Sun system, there now exists a very wide parameter space for physical models to explain the origin of the Moon by a giant impact, with the Moon formed from a circum-terrestrial disc of molten debris ejected largely from the Earth. This class of models can explain the Earth-Moon angular momentum and early thermal history of the Moon [4,5]. However, as currently formulated, all of these models predict wholesale melting and partial vaporization of the silicate material that enters proto-lunar orbit, and total evaporation of the most volatile elements. Thus all of these models fail to account for the presence of water in the Moon's interior.

Water in the lunar interior is at odds not only with existing formation models, it is also counter to one of the longest-standing observations in lunar geochemistry, namely the volatile-depleted nature of the Moon compared with the Earth. There exists a large body of evidence that the abundances of volatile elements in lunar basalts are present at levels that are 10-100x lower than their abundances in terrestrial mid-ocean ridge and ocean-island basalts [e.g. 6,7]. This fundamental observation was not extended to the highly-volatile atmophile elements due to a combination of factors; the barely-detectable concentrations in lunar samples, the implantation of hydrogen and other volatiles by solar wind, and suspected contamination by micrometeorite material and terrestrial atmosphere. Nevertheless, the detection and abundance of magmatic water in lunar glasses and minerals, as well as other volatiles like fluorine and chlorine [1-3], is an apparently contradictory result in the context of prior laboratory studies of lunar samples. This contradiction has led to the suggestion that perhaps the water-bearing samples are a lunar anomaly, and do not say anything particularly fundamental about the formation and evolution of the Moon [8].

Here we will demonstrate that most of these apparent contradictions – the geochemical ones at least – have arisen due to the previously unappreciated importance of a single widespread process, magmatic degassing. Degassing occurs in all eruptions of magma, with consequent release of volatile elements into an exsolved vapor phase, and has thus affected all lunar volcanic samples.

Samples and Analytical Techniques: We examined the Apollo 15 very-low Ti and low Ti glasses (15426/27) and the Apollo 17 high Ti glasses (74220) as well as the olivine-hosted melt inclusions and the host glass beads from 74220. The major element and partial volatile (H, F, S, and Cl) contents for all samples have been reported previously [1-3]. The major element compositions were obtained using a Cameca SX-100 electron microprobe at the American Museum of Natural History for the lunar glass beads and a JEOL Superprobe at the Geophysical Lab, CIW for the melt inclusions and host glass beads.

Results: At the global scale, the significance of the lunar volcanic glasses depends to some degree on their petrogenetic connection with mare basalts, which are thought to make up ~17% of the surface area of the Moon [9]. Many suites of volcanic glasses have been dated, and the histogram of their eruption ages corresponds very closely with the formation ages of Apollo mare basalts and basaltic lunar meteorites. However, Longhi [10] made the observation that many suites of volcanic glasses, upon cooling and crystallization, would produce lower-MgO basalts that matched only a subset of mare basalts in the Apollo collection analyzed at that time. And the converse was also true, that many inferred high-MgO parents of medium-TiO2 mare basalts did not match the composition of any of the lunar volcanic glass categories described by Delano [11].

Data published since 1987 includes many more analyses of major and trace elements, including the compositions of mare basalt clasts sampled from lunar soils and regolith breccias. Among fine-grained crystalline mare basalts measured for major elements, inferred parental magma compositions for those with low TiO2 (<2%) and medium TiO2 (4-6%) are well-matched by the lunar volcanic glasses. In the same way, high-TiO2 mare basalt compositions (> 6%) also can be explained by fractionation of olivine + FeTi oxides (spinel, ilmenite, armalcolite) from parent

magmas represented by high-TiO2 lunar volcanic glasses. There exists a gap in the lunar volcanic glass compositions between 1.0-3.5% TiO2 with no corresponding gap in mare basalt compositions, however there also exist a number of crystalline mare basalt compositions with 12-19% MgO within this range of TiO2. Though it can be debated whether these high-MgO mare basalts represent actual liquid compositions, it appears that fractionation of olivine, spinel, ilmenite and armalcolite from lunar volcanic glass compositions, or mixtures of such compositions, can explain the entire compositional range of lower-MgO mare basalts from all Apollo sampling sites.

The above discussion serves to emphasize an important point - that lunar volcanic glasses are not a mere anomaly produced by pyroclastic eruption of exotic lunar magma sources that happened to be particularly volatile-rich. Rather, they are the most primitive magmas produced by melting and melt migration processes in the lunar mantle, and they appear to be parental to the entire compositional spectrum of lunar mare basalts. As such they provide the most direct information about the volatile content of the lunar interior in the time period after solidification of the lunar magma ocean.

Using the highest volatile element abundances in the lunar melt inclusions from 74220, and average trace element abundances of orange glass from 74220, we can estimate volatile/refractory element ratios for the mantle source of 74220 magma: H_2O/Ce (60), F/Nd (4), S/Dy (90) and Cl/Nb (0.17). These volatile/refractory ratios are lower limits due to the fact that the melt inclusions define a degassing trend, so the volatile element abundances themselves are lower limits on the volatile content of primary 74220 magma.

Conclusions: The derived volatile/refractory ratios for the 74220 primary magma are at most only 2-10 times lower than the same values for the Earth, and these ratios are not expected to change significantly during LMO crystallization, save for the effects of LMO degassing which appears to have affected KREEP, as reflected in low H_2O contents of apatite from KREEP-related samples [12]. The mild volatile depletion of H_2O, F, S and Cl are consistent with prior estimates of the Moon's volatile depletion derived from the geochemistry of lunar volcanic glasses [13], and is also consistent with the Rb/Sr and U/Pb ratios of the lunar interior inferred from Sr and Pb isotope studies of well-dated lunar samples [e.g. 14,15]. Overall, these observations indicate that the Moon was only moderately depleted in volatile elements at the time of the lunar magma ocean, and may have even been similar to the Earth considering that our derived volatile/refractory element ratios are lower limits.

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