THE ABUNDANCE AND ISOTOPIC COMPOSITION OF HYDROGEN IN LUNAR MELT INCLUSIONS.

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Introduction: Since the first report of the detection of water in lunar volcanic glasses (LVG) [1], the concentration and origin of this water is vigorously debated. Indeed, the bulk Moon H_2O content estimated on the basis of refractory elements abundances (Fe/Zn) points towards an anhydrous Moon (<1ppm H_2O) [2], while *in-situ* measurements on various lunar phases, such as olivine-hosted melt inclusions (MIs) [1, 3-4], LVG [1,5], plagioclase [6] and apatite [7-8] strongly suggest a wetter Moon, with estimates ranging from ~1 to 450 ppm H_2O for the bulk silicate Moon (BSM) [1,3-6]; albeit still depleted relative to the bulk silicate Earth. Among all lunar phases, silicate-hosted MIs are thought to be more robust for preserving pre-degassed volatiles signature compared to later-formed phases such as apatite, although syn- and post-eruption processes such as post-entrapment crystallisation (PEC), as well as, secondary processes such as cosmic ray spallation effects, need to be carefully considered in the case of MIs.

In terms of hydrogen isotopic composition (δD), multiple lunar reservoirs have been identified, with values ranging between -300 and +300 ‰ [6-9]. As the parent magma may have undergone significant degassing by the time apatites crystallised, MIs potentially offer an opportunity to determine the juvenile δD value of the mantle source regions of mare basalts. Moreover, inferring the H_2O contents of parent magmas using igneous apatites is non-trivial compared to silicate-hosted MIs. Only a few δD values have been reported for lunar MIs so far. 74220 and 74002 MIs and glassy beads recorded a juvenile lunar δD between +187 and +274‰ [10-11]. A study on Apollo 12 basaltic MIs [12] reported a lower range of values from -183 to +138‰ (these values are not corrected for spallation and thus should be viewed as upper limit), arguing for D/H exchange with the lunar regolith during cooling of the Apollo 12 olivine basalts. We have analysed 56 MIs hosted in either olivine or pyroxene from nine different basalt types collected from four Apollo landing sites, in order to constrain the initial H_2O abundance and H isotopic signature of the mantle source regions and document any lateral heterogeneity for H in the lunar mantle as sampled by mare magmas.

Samples: The samples selected are low-K ilmenite basalts 10020 and 10058, low-Ti Apollo 12 suite basalts 12002, 12004, 12008, 12020 and 12040, high-Al basalt 14072 and low-Ti basalt 15016. We selected some samples (10020 and 15016) for which H_2O abundances were previously measured in homogenized and in some crystallised olivine-hosted MIs [4]; while H isotopic compositions and abundances have been reported for MIs in 12040 [12]. Other criteria for sample selection were based on the confirmed presence of MIs as well as mare basalts with a range of exposure ages (i.e. 21 to ~400 Ma).
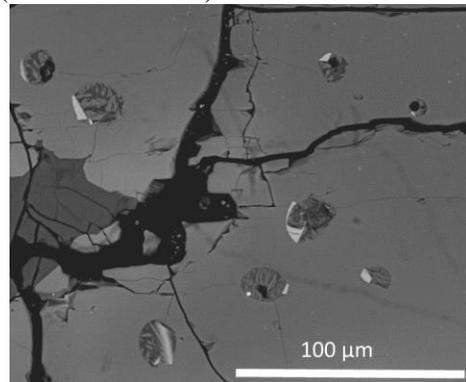

Figure 1: Back Scattered Electron (BSE) image of ol-hosted MI assemblage in 12004,51.

Analytical methods: Olivine and pyroxene phenocrysts containing MIs were identified using optical microscopy and a FEI Quanta 200 3D scanning electron microscope (Fig. 1) at The Open University. Chemical composition of MIs and their hosts were also measured using Cameca SX 100 electron micro-probe.

Hydrogen concentration and isotopic composition. Measurements of D/H ratios and H_2O concentrations in the olivine (ol-) and pyroxene (px-) hosted MIs were conducted using the Cameca NanoSIMS 50L at The Open University. The H^-, D^-, $^{13}C^-$ and $^{18}O^-$ secondary ions were measured using a Cs^+ primary beam of 550 pA. $^{13}C^-$ was used to monitor contamination on the sample. The primary beam was rastered over a 8×8 µm². Beam blanking limited data collection to the central 4×4 µm² (25%) of the rastered area, with each measurement consisting of 2000 cycles (~20 mins).

Results: Altogether, 42 ol-hosted MIs and 14 px-hosted MIs were analysed. The measured H_2O contents range from 2±1 to 194±51 ppm and from 6±1 to 212±27 ppm in ol- and px-hosted MIs, resp. (corrected for PEC - Fig. 2). δD values in these 9 samples cover a relatively large range of values, from -912±553‰ to +1942±611 ‰ (after spallation correction). In fact,

each sample generally display a significant range too, displaying both positive and negative trends in H_2O-δD space (Fig. 2). We can group samples into three groups: Apollo 11 samples, Apollo 12 samples and "unusual" samples (i.e. 12040, 14072 and 15016), which exhibit very low δD values following positive trends.
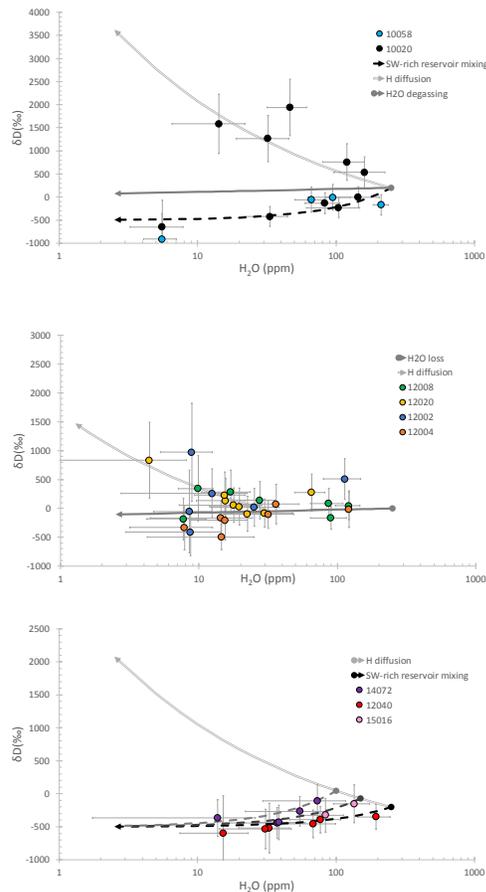

Figure 2: H_2O (ppm) vs. δD (‰) for lunar basaltic silicate-hosted melt inclusions.

Discussion: *Syn- and Post-eruption processes altering the MI H_2O-δD signature.* The large variations documented for both δD values and H_2O abundances among the lunar MIs, as well as the trends observed in H_2O-δD systematics (Fig. 2), suggest that some processes have modified the primordial H inventory and isotope signature of these MIs. The apparent relative slow cooling of lunar MIs, reflected by their high PEC rate, as well as steep negative trends in H_2O-δD space (Fig. 2) for Apollo 11 and Apollo 12 samples, are concordant with diffusional proton loss. Melt inclusions from Apollo 12 basalts also show a slightly positive trend, concordant with shallow degassing of H_2O prior to MI entrapment. Finally, steeper positive trends are observed for Apollo 11 MIs as well as the three "unusual" samples 12040, 14072 and 15016. Processes that

could account for a steep H_2O-δD positive trend are limited, and mixing with a solar wind (SW) rich reservoir seems the most plausible explanation. Indeed, 12040 and 15016 basalts have very large CRE ages, and their apatites exhibit lower δD than typical mare basalts, which have been interpreted in the context of assimilation of SW implanted lunar regolith [13]. Sample 14072, with an CRE age of only 21 Ma, is one of the most reduced basalts retrieved from the Moon, where the reducing agent was suggested to be the solar wind [14]. As such, SW seems to be an important contributor of H into lunar magma. Based on modelling for the effects of all these processes on our set of studied mare basalts, we estimate initial δD values of basaltic parent melts between -200‰ to +200‰, concordant with a chondritic hydrogen isotopic signature for the Moon.

Hydrogen concentration in lunar mantle. The range in H_2O contents in ol-hosted MIs (2-212 ppm) is in good agreement with the range of 5-131 ppm measured in 10020 and 15016 homogenized MIs [4] and the range of 28-156 ppm in crystallised 12040 MIs [12]. The highest water content recorded by silicate-hosted MI in each sample varies from 65 ppm (in 12020) to 212 ppm (in 10058). For instance a glassy MI found in 12040 recorded 194 ppm H_2O content. As such, these values are likely to be representing the lower limit because of H loss by various processes. We considered the highest H_2O content measured (i.e. 212±27 ppm) as the closest to the pre-eruptive abundance of the mare basaltic parent melt. Assuming 3 to 30% partial melting in the lunar mantle, we estimate a water content for the BSM in the order of 10 to 50 ppm. This range is towards the lower range of previous estimates (~1-450 ppm) and should be seen as a lower limit because of the likely loss of H and H_2O from lunar MIs.

This study highlights the fact that MIs are not entirely closed system with respect to H gain and/or loss and associated H isotope fractionation processes. However, they remain a good proxy to disentangle various magmatic and secondary processes as long as several (>5) MIs are analysed in each studied sample.

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