The hydrogen isotopic composition of lunar melt inclusions: An interplay of complex magmatic and secondary processes

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Abstract

Since the discovery of water (a term collectively used for the total H, OH and H₂O) in samples derived from the lunar interior, heterogeneity in both water concentration and its hydrogen isotopic ratio has been documented for various lunar phases. However, most previous studies have focused on measurements of hydrogen in apatite, which typically forms during the final stages of melt crystallisation. To better constrain the abundance and isotopic composition of water in the lunar interior, we have targeted melt inclusions (MIs), in mare basalts, that are trapped during the earliest stages of melt crystallisation. Melt inclusions are expected to have suffered minimal syn- or post-eruption modification processes, and, therefore, should provide more accurate information about the history of H in the lunar interior. Here, we report H /¹⁸O measurements as calibrated water concentrations, and hydrogen isotope ratios obtained by secondary ion mass spectrometry (SIMS) in a large set of basaltic MIs from Apollo mare basalts 10020, 10058, 12002, 12004, 12008, 12020, 12040, 14072 and 15016. Our results demonstrate that partially crystallised MIs from lunar basalts and their parental melts were influenced by a variety of processes such as hydrogen diffusion, degassing and assimilation of material affected by solar-wind implantation. Deconvolution of these processes show that lunar basaltic parental magmas were heterogeneous and had a broadly chondritic hydrogen isotopic composition with δD values varying between −200 and +200‰.

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1. INTRODUCTION

Since the discovery of indigenous water in lunar volcanic glasses (Saal et al., 2008), the abundance and origin of water in the lunar mantle has been vigorously debated (it is important to note that the term “water” used here collectively refers to all major forms of hydrogen (i.e., H, OH, H₂O), being measured in the target lunar mineral/phase). Estimates for the bulk-Moon H₂O content (calculated as 1000 μg/g) based on measured ratios of moderately volatile elements (e.g., Zn/Fe) in lunar samples and volatilities of respective elements point to an anhydrous Moon (<1 μg/g H₂O) (Albarede et al., 2015). On the other hand, measurements of water (H, OH, H₂O) abundances in lunar volcanic glasses (LVG) and olivine-hosted MIs (Saal et al., 2008; Hauri et al., 2011; Füri et al., 2014; Chen et al., 2015; Ni et al., 2019), plagioclase (Hui et al., 2013, 2017), and apatite (Boyce et al., 2010; McCubbin et al., 2010a, 2010b; Greenwood et al., 2011; Barnes et al., 2013, 2014; Tartèse et al., 2013, 2014; Boyce et al., 2015) indicate a H₂O-richer Moon, with estimates ranging from ~1 to ~450 μg/g.
g H₂O for at least some portions of the lunar mantle (McCubbin et al., 2010b; Hauri et al., 2011, 2015; Hui et al., 2013, 2017; Tartèse et al., 2013; Füri et al., 2014; Chen et al., 2015; Ni et al., 2019). This range of water content for the lunar mantle is still an order of magnitude lower than some estimates for the water content of the bulk silicate Earth (ca. 1000–3000 µg/g H₂O (Marty, 2012); 1100 ± 220 µg/g H₂O (Palme and O'Neil, 2014); 3900 ± 12700 /C0 µg/g H₂O (Peslier et al., 2017; and ref. therein)). Nevertheless, the upper end of the estimated range of water content for the lunar mantle is consistent with some estimates of the water content of the Earth’s primitive mantle (ca. 300 ± 100 µg/g (Halliday, 2013); 268 ± 134 µg/g (Zhang, 2014)). Overall, Taylor (2014) states that it would seem unusual if the water content of the Moon were similar to that of Earth’s mantle. It has also been suggested that water is heterogeneously distributed among the different lunar reservoirs (Anand, 2010; McCubbin et al., 2011; Robinson and Taylor, 2014), with source regions for mare basalt and pyroclastic volcanic samples being richer in water compared to the source regions for non-mare intrusive rocks (Barnes et al., 2014; Robinson et al., 2016). As a result of the incompatible nature of H during crystallisation of major silicate minerals such as olivine, pyroxene, and plagioclase, H₂O enrichment is expected in later formed products of the lunar magma ocean (LMO) crystallisation. The apparent discrepancy between the water contents of mare and non-mare rocks is thus at odds with non-mare materials being formed from late-stage LMO products. Differences in water abundance between mare and non-mare source regions may be linked to their respective ages of formation; the younger mare basalts and pyroclastic deposits having incorporated late-delivered components (Tartèse and Anand, 2013; Barnes et al., 2016). Another possible explanation for the discrepancy between the water contents of mare and non-mare material may be related to degassing of H₂O towards the end of the LMO crystallisation leaving late-stage LMO products depleted in H₂O (Hui et al., 2017). Among basaltic and volcanic products, the higher water concentration of the high-Ti 74220 primitive melt, calculated from diffusion modelling of volcanic glasses (Saal et al., 2008) and recorded in their MIs (Hauri et al., 2011), has been used to calculate a water content for their mantle source region of ~100 to 300 µg/g H₂O. This sample has been considered an anomaly, and, thus not a representative of the lunar interior, implying local heterogeneities in the lunar mantle (Albarède et al., 2015). However, recent work on MIs from Apollo 11, Apollo 12, and Apollo 15 mare basalt suites are consistent with a lunar mantle with a water content of ~80–100 µg/g (Chen et al., 2015; Ni et al., 2019).

The primordial hydrogen isotopic composition of indigenous lunar water has been inferred to be between ~281 ± 100‰; (H Isotopic composition is reported using the δD notation, which represents the deviation from the H isotope composition of terrestrial oceans in parts per thousand, following δD = [(D/TVSMOW)/D/HVSMOW] × 1000, where D/HVSMOW = 15.76 × 10^-6; Hagemann et al., 1970; Gonfiantini, 1978). Hydrogen isotope measurements on lunar volcanic glasses suggest an initial source with a δD value between +187 ± 19‰ and +274 ± 42‰ (Saal et al., 2013; Füri et al., 2017 and ref. therein). Apatite from mare basalt generally have δD values > +500‰ (Barnes et al., 2013; Tartèse et al., 2013), which have been interpreted as resulting from the fractionation of D/H ratios in late-stage basaltic melts after extensive H₂ degassing from an initial H isotope composition similar to carbonaceous chondrites. Apatite from non-mare materials such as the Mg-suite and alkali-suite display lower average δD values of ~281 ± 49‰ (Barnes et al., 2014). In case of evolved-rocks such as quartz monzodiorites (QMDs), from the Apollo 15 collection, apatite record some of the lowest δD values ever reported for lunar samples (~754 ± 57‰; Robinson et al., 2016), suggesting that H isotopes in their magmas were not fractionated by H₂ degassing, and that there may exist some local heterogeneities in terms of water reservoirs in the lunar interior (Robinson and Taylor, 2014; Robinson et al., 2016). The whole picture is complicated by the fact that magmatic and secondary processes such as degassing, spallation reaction producing D, and/or incorporation of regolith, enriched in solar wind H (Stephant and Robert, 2014; Treiman et al., 2016; Singer et al., 2017), as well as speciation of H in lunar melts (Elkins-Tanton and Grove, 2011; Renggli et al., 2017) can all potentially induce δD variations among lunar samples, and could be, in part, responsible for the apparent δD heterogeneity observed among various lunar reservoirs. For instance, Hui et al. (2017) recently proposed that heterogeneous δD values among different lunar reservoirs could result from degassing of the LMO, with the deeper and undegassed lunar interior being characterised by a δD value of ~281 ± 49‰, as recorded by apatite in Mgsuite norites (Barnes et al., 2014), and a degassed interior reservoir characterised by δD values around +310 ± 110‰, as measured in plagioclase from ferroan anorthosite 60015 (Hui et al., 2017). Desch and Robinson (2019) proposed an alternative hypothesis to explain the heterogeneity in δD among different lunar reservoirs by suggesting that the Moon-forming impactor Theia, carried a nebular H isotope signature (i.e., −865‰; (Geiss and Gloeckler, 1998)), which might be reflected in the very low-δD values measured in some of Apollo 15 QMDs (~754 ± 57‰; Robinson et al., 2016).

Among the variety of lunar phases studied so far, MIs are potentially the ideal candidates for unravelling the abundance and H isotopic composition of primordial lunar water. Melt inclusions are small droplets of silicate melts trapped during phenocryst growth at magmatic pressures and temperatures, which theoretically shield them from subsequent degassing or crystal fractionation effects during the eruption and emplacement of a magma (Walker et al., 1976; Roedder, 1979; Lowenstern, 2003; Métrich et al., 2008; Moore et al, 2015; Cannatelli et al., 2016). As such, MIs supposedly record the volatile composition of the magma (such as H₂O, Cl, CO₂, S, F) at the time of melt entrapment.

The speciation of hydrogen in amorphous silicates such as melt inclusions can occur in different forms (e.g., H, H₂, OH, H₂O, CH₄, H₂S, NH₃) depending on parameters such as pressure, temperature, melt composition, the concentra-
tions of other volatiles (C, N, F, Cl, S), water and oxygen fugacities (Holloway and Blank, 1994; Elkins-Tanton and Grove, 2011; Peslier et al., 2017; Renggli et al., 2017; Dalou et al., 2019; Grewal et al., 2020). In fact, H₂O can be dissolved as OH⁻ with decreasing temperature of the melt (Nowak and Behrens, 1995). Given the oxygen fugacity of lunar samples, Elkins-Tanton and Grove (2011) stated that atomic H will be as abundant as H₂O in lunar melt phases, while Renggli et al. (2017) found that H₂ is the most abundance hydrogen species in lunar gas. Grewal et al. (2020) stated that while much of H would be present in N-H or C-H bearing species, H would also be present in the form of OH in the silicate melt if the bulk H content of the silicate melt is much higher than the bulk N content. It is important to note that for SIMS measurements, it is not possible to confirm the speciation of hydrogen. As such, even though hydrogen might be distributed among different species in the same melt, throughout this paper, we have chosen to report H²/¹⁸O measured in lunar MIs as H₂O or water.

A major challenge in using MIs for inferring the volatile composition of a melt, and especially hydrogen, is that some magmatic and secondary processes can alter both the H₂O content and δD value of a MI after entrapment. This, issue can be further compounded by the hydrogen speciation, that could also induce some isotopic fractionation. Indeed, H₂O loss (i.e., shallow level degassing; Hauri, 2002), H⁺ diffusion through the host (Hauri, 2002; Massare et al., 2002; Severs et al., 2007; Gaetani et al., 2012; Bucholz and Gaetani, 2013; Chen et al., 2013; Ni et al., 2017), as well as post-entrapment crystallisation (PEC) (Danyushevsky et al., 2002; Steele-MacInnis et al., 2011) could alter the original water budget and hydrogen isotopic signature. However, because these processes affect both H₂O and δD, they produce systematic variations that can be identified using a coupled H₂O-δD dataset for MIs.

Despite many challenges, water concentrations in MIs have been used for investigating H₂O abundances in planetary bodies such as the Earth (e.g., Esposito et al., 2012; Hauri, 2002; Wallace, 2005), Mars (e.g., Giesting et al., 2015; Usui et al., 2012) and the Moon (e.g., Chen et al., 2015; Saal et al., 2013; Hauri et al., 2011; Singer et al., 2017; Ni et al., 2019; Greenwood et al., 2019). Lunar basalts from Apollo 11 and Apollo 12 are known to contain abundant MIs, as first demonstrated in the pioneering work of Roedder and Weiblen (1970, 1971). However, the first analysis of water concentration and δD in lunar MIs was achieved only recently, in sample 74220 (Hauri et al., 2011; Saal et al., 2013). Results indicated an initial H₂O content of ~100 to 300 µg/g (Hauri et al., 2015) for the lunar mantle, associated with a δD value of +187 ± 19‰ (Saal et al., 2013). Results from these MIs are comparable to those obtained on volcanic glasses in sample 74002 for which a δD value of +274 ± 42‰ was reported by Fürri et al. (2017). Based on H₂O/Ce ratios measured in MIs from various mare basalts, water concentrations of around ~80–100 µg/g have been estimated for their lunar mantle source regions (Chen et al., 2015; Ni et al., 2019), which are consistent with estimated water concentrations in the mantle source regions of pyroclastic glasses. So far only two studies have reported the D/H ratio of water in MIs in mare basalts (Apollo 12 basaltic suite; Singer et al., 2017; Greenwood et al., 2019). These studies reported a range of δD values (−183 ± 212‰ to +138 ± 61‰) all of which were lower than δD values recorded in pyroclastic glasses and their MIs (note that these values are not corrected for spallation-produced D and, therefore, should be viewed as an upper limit). These lower δD values in mare basalt MIs were interpreted in terms of an exchange of deuterium and hydrogen with the lunar regolith during cooling of the Apollo 12 olivine basalts (Singer et al., 2017; Greenwood et al., 2019).

To develop a comprehensive understanding of D/H ratios in MIs from mare basalts, and to provide more robust constraints on the D/H ratio(s) of water in mare-basalt source regions, we have analysed the H concentration and its associated H isotopic composition in olivine- and pyroxene-hosted MIs from nine different samples from four Apollo missions. We converted the H²/¹⁸O ratio measured into equivalent H₂O concentration, as stated previously. These data are then used to constrain the abundance and source of H in their respective parent-melt and investigate any variations among respective volatile reservoirs. We have also analysed water abundance and isotopic composition in apatite from the same samples where literature data were not available in order to investigate the relationship between water abundance and D/H ratio between earlier-formed MIs and later-formed apatite in a given sample.

2. MATERIALS AND METHODS

2.1. Standards

Several terrestrial standards were used for water abundance calibrations and instrumental mass fractionation (IMF) corrections of data acquired on MIs and apatite. The first set of standards, used for MI analyses, includes: San Carlos olivine, which was used effectively as a dry standard for background monitoring; terrestrial basaltic glasses from the Southwest Indian Ridge DR5, DR15 and DR20 for IMF correction and for H₂O calibration. These standards were mounted in 10 mm diameter aluminium mounts filled with indium, following the protocol established in previous studies (Aubaud et al., 2007; Mosenfelder et al., 2011). As was done previously in several studies of hydrogen in nominally anhydrous minerals (NAMs) (Aubaud et al., 2007; Hauri et al., 2002; Koga et al., 2003; Mosenfelder et al., 2011; Tenner et al., 2009), these standards were baked overnight at 115 °C before being pressed into an indium mount. The second set of standards for phosphate analyses includes San Carlos olivine, for background monitoring, and apatites Ap003, Ap004 and Ap018 (McCubbin et al., 2012). These standards were also mounted in indium, in the same manner as the first set. Both sets of standards were baked in an oven at ~50 °C overnight for ~17 h before being gold-coated and introduced into the NanoSIMS. The chemical composition, H₂O concentrations and δD values of the terrestrial standards are provided in supplementary Table S1.
2.2. Samples

Forty-two olivine-hosted MIs and fourteen pyroxene-hosted MIs were selected from nine polished thin sections of Apollo basalt samples 10020,31; 10058,254; 12002,562; 12004,51; 12008,18; 12020,8; 12040,44; 14072,13 and 15016,14; prepared at NASA Johnson Space Center using a water-free medium. A selection of backscattered electron [BSE] images are presented in Fig. 1 (a larger set of BSE images can be found in supplementary Fig. S1). The samples were selected based on the probability of finding MIs. Samples from the Apollo 12 collection were thus selected since they have been extensively studied previously for MIs (Roedder and Weiblen, 1971; Bombardieri et al., 2005; Chen et al., 2015; Singer et al., 2017). Samples from other Apollo landing sites (i.e., Apollo 11, 14, 15) were also selected to expand the spatial coverage of the sample set and explore any potential variations among their hydrogen abundance and isotopic composition. For inter-laboratory comparisons, a few samples in which MIs were analysed in previous studies were also selected (Chen et al., 2015; Ni et al., 2017; Singer et al., 2017).

Samples 10020 and 10058 are high-Ti/low-K basalts (Fig. 2), with 10020 having a fine-grained texture and 10058 having a coarser-grained texture. Their cosmic ray exposure (CRE) ages are 130 Ma and 70 Ma, respectively (Guggisberg et al., 1979). In 10020, the presence of MIs in olivine phenocrysts has been documented in the literature (Meyer, 2009). In contrast, olivine is rare in 10058 (Beatty and Albee, 1978), and therefore only pyroxene-hosted MIs could be studied. The H₂O content and δD values of some apatite grains in 10058 were reported previously by Tartèse et al. (2013).

Of the Apollo 12 suite, five samples have been investigated in this study: 12002, 12004, 12008, 12020, 12040. All of these basalts are low-Ti basalts (Fig. 2). The medium-grained porphyritic olivine basalt 12002 has a CRE age between 92 Ma (Bogard et al., 1971) and 161 ± 20 Ma (Alexander, 1971). The older CRE age was chosen for spallation correction because Füri et al. (2017) showed that CRE ages of most Apollo samples have likely been underestimated. The porphyritic olivine basalt 12004 has 40% of its mass represented by olivine and pyroxene phenocrysts (Meyer, 2009). Hintenberger et al. (1971) determined CRE ages for 12004 using 3He (60 Ma), 21Ne (53 Ma) and 38Ar (45 Ma). It has been recalculated recently by Füri et al. (2017) with values spanning between 60 and 70 Ma; we selected an average exposure age of 66 ± 12 Ma. Basalt 12008 is composed of olivine phenocrysts surrounded by dendritic pyroxenes. The presence of circular olivine-hosted MIs has been reported in this sample (Meyer, 2009). Stettler et al. (1973) determined a 38Ar exposure age of 50 Ma. Basalt 12020 is a medium-grained olivine microgabbro (Klein et al., 1971). Its 21Ne exposure age was estimated first at 71 Ma (Hintenberger et al., 1971) and then recently re-estimated between 73 Ma and 111 Ma (Füri et al., 2017). We selected an average CRE age of 91 ± 15 Ma for this study. Low-Ti basalt 12040 is a slowly cooled olivine basalt (Walker et al., 1976) with a high proportion of mafic minerals. The widespread occurrence of MIs in olivine and pyroxene has been highlighted since the return of this sample (Newton et al., 1971). As such, H in MIs in 12040 has been studied before (Chen et al., 2015; Singer et al., 2017). However, basalt 12040 has a very old CRE age of ~285 ± 50 Ma (Burnett et al., 1975). Additionally, previous studies involving H₂O-δD systematics in apatite and MIs have raised the possibility that this sample may have incorporated solar wind hydrogen (Boyce et al., 2015; Treiman et al., 2016; Singer et al., 2017).

High-Al basalt 14072 is an olivine basalt with medium-sized olivine phenocrysts, also classified as a low-Ti basalt (Fig. 2). The Apollo 14 mission landed on the Fra Mauro Formation, which is part of the ejecta blanket that formed from the excavation of the Imbrium Basin at ~3.93 Ga (Nemchin et al., 2009; Snape et al., 2016). The 38Ar exposure age of sample 14072 has been estimated to be 21 Ma (York et al., 1972).

Finally, 15016 is a medium-grained, vesicular, olivine-normative (Meyer, 2009) low-Ti basalt (Fig. 2). Similar to sample 12040, it is a slowly cooled basalt. The CRE age of 15016 has been re-evaluated recently by Füri et al. (2017) to be between 378 ± 66 and 422 ± 73 Ma. As such, we decided to use the average of 400 ± 73 Ma for this study. The H₂O abundances and δD values of apatite grains in 15016 have been reported previously (Barnes et al., 2019).

Almost all of the studied forty-two olivine-hosted MIs and fourteen pyroxene-hosted MIs are partially crystallised, with a few exceptions of “glassy” MIs (only four MIs have a post-entrapment crystallisation (PEC) percentage, i.e., the percentage of daughter minerals, <10%). While some previous workers have argued in favour of homogenisation experiments on MIs in order to ascertain the initial H₂O abundances of their melts (Esposito et al., 2012; Chen et al., 2015), a recent study on MIs from Apollo 12 basalts has shown that H₂O contents, measured in partially-crystallised MIs, do not exhibit significant variations compared to glassy ones (Singer et al., 2017; and references therein).

2.3. Scanning Electron Microscope and Electron Microprobe

Backscattered electron imaging (Fig. 1 – see Fig. S1 for BSE images of all MIs) and chemical characterisation of MIs and their host silicates in the studied Apollo samples were performed using the FEI Quanta 200 3D scanning electron microscope (SEM) and with the Cameca SX-100 electron microprobe (EPMA) at The Open University. Major-element mineral chemistry was measured using a 15 kV accelerating voltage and a 20nA current. The beam size was set to 1 μm for silicates and was defocused to 3 μm for MIs. The measured chemical compositions of MIs are presented in supplementary Table S2. The size of MIs ranges from 5 to 120 μm in diameter (cf. Table 1). In order to avoid potential migration of volatiles (Goldoff et al., 2012), EPMA analyses were performed after NanoSIMS analyses. However, because of the small sizes of most MIs, the cratered spots created during NanoSIMS analysis prevented or compromised EPMA data collection on most
Fig. 1. A representative selection of BSE images for olivine-hosted and pyroxene-hosted MIs in the studied Apollo thin sections. (A) Pyroxene-hosted MI #5 in sample 10058; (B) Pyroxene-hosted MI #1 in sample 12002; (C) Olivine-hosted MI #27 in sample 12004; (D) Olivine-hosted MI #6B in sample 12008; (E) Olivine-hosted MI #10 in sample 12020; (F) Assemblage of two olivine-hosted MIs #4A and #4B in sample 12040. MI #4A shows a shrinkage bubble; (G) Olivine-hosted MI #15 in sample 14072; H) Olivine-hosted MI #23 in sample 15016.
MI. Consequently, some EPMA analyses have low oxide totals (95 to 98%).

2.4. NanoSIMS

2.4.1. Melt inclusion measurements

Measurements of D/H and $^{18}$O ratios (reported in terms of equivalent H$_2$O concentrations) in the olivine- and pyroxene-hosted MI were performed with the Cameca NanoSIMS 50L at The Open University in two sessions (10020, 12004, 12040, 14072 and 15016 during session 1; 10020, 10058, 12002, 12008, 12020 during session 2). The H$^+$, D$^+$, $^{13}$C$^-$ and $^{18}$O$^-$ secondary ions were measured using a Cs$^+$ primary beam of 550 pA. The ion $^{13}$C$^-$ was used to monitor any potential terrestrial contamination and any crack(s) in the analysis area. The primary beam was rastered over an 8 $\mu$m $\times$ 8 $\mu$m area. Each analysis surface area was divided into 64 $\times$ 64 pixels, with a counting time of 0.132 ms per pixel. Blanking was performed, and ion counts from only the 4 $\mu$m $\times$ 4 $\mu$m (25%) interior of the rastered areas were recorded, with each measurement consisting of 200 cycles. Prior to each analysis, the surface was pre-sputtered for 2 min using the same primary beam current. Vacuum in the analytical chamber was maintained at or below 5 $\times$ 10$^{-10}$ Torr throughout both sessions. Samples were kept under high vacuum for at least 24 h prior to analysis. An electron gun was used for charge compensation and tuned to an electron current of ~1800 nA. A H$^+$/H$^{18}$O$^-$ vs. H$_2$O calibration curve, based on analyses of DR5, DR15, and DR20 basaltic glasses, was used to determine H$_2$O concentrations in MIs. Background for H$_2$O concentrations was corrected using the average H$^+$/H$^{18}$O$^-$ ratio of six analyses on San Carlos olivine, estimated to be 10 ± 2 $\mu$g/g and 13 ± 3 $\mu$g/g, for sessions 1 and 2, respectively. Errors estimated for H$_2$O concentrations account for the errors from counting statistics, from the background estimation and from uncertainties on the calibration lines. Slopes of the calibration lines were calculated using the R programming language for statistical computing, which yielded 8.71 ± (0.63) $\times$ 10$^{-5}$ (n = 17, ±2SD) and 1.18 (±0.11) $\times$ 10$^{-5}$ (n = 12, ±2SD) for sessions 1 and 2, respectively (Fig. S2).

Most MIs in Apollo samples are partially crystallised. Hence, their measured volatile contents had to be corrected accordingly, using the established method of post-entrapment crystallisation (PEC) correction. We calculated the PEC percentage, i.e., the percentage of crystallised daughter minerals in the MI, in each case, using the Petrolog3 program, following the method described in Danyushevsky and Plechov (2011). The forsterite (Fo) contents (or Mg# of pyroxene) of host phenocrysts, coupled with their bulk-rock composition, were used to calculate the percentage of PEC in each case (c.f. Table S2). Using these PEC values, water abundances were corrected following equation (1):

$$\text{H$_2$O$_{corrected}$} = \left(\frac{100 - \text{PEC}\%}{100}\right) \times \text{H$_2$O$_{measured}$}$$ (1)

The calculated PEC percentages alongside corrected water contents are given in Table 1, and the latter are used in the rest of the manuscript.

For hydrogen isotopic measurements, an IMF factor $\alpha$ of 1.10 ± 0.06 (session 1; n = 17, ±2SD) and 1.01 ± 0.05 (session 2; n = 12, ±2SD) was calculated based on repeated analyses of the MORB standards. The measured D/H ratios are expressed using the $\delta$D notation defined earlier. The raw measured D/H ratios were corrected for IMF, followed by corrections for the background and for the effects of spallation reactions, using a D production rate of 2.17 $\times$ 10$^{-12}$ mol D/g/Ma (Füri et al., 2017). This production rate has been estimated based on H$_2$O-poor olivine and is appropriate for silicates and their MIs (see Füri et al., 2017). As such, all discussion on MIs in this manuscript

Fig. 2. Bulk-rock MgO vs TiO$_2$ composition of the studied Apollo samples. Bulk-rock compositions are from Rhodes and Blanchard (1980) for 10020 and 10058; Willis et al. (1971) for 12002; Maxwell and Wiik (1971) for 12004; Rhodes et al. (1977) for 12008; Kushiro and Haramura (1971) for 12020 and 12040; Taylor et al. (1972) for 14072; Rhodes and Hubbard (1973) for 15016. The full range of compositional variations recorded in basalts from Apollo collections studied here (Apollo 11, 12, 15 and 17) is highlighted using elliptical outlines.
Table 1
Water content and hydrogen isotopic composition of lunar MIs in Apollo samples 10020, 10058, 12002, 12004, 12008, 12020, 12040, 14072, 15016. H2O measured and H2O corrected from PEC are included. δD_corrected corresponds to δD corrected for IMF and background. δD_spallation are corrected using the D production rate of Füri et al. (2017). PEC (%) correspond to the percentages of daughter minerals in the MIs and have been calculated using Petrolog3 (see text for details). Mg# of the host has been calculated as Mg# = Mg/(Mg + Fe). MI diameter has been measured taking the largest diameter of the MI.

| Sample/Host | MI #  | H2O measured (µg/g) | H2O corrected (PEC) | 2σ | δD (%) corrected | 2σ | δD (%) spallation | 2σ | PEC (%) | Host Mg# | MI diameter (µm) |
|-------------|-------|---------------------|---------------------|-----|-----------------|-----|-------------------|-----|---------|----------|-----------------|
| 10020.31    |       |                     |                     |     |                 |     |                   |     |         |          |                 |
| Olivine     | MI 12 | 56                  | 46                  | 15  | 2236            | 610 | 1942              | 611 | 17      | 69.4     | 22              |
| Olivine     | MI 13 | 50                  | 32                  | 13  | 1596            | 499 | 1265              | 501 | 36      | 73           | 27              |
| Olivine     | MI 22A| 29                  | 14                  | 8   | 2151            | 639 | 1585              | 643 | 52      | 70.9     | 53              |
| Pyroxene    | MI 20A| 166                 | 105                 | 44  | −131            | 210 | −234              | 210 | 37      | 70.2     | 5              |
| Pyroxene    | MI 20B| 230                 | 145                 | 60  | 70              | 229 | −4                | 229 | 37      | 70.2     | 5              |
| Olivine     | MI 6A | 222                 | 120                 | 40  | 834             | 397 | 759               | 397 | 46      | 72.6     |                 |
| Olivine     | MI 6B | 124                 | 83                  | 23  | 4               | 225 | −134              | 225 | 33      | 72.6     |                 |
| Olivine     | MI 6C | 55                  | 33                  | 11  | −112            | 212 | −421              | 216 | 40      | 72.3     |                 |
| Olivine     | MI 32 | 10                  | 6                   | 2   | 1057            | 531 | −646              | 578 | 45      | 71.7     |                 |
| Olivine     | MI 10 | 366                 | 161                 | 65  | 579             | 338 | 533               | 338 | 56      | 72.5     | 26              |

(continued on next page)
Table 1 (continued)

| Sample/Host | MI #     | H₂O measured (μg/g) | H₂O corrected (PEC) | 2σ | △D (%) corrected | 2σ | △D (%) spallation | 2σ | PEC (%) | Host Mg# | MI diameter (μm) |
|-------------|----------|---------------------|---------------------|----|------------------|----|--------------------|----|----------|-----------|-----------------|
| Olivine     | MI 15    | 34                  | 22                  | 7  | 253              | 295| −94                | 304| 35       | 63.7      | 68              |
| Pyroxene    | MI 2     | 38                  | 20                  | 8  | 342              | 313| 32                 | 321| 49       | 66.2      | 22              |
| Pyroxene    | MI 17    | 30                  | 15                  | 6  | 631              | 391| 230                | 402| 48       | 67.2      | 17              |
| Olivine     | MI 2     | 117                 | 77                  | 31 | −72              | 185| −393               | 200| 34       | 52.3      | 23              |
| Olivine     | MI 4A    | 194                 | 194                 | 51 | −156             | 182| −349               | 187| 0        | 53.9      | 5               |
| Olivine     | MI 4B    | 50                  | 33                  | 13 | 234              | 334| −520               | 376| 34       | 53.9      | 19              |
| Olivine     | MI 12    | 63                  | 31                  | 17 | 62               | 267| −534               | 300| 51       | 58.3      | 42              |
| Olivine     | MI 16    | 30                  | 15                  | 8  | 656              | 493| −597               | 570| 49       | 58.2      | 36              |
| Olivine     | MI 21A   | 118                 | 68                  | 31 | −136             | 198| −456               | 211| 42       | 59.2      | 28              |
| Pyroxene    | MI 24A   | 22                  | 12                  | 6  | 171              | 362| n.d.               | 46  | 73.3     | 17        |                 |
| Olivine     | MI 2A-a  | 85                  | 38                  | 22 | −410             | 235| −442               | 235| 56       | 70.9      | 120             |
| Olivine     | MI 2A-d  | 125                 | 55                  | 33 | −244             | 225| −266               | 225| 56       | 70.9      | 120             |
| Olivine     | MI 2B    | 167                 | 73                  | 44 | −91              | 250| −108               | 250| 56       | 71.9      | 22              |
| Olivine     | MI 15    | 47                  | 14                  | 12 | −308             | 277| −368               | 278| 70       | 76.3      | 42              |
| Olivine     | MI 39    | 54                  | 39                  | 14 | −382             | 261| −433               | 261| 28       | 58.4      | 30              |
| Olivine     | MI 23    | 14                  | 8                   | 4  | 1784             | 747| n.d.               | n.d.| 43       | 54.6      | 16              |
| Olivine     | MI 35    | 3                   | 2                   | 1  | 8335             | 2662| n.d.               | n.d.| 25       | 43.8      | 21              |
| Pyroxene    | MI 1     | 150                 | 135                 | 39 | 197              | 275| −152               | 287| 10       | 49.0      | 6               |
| Pyroxene    | MI 9     | 112                 | 84                  | 29 | 145              | 232| −325               | 257| 25       | 52.6      | 6               |

uses spallation corrected △D values. Due to the low water contents measured in the studied MIs, the correction of △D values for spallation effects is significant for most samples, with the exception of 14072 which has a low CRE age of 21 Ma. Samples 12040 and 15016 have very long exposure ages at 285 ± 50 and 400 ± 73 Ma, respectively. As a result, the amount of D produced by spallation is significant, and therefore, MIs with H₂O concentrations <5 μg/g have undetermined spallation-corrected hydrogen isotopic ratio. Uncertainties associated with △D values include uncertainties in counting statistics as well as in IMF estimation, in background △D values, and in spallation corrections. All NanoSIMS spots were checked after analysis using SEM imaging to confirm that analyses targeted the MI and not the surrounding host minerals. The full MI dataset is presented in Table 1.

2.4.2. Apatite measurements
The H²/H₁₈O ratio and H isotope composition of a number of apatite grains in samples 10020, 12002, 12004, 12040 and 14072 were measured, in two different sessions, using a Cameca NanoSIMS 50L at The Open University, following the protocol detailed in Barnes et al. (2013) and Tartèse et al. (2013). In brief, a large Cs⁺ primary beam of ca. 250 pA current with an accelerating voltage of 16 kV was rastered on the sample surface over 12 μm × 12 μm area during a 3 min pre-sputter to eliminate any surface contamination. For analysis, secondary ions of ¹H⁺, ²H⁺, ¹³C⁻ and ¹⁸O⁻ were collected simultaneously from the central areas of 6 μm × 6 μm to 10 μm × 10 μm rasters, with a 25% blanking on electron multipliers, for ~10 min. An electron gun was used for charge compensation and tuned to minimise its contribution to the background H. The ion ¹³C⁻ was used to monitor any potential terrestrial contamination and cracks during analyses. The mass resolving power was set to ~4000, sufficient to readily resolve ³H⁺ from molecular H₂. Vacuum in the analytical chamber was maintained at or below 5 × 10⁻¹⁰ Torr during both sessions. Samples were kept under high-vacuum for at least 24 h prior to analysis.

Apatite H₂O contents were calibrated using the measured ³H/H¹₈O ratio and the calibrations derived using reference apatite samples with known H₂O contents, comprising Ap003 (600 ± 400 μg/g H₂O), Ap004 (5500 ± 500 μg/g H₂O), and Ap018 (2000 ± 400 μg/g H₂O) (McCubbin et al., 2012). Two distinct sessions were necessary to perform apatite measurements. Samples 12040 and 14072 were analysed during session 1 and samples 10020, 12002, and 12004 were analysed during session 2. The uncertainties on the slopes of the calibration lines used to calculate apatite H₂O contents were ±5.8% and ±5.0% (95% confidence interval) for the first and second session, respectively (Fig. S3). During the first session, background H₂O of 14 ± 8 μg/g (2σ) was estimated based on repeat analysis of San Carlos olivine (n = 8) and was subtracted from the measured H₂O in Apollo samples. Measured D/H ratios were corrected for IMF using repeat analysis of Ap004 (△D = −45 ± 5‰, McCubbin et al., 2012), which
yielded an IMF of 251 ± 50‰ (2σ, n = 8). For the second session, the background estimated from San Carlos olivine analyses was 44 ± 6 μg/g H2O (2σ, n = 4) whereas the IMF was 100 ± 42‰ (2σ, n = 4).

The IMF- and background-corrected δD values were corrected for the effects of spallation reactions, using a D production rate of Merlivat et al. (1976). As apatite in samples 10020, 12002 and 12004 have relatively higher water contents (>700 μg/g H2O), the spallation correction is negligible (maximum shift in δD values by 11‰, which is within the overall measurement uncertainty of δD values). Apatite in 14072 and 12040 have much lower water contents. However, 14072 has a CRE age of 21 Ma. Therefore, the spallation correction for 14072 apatite is also negligible (shift in δD values by < 20‰). Because 12040 has an extremely old CRE age (285 ± 50 Ma), the associated spallation corrections result in significant changes in δD values. Thus, we caution against overinterpreting the data for 12040, especially keeping in mind that spallogenic D production rates for apatite have not yet been determined. All discussion on apatite δD in this work from here on refers to spallation corrected δD values.

The apatite H2O contents and δD values are reported in Table 2, which include the reproducibility obtained on repeated analysis of Ap004, the internal precision of each analysis, and the uncertainties associated with cosmic-ray spallation correction.

### 3. RESULTS

#### 3.1. Chemistry of melt inclusions

The major-element composition of MIs (uncorrected for PEC) are displayed in Fig. 3 (Fig. S4). These plots illustrate the compositional evolution of the parental melts in each case. Data for homogenised MIs (from Chen et al., 2015) are plotted along with our data for crystallised MIs. Homogenised MIs plot within the range defined by bulk-rock composition, while crystallised MIs display a large range in composition, revealing the evolution of the parent melt at their time of trapping. Major-element compositions suggest that the studied MIs could have potentially recorded a larger span of melt crystallisation, and thus represent a snapshot of melt composition at the time of their trapping. Indeed, the original composition of MIs were also affected by PEC. It is interesting to note that MI 6 hosted in pyroxene in sample 10058 has a very high SiO2 content of 90 wt. % This is most probably an evidence of silicate liquid immiscibility as this glass inclusion is near a plagioclase, which have been observed previously in Apollo 11 rocks (Roedder and Weiblen, 1970).

A major concern regarding MIs is the possibility that they have re-equilibrated with their host during natural cooling. This re-equilibration manifests itself as Fe-loss from the MIs (Danyushevsky et al., 2002; Kent 2008 and refs therein). If the MIs in Apollo basalts had undergone
Fig. 3. Major-element composition of MIs (uncorrected for PEC) and bulk-rock samples, expressed in terms of oxide weight% (wt%). The high-Ti basalts (10020 and 10058) are plotted in the left column whereas the low-Ti basalts (Apollo 12002, 12004, 12008, 12020, 12040, 14072 and 15016) are plotted in the right column. Data from Chen et al. (2015) on homogenised MIs from 10020 and 12008 are also plotted for comparison purposes. Blue lines represent predicted liquid lines of descent.
such Fe loss, their composition would plot below the liquid line of descent predicted from bulk-rock FeO vs. MgO (c.f. Fig. 3). Similarly, a negative correlation between the Mg# of the host and FeO content of an inclusion should be seen as a result of Fe-loss during re-equilibration between olivine and melt (Yaxley et al., 2004; Kent et al., 2008) (c.f. Fig. 4).

Fig. 4. Melt-inclusion host phenocryst Mg# vs. MI FeO abundance (uncorrected for PEC). Mg# is defined as the mole fraction Mg/(Fe + Mg).

Fig. 5. δD (‰) vs. H2O (µg/g) in silicate melt inclusions for each Apollo sample studied here: (A) 10020, (B) 10058, (C) 12002, (D) 12004, (E) 12008, (F) 12020, (G) 12040, (H) 14072, (I) 15016. Data points represented by a circle or a square represent either an olivine-hosted or pyroxene-hosted MI, respectively. H2O contents represented here are corrected for PEC; δD values are corrected for spallation using the production rate of Furi et al. (2017). Please note that y-axis for 10020 (graph A) is different than the other graphs.
Neither of these two characteristics apply for the large majority of the MIs in the studied Apollo basalts, arguing against a re-equilibration of the MIs with their host crystals.

### 3.2. Water content and hydrogen isotopic ratios

#### 3.2.1. 10020

Eight olivine-hosted MIs and two pyroxene-hosted MIs were analysed in sample 10020. These inclusions have a PEC values between 17 and 56%. After PEC correction, H$_2$O contents range from 6 ± 2 to 161 ± 65 μg/g. Hydrogen isotopic composition of olivine-hosted MIs show a very large range of δD values from −646 ± 578 to +1942 ± 611‰. In contract, the pyroxene-hosted MIs have more restricted δD values of −234 ± 210 and −4 ± 229‰. Interestingly, H$_2$O-δD systematics in 10020 MIs seem to follow two opposite trends (Fig. 5A and Fig. 6). The R$^2$ values are 0.74 and 0.90, for the negative and the positive trends, respectively. The MI with the highest H$_2$O content (i.e., 161 μg/g) is associated with a δD value of +533 ± 338‰.

A single analysis in apatite yielded a water concentration of 1440 ± 251 ppm and an associated δD value of +595 ± 339‰ (Fig. 7).

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**Fig. 6.** δD (‰) vs H$_2$O (μg/g) in silicate melt inclusions for all samples in this study plotted together with the literature data from Singer et al. (2017). For MIs analysed in this study, H$_2$O contents are corrected for PEC and δD values are corrected for spallation using the production rate of Čích et al. (2017). Round and square symbols are for olivine-hosted MI and pyroxene-hosted MI, respectively. Star symbols refer to Singer et al. (2017) MI data on samples 12018, 12035 and 12040, corrected for spallation using the production rate of Füri et al. (2017).

**Fig. 7.** Apatites H$_2$O-δD systematics, in μg/g and permil, respectively. The data plotted for samples 10020, 12002, 12004, 12040 and 14072 are from this study. Data for 10058 and 15016 are from Tartese et al. (2013) and Barnes et al. (2018), respectively. Samples 10020 and 10058 are high-Ti basalts while the others are low-Ti basalts. Literature data for apatite from low-Ti and high-Ti basalt are from Greenwood et al. (2011), Barnes et al. (2013), Tartese et al. (2013), Boyce et al. (2015); high-Al basalt apatite are from Greenwood et al. (2011); for Mg- and Alkaline-suite apatite are from Greenwood et al. (2011) and Barnes et al. (2014); QMD evolved lithologies apatite are from Robinson et al. (2016). δD values of 10058, 12002, 12004, 12040, 14072 and 15016 are corrected for spallation using the production rate of Merlivat et al. (1976), in order to compare our data with the literature data on lunar apatite.
3.2.2. 10058

Sample 10058 is devoid of olivine phenocrysts. As such, only seven pyroxene-hosted MIs were identified in the 10058 thin section, four of which were analysed. The measured H$_2$O concentration ranges from 6 ± 1 to 212 ± 27 μg/g, after PEC correction (16 to 42 % PEC). δD values in these MIs range from −912 ± 553 to −7 ± 281‰. The MI with the highest H$_2$O content (i.e., 212 μg/g) is associated with a δD value of −169 ± 222‰ (Fig. 5B).

Tartèse et al. (2013) analysed apatite grains in sample 10058 and reported water concentration of ~1350 ± 400 μg/g (2sd) with associated δD values ranging between 600 and 1100‰ (Fig. 7).

3.2.3. 12002

In sample 12002, MIs yielded a slightly more restricted range of water contents from 9 ± 4 to 113 ± 34 μg/g H$_2$O (40 to 73 % PEC). The five olivine-hosted MIs and the one pyroxene-hosted MI have δD values covering a range from −412 ± 407 to +972 ± 850‰. The δD value of +508 ± 352‰ of the MI with the highest H$_2$O content (113 μg/g) is similar to that in 10020 (Fig. 5C).

Two apatite grains were analysed and yielded water concentrations of 794 ± 59 μg/g and 1286 ± 91 μg/g, with δD values of 568 ± 235‰ and 1102 ± 306‰ (Fig. 7).

3.2.3. 12004

Seven MIs were measured in 12004, among which five were in olivine and two in pyroxene. These MIs yielded a water content from 8 ± 5 μg/g to 121 ± 57 μg/g (40 to 63% PEC) (Fig. 5D). The δD values range from −496 ± 219‰ to +73 ± 342‰. In this case also, the highest δD value was measured in a pyroxene-hosted MI. The highest water content of 121 μg/g is also similar to that measured in MI in 12002 and is associated with a δD value of −13 ± 318‰.

A single apatite analysis yielded a H$_2$O abundance of 746 ± 56 μg/g and a δD value of 961 ± 297‰ (Fig. 7).

3.2.5. 12008

Six olivine-hosted MIs were analysed in 12008, with MI #11 being analysed twice (11a and 11b) in order to test any heterogeneity in δD and H$_2$O in a crystallised MI. MIs in 12008 have relatively lower percentages of PEC between 8 and 47%. The H$_2$O contents range from 8 ± 4 μg/g to 121 ± 24 μg/g and δD values from −185 ± 362‰ to 345 ± 567‰ (Fig. 5E). The two analyses in MI #11 yielded H$_2$O abundances of 28 and 87 μg/g, which can be explained by a different proportion of crystals and melt in the area analysed. However, the δD values of the two analyses are similar within errors, i.e., 87 ± 260 and 142 ± 333‰, which gives confidence in the broad reproducibility of δD measurements in partially crystallised MIs. The olivine-hosted MI with the highest water content (121 μg/g) has a δD value of +46 ± 243‰.

3.2.6. 12020

Six olivine-hosted MIs and two pyroxene-hosted MIs yielded water contents from 4 ± 4 μg/g to 65 ± 16 μg/g, with percentage of PEC varying between 23 and 74%. The δD values range from −94 ± 304‰ to +834 ± 657‰. The olivine-hosted MI #10, which yielded 65 μg/g H$_2$O, has the lowest percentage of PEC (23%) and as an appearance of an almost glassy MI (Fig. 5F). It is associated with a δD value of +276 ± 320‰.

3.2.7. 12040

In 12040, one pyroxene-hosted MI and six olivine-hosted MIs were analysed, among which one is glassy (although with a shrinkage bubble – Fig. 1). The H$_2$O contents in olivine-hosted MIs range between 15 ± 6 μg/g and 194 ± 51 μg/g, while the pyroxene-hosted MI yielded 12 μg/g H$_2$O. The δD values range from −597 ± 570‰ to −349 ± 187‰ (Fig. 5G). The low H$_2$O content measured in the pyroxene-hosted MI in 12040 precluded calculation of a reliable δD value because of the sample’s long CRE age of 285 ± 50 Ma. The glassy MI #4A contains the highest water concentration and is associated with a δD of −349 ± 187‰.

Nine measurements were performed on four apatite grains. Their water abundances range from 25 ± 2 to 91 ± 9 μg/g while the associated δD values range from −191 ± 404‰ to +232 ± 429‰ (Fig. 7), which is consistent with previously reported D/H measurements in apatite in 12040 that range from −150 ± 26‰ to +27 ± 91‰ (Greenwood et al., 2011; Boyce et al., 2015), although these literature values are uncorrected from spallation correction.

3.2.8. 14072

Five analyses were performed in four olivine-hosted MIs in sample 14072. The measured water concentrations range from 14 ± 12 μg/g to 73 ± 44 μg/g (28 to 70% PEC) while the associated δD values range from −442 ± 235‰ to −108 ± 250‰ (Fig. 5H). Sample 14072 has a very short CRE age of ~21 Ma. The correction from δD produced by spallation is thus limited to a maximum of ca. 50‰. The MI with the highest water content records the highest δD value (i.e., −108 ± 250‰).

Five apatite grains have also been analysed (Table 2) and yielded a range of H$_2$O contents from 68 ± 4 μg/g to 323 ± 19 μg/g, with δD values ranging from +13 ± 410‰ to +437 ± 308‰ (Fig. 7).

3.2.9. 15016

In 15016, two olivine-hosted MIs and two pyroxene-hosted MIs were analysed. Water abundances measured in the olivine-hosted MIs are very low, between 2 ± 1 μg/g and 8 ± 4 μg/g H$_2$O (10 to 43% PEC). Because sample 15016 has a very long CRE age of ~400 ± 73 Ma (Füri et al., 2017), no reliable spallation corrected δD values could be calculated. Pyroxene-hosted MIs contain between 84 ± 29 μg/g and 135 ± 39 μg/g H$_2$O, with associated δD values of −325 ± 257‰ and −152 ± 287‰, respectively (Fig. 5I).

Barnes et al. (in press) analysed apatite in samples 15016 and reported water concentrations ranging from 55 to 379 μg/g with associated δD values ranging between −83 ± 107‰ and +494 ± 306‰ (Fig. 7).
3.3. Link between the volatile composition of MI and their petrography and chemistry

The estimated water contents in MIs are plotted against the Mg# of their host and against the MI diameter (Fig. 8). A negative correlation between the MI water content and the Mg# of its host should indicate the relative time of entrapment of the MIs, since Mg# of olivine and pyroxene would decrease with progressive melt crystallisation while H should increase as it is incompatible in all major rock-forming silicate (e.g., olivine, pyroxene, plagioclase). It is important to note that this is true only if no other magmatic or secondary processes have altered the water content of MIs, post entrapment. Among all the MIs analysed in this study, the water contents in some of the Apollo 12 MIs show this expected correlation with their hosts’ Mg# (Fig. 8A). The most notable trend is seen for ol-hosted MIs in 12040 (Fig. 8A) where the highest water content was measured in a MI trapped in olivine with the lowest Mg#. This may imply that, overall, MIs in 12040 formed from a more evolved parental melt compared to parental melts for other Apollo 12 samples. In contrast, the estimated water content in MIs from samples 10020 and 10058, as well as 14072 and 15016 do not show any such correlation with their host Mg#. Although a heterogeneity in melt composition cannot be ruled out, it is also possible that some other process may have erased the effect of crystallisation on MI water content in these cases. Regardless of either possibilities, it is interesting to note that at comparable host Mg#, the MIs are more water-rich in Apollo 11 samples compared to those in Apollo 12 samples (Table 1Fig. 8). However, no correlation is obvious between the host Mg# and the δD measured in MIs (Fig. 8D), which is consistent with the fact that no significant isotopic fractionation is expected during basaltic melt crystallisation (Kyser and O’Neil, 1984; Bindeman et al., 2012).

Previous studies have demonstrated a dependence of the water content in MI with the MI radius as a result of a more rapid re-equilibration among small MIs (<25 μm) compared to larger ones (Chen et al., 2013; Ni et al., 2017). This trend is not observed among the MIs studied here (Fig. 8C and D). However, Chen et al. (2013) and Ni et al. (2017) predominantly observed this correlation in the case of homogenized MI in which H diffusion was most likely enhanced during homogenisation experiments.

4. DISCUSSION

4.1. Reliability of H₂O-δD systematics in lunar MIs

Because MIs are the best available tool for assessing volatiles signatures of the primary basaltic magmas, numerous studies have examined various processes that can influence their original signatures subsequent to entrapment in a silicate-host. The modification of the original volatile inventory of MIs is principally caused by re-equilibration between the MI and an external melt, the composition and oxidation state of which changes during ascent and eruption (Mackwell and Kohlstedt, 1990; Kohlstedt and Mackwell, 1998; Hauri, 2002; Demouchy and Mackwell, 2006; Gaetani et al., 2012; Bucholz and Gaetani, 2013; Le Voyer et al., 2014). Small MIs are more susceptible to mod-

Fig. 8. H₂O content (μg/g) and δD values (‰) of MIs in Apollo samples compared to Mg# of their host (Mg# is defined as the mole fraction Mg/(Fe + Mg)) and the diameter of the MI (μm). The grey shading emphasises the correlation between H₂O content in MIs and their host #Mg for Apollo 12 basalts.
ification (Bucholz and Gaetani, 2013; Chen et al., 2013; Ni et al., 2017), which is the case for lunar MIs. Moreover, the large variations documented for both δD values and H₂O abundances among the lunar MIs, as well as some trends observed in H₂O-δD systematics (Fig. 5), suggest that some processes have altered the primordial H inventory and isotope signature of these MIs. Hauri (2002) compiled an exhaustive list of such typical processes for terrestrial MIs, and here we will evaluate our measurements in light of some of these processes to assess whether lunar MIs are faithful recorders of lunar H₂O-δD systematics. These processes include post-entrapment growth of daughter crystals, (e.g., Danyushevsky et al., 2002; Steele-MacInnis et al., 2011), formation of vapour bubbles within inclusions (Moore et al., 2015), diffusive loss of H through the host (Gaetani et al., 2012; Bucholz and Gaetani, 2013), isotopic exchange with another H reservoir (Shaw et al., 2008), and shallow level degassing of melt prior to entrapment (Hauri, 2002). Most of these processes, which occur during ascent and eruption of basaltic magma, result in positive and negative trends between H₂O abundances and δD values. These trends are pictorially represented in Fig. 9. Some of these processes require different speciation of H that can be found in lunar melt (Elkins-Tanton and Grove, 2011; Renggli et al., 2017; Dalou et al., 2019). Another important factor to take into consideration is an exogenous process that can also alter the δD-H₂O systematics of a lunar melt inclusion, post entrapment. See text for further discussion.

4.2. Basalt crystallisation

Before looking at magmatic and secondary processes that could induce hydrogen isotopic fractionation, the effect of melt crystallisation needs addressing, as it is often involved in giving rise to a range in H₂O contents among MIs, from a single sample, if they are trapped at different stages of magma evolution. Indeed, the incompatibility of hydrogen in nominally anhydrous mineral increases the water content in the remaining melt. MIs trapped later in the crystallisation sequence are thus expected to be more water-rich than earlier-trapped MIs. A negative correlation between H₂O content of MIs and their host Mg# is observed among some Apollo 12 basalt samples (cf. Fig. 8A). This correlation suggests that H₂O contents in MIs from Apollo 12 basalts were mostly governed by the fractional crystallisation of their parental melts (see Fig. 10B). As such, the δD-H₂O systematics of MI trapped in a host with the highest Mg# in Apollo 12 samples would therefore be closest to their initial parental melt volatile signature. For other samples (10020, 10058, 14072, 15016) which do not show such a correlation, other additional processes might have been involved. In these cases, the volatile-richer MI would be chosen as reflecting the initial melt, which for Apollo 11 samples match with high Mg# of silicate hosts.

4.3. Post-entrapment crystallisation (PEC)

Due to the relatively slow cooling rates of lunar melts (Holness et al., 2012; Walker et al., 1976; Tikoo et al., 2012), most of the MIs found in mare basalts are partially crystallised (Roedder, 1984). The formation of daughter minerals in MIs is characterised by some compositional changes causing Fe-loss: olivine crystallises on the inclusion wall and re-equilibrates with the host, typically resulting in a net Fe-loss in the trapped melt and an enrichment in the host (Danyushevsky et al., 2002; see EPMA data in supplementary Table S2). Therefore, recognising such negative and positive trends in MI H₂O-δD dataset, and comparing them against various modelled curves, should allow estimation of the initial H₂O-δD systematics of the parental melts of the studied samples.
Fig. 10. Processes modifying the H$_2$O-$\delta$D systematics of lunar MIs. Also see Fig. 9 for a schematic of all possible processes and their trends. H$_2$O contents represented here are corrected for PEC; $\delta$D values are corrected for spallation using the production rate of Füri et al. (2017). (A) Apollo 11 basaltic samples 10020 and 10058. Apollo 10020 MIs plot along two trends, H$^+$ diffusion through the host (light grey curves) and mixing with a D-poor reservoir ($\delta$D = $-500\%$) (black dashed curves). (B) Apollo 12 basaltic suite (samples 12002, 12004, 12008, 12020). MIs follow a trend defined by fractional crystallisation (blue arrow). Few MIs are also affected by H$^+$ diffusion (light grey curves). (C) Apollo low-Ti samples 12040, 14072 and 15016. All these samples fall on a mixing trend with a solar wind rich reservoir ($\delta$D = $-500\%$) (black dashed curves). See text for details. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
have shown that there is no matrix effect associated with hydrogen isotopic measurement in a partially crystallised MI. Moreover, no trend is observed between the PEC percentage of the MI and its $\delta D$, which should be expected if PEC had an influence on the $\delta D$ values. As such, we do not consider PEC to have played a role in any of the trends observed between $H_2O$ and $\delta D$ values of the lunar MIs investigated here.

The total range of water concentration reported in MIs across the nine Apollo samples span from 2 µg/g to 212 µg/g (Table 3). Also listed are the $H_2O$ contents determined in homogenised as well as unhomogenised (i.e., crystallised) MIs from 10020, 12008, 12040 and 15016 in previous studies (Chen et al., 2015; Singer et al., 2017; Ni et al., 2019). For these four samples, previously reported ranges in water contents for both crystallised and homogenised MIs fit within our measured range of water contents, once PEC corrections have been implemented (Table 3). It is noted that previously reported ranges are narrower than the ranges seen in our dataset. This could indicate some heterogeneity across individual samples. Moreover, lower water contents are generally noted for MIs that were subjected to homogenisation experiments, possibly reflecting a loss of water during homogenisation of smaller MIs (Chen et al., 2013; Ni et al., 2017).

4.4. Presence of shrinkage bubble

Theoretically, formation of a bubble after trapping could alter the primordial $\delta D-H_2O$ systematics as volatiles will preferentially be partitioned in the bubble. As such, the formation of a shrinkage bubble in a suite of MIs with uniform volatile contents can generate a range in $\delta D-H_2O$ systematics (Moore et al., 2015). In the studied samples however, it is difficult to assess the possible effect of bubble formation as (i) pre-existing bubble(s) could have been removed during sample cutting and polishing, and (ii) no correlation with water content is observed between MI with an apparent bubble at the surface and those with no visible bubble. For instance, MI #4 from sample 12040 contains a shrinkage bubble (Fig. 1) while being one of the most $H_2O$-rich MI measured in this study (i.e., 194 ± 51 µg/g). Other MIs with apparent shrinkage bubble are MI #13 in 10020, MI #9 in 12020, MI #12, #16 and #21 in 12040, MI #2A and #2B. Without better constraints on the presence or absence of a bubble in an individual MI, we can only acknowledge the possibility of potential effects of bubble formation on volatiles in MIs but are unable to evaluate it further.

4.5. Diffusional proton loss through the host silicate

Diffusional proton ($H^+$) loss from a MI through its host can happen during ascent and eruption of basaltic melts. Protons diffuse quickly in pyroxene and olivine hosts (Ingrin and Blanchard, 2006), and MI can lose a few wt% $H_2O$ as well as increase its $\delta D$ value by a few hundreds of parts per mil over a timescale of hours to a day (Danyushevsky et al., 2002; Gaetani et al., 2012; Bucholz and Gaetani, 2013; Chen et al., 2015). Dry MIs carried in a $H_2O$-rich magma (in a magma-mixing scenario) could potentially gain H instead of losing it (Portnyagin et al., 2008; Gaetani et al., 2012; Hartley et al., 2015). Two mechanisms are associated with diffusional $H^+$ loss (Le Voyer et al., 2014; Roskosz et al., 2018): (i) proton-polaron process, where the charge balance during $H^+$ diffusion is compensated via iron oxidation (Kohlstedt and Mackwell, 1998; Demouchy and Mackwell, 2006); (ii) proton-vacancy process, where the charge balance during $H^+$ diffusion is associated with rearrangement of metal vacancies (Mackwell and Kohlstedt, 1990; Kohlstedt and Mackwell, 1998). These $H^+$ diffusion processes form negative trends in $\delta D$ vs. $H_2O$ diagrams in the case of $H^+$ loss from MI, as protons diffuse quicker than deuterons (i.e., about 13–
18%, Bucholz and Gaetani, 2013). Shaw et al. (2008) listed the following pieces of evidence which would argue against diffusional $H^+$ loss through a MI host: (i) proof of rapid cooling of the melt - i.e., the absence of daughter minerals, a percentage of PEC < 5%, no Mg-Fe zoning at the inclusion rims - and (ii) the absence of correlation between δD, H$_2$O and MI size (cf. Fig. 8), where smaller MIs can lose H$_2$O more easily (Hauri, 2002; Bucholz and Gaetani, 2013). The MIs in studied Apollo basalts exhibit features none of which meet the above two criteria: they possess daughter minerals with high percentage of PEC, they have relatively slow cooling rates, they are relatively small (most are < 20 μm in size) and some samples exhibit negative δD-H$_2$O correlations, which make them good candidates for having been affected by diffusional proton loss. Moreover, protons could be important H-species in reduced lunar melts (Ekins-Tanton and Grove, 2011).

Some MIs from the Apollo 11 high-Ti basalts show a negative H$_2$O-δD trend (Fig. 10A; $R^2 = 0.71$) that could be explained by H$^+$ diffusion out of MIs. We modelled the diffusional H$^+$ loss through a Rayleigh distillation process (eq. (2)), assuming a maximum decoupling between hydrogen and deuterium diffusion coefficients $D_H$/$D_D$ of 1.41 (i.e., $\sqrt{2}$) for a dilute ideal gas, as Roskosz et al. (2018) obtained a similar experimental value (1.46) by dehydration of an anhydrous silicate melt at 800°C and Peslier et al. (2019) obtained a fractionation factor of 1.25 to 2 for augites in nakhlites. As such, diffusional H loss fitting curves have thus to be seen as an upper limit for isotopic fractionation in lunar MIs (Fig. 10A – light grey curves).

$$D/H_t = D/H_0 \times f^{n-1}$$  \hspace{1cm} (2)

As a starting composition of the melt, we chose a water concentration of 250 μg/g, close to the highest water concentration measured in our Apollo 11 MI (i.e., 212 μg/g in 10058), and a δD value of +200 ± 100‰, as representative of the weighted average of the H$_2$O-rich MI from 10020 and 10058. This initial Apollo 11 reservoir has a similar δD value to the one estimated from lunar volcanic glasses and MIs of 74220 and 74002 samples (i.e., +187 ± 19‰ (Saal et al., 2013); +274 ± 42‰ (Füri et al., 2017)). A similar Rayleigh distillation process can be modelled to explain the negative trend observed among some of the Apollo 12 MIs starting from a lower δD value (-100‰; Fig. 10B).

4.6. Isotopic exchange

Hydrogen isotopic exchange can occur between a melt inclusion and the crystallising magma through the host crystal if the hydrogen isotope composition of water in the parent magma and in the MI differ (Shaw et al., 2008). However, the rate of such exchange is likely to be small compared to other post-eruptive processes, meaning that this signature may not be measurably large and/or is easily overprinted. Nevertheless, Singer et al. (2017) have argued that isotopic exchange did happen between Apollo 12 basaltic magmas and a low-δD reservoir during slow cooling of the basalts. A low-δD reservoir could be the lunar regolith, which is constantly implanted with solar wind hydrogen (Stephan and Robert, 2014; Treiman et al., 2016). In terms of 5D-H$_2$O systematics, this would be seen as a drop towards more negative δD values, at a given H$_2$O content (Fig. 9). This process is likely to be relevant for the slowly cooled samples 12040 and 15016, as well as for sample 14072 since these three low-Ti basalts recorded low-δD values between ~ -500‰ and ~ -200‰. Similarly, δD of apatites in each of these samples recorded lower δD values compared to other are basalts (Fig. 7).

4.7. Shallow degassing prior to entrapment

It has been shown that H$_2$O degassing from a melt results in a decrease of δD values of the residual melt, leading to a slightly positive δD vs. H$_2$O trend (Kysier and O’Neill, 1984; Pineau et al., 1998; Hauri, 2002). However, this isotopic fractionation is limited (δD changes ≤ 100‰; Newman et al., 1988; Pineau et al., 1998; Hauri, 2002). Additionally, given the reduced nature of lunar interior, H$_2$ and H could be a more dominant degassing species, making H$_2$O unlikely to degas from parental melt (Hirschmann et al., 2012; Saal et al., 2013; Sharp et al., 2013; Tartiése et al., 2013; Renggli et al., 2017). As such, H$_2$O degassing is not considered here.

4.8. Exogenous processes

The Moon is devoid of a protective atmosphere and subject to exogenous processes such as solar wind implantation (Keller and McKay, 1997; McCord et al., 2011) and spallation reactions induced by solar and galactic cosmic rays (Merlivat et al., 1976; Saal et al., 2013; Füri et al., 2017). Protons of solar wind can be implanted down to ~200 nm below the surface (Keller and McKay, 1997) and bond to oxygen atoms of silicate grains to form hydroxyl molecules (OH) (Ichimura et al., 2012; Bradley et al., 2014). The solar wind is devoid of deuterium (with a δD of ~ −1000‰; (Hashizume et al., 2000; Wiens et al., 2004)). Therefore, any mixing of the initial melt with surface material may cause a reduction in the initial δD values and H$_2$O content (Fig. 9). Implantation of solar wind has been recorded mostly in lunar agglutinates (Liu et al., 2012; Stephan and Robert, 2014). Treiman et al. (2016) proposed that this D-poor surface reservoir can be incorporated and mixed into mare basalt melts either by assimilation of regolith or by vapor transport from regolith heated by the lava flow, also called metasomatism (Rumpf et al., 2013). Indeed, Low-Ti mare basalts 12040 and 15016 are both slowly cooled basalts (Walker et al., 1976; Tikoo et al., 2012), and it has been argued that hydrogen assimilation from the underlying regolith could explain the low δD values of their apatite (Treiman et al., 2016; Barnes et al., 2019) compared to “typical” mare basaltapatite that is characterised by elevated D/H ratios (δD > 500‰) (cf. Fig. 7). Alternatively, it has also been argued that low δD values in MIs of basalt 12040 could have resulted from isotopic exchange with a D-poor reservoir enriched in solar wind hydrogen (see Section 4.5 – Singer et al., 2017; Greenwood et al., 2019). Finally, H$_2$O-D positive trends observed among Apollo 17 lunar volcanic glasses and MI have been assigned to solar wind
mixing with the pyroclastic melt (Füri et al., 2017 and ref. herein). As such, solar wind is considered as a substantial contributor of hydrogen and may be responsible for low-δD values recorded in various lunar samples.

Interestingly, MIs from 12040 and 15016 show a range of H2O-δD values that can be ascribed to mixing with a D-poor and H2O-poor reservoir (Fig. 10C – dashed line). One potential issue that is worth considering relates to the effect of spallation corrections on the δD values of samples that have very long CRE ages, i.e., ~285 Ma and ~400 Ma for 12040 and 15016, respectively (note that we used the new D production rate from Füri et al., 2017).

Considering the low water content of MIs in 12040 and 15016, the long CRE ages of these samples, and the large uncertainty on the D production rate (Merlivat et al., 1976; Füri et al., 2017), one might suggest that the observed positive H2O-δD trends result from an over-correction of D produced by spallation (Hauri et al., 2017). Here we consider that the δD values of 12040 and 15016 MIs with water concentrations lower than 25 μg/g are unreliable due to their extreme CRE ages. However, high-Al basalt 14072 follows the same trend defined by 12040 and 15016 (Fig. 10C), while having a relatively short CRE age of 21 Ma (York et al., 1972). The maximum D production associated with spallation reactions for 14072 is associated with a shift of δD values by up to 50‰, and it is unlikely that its positive H2O-δD trend is a result of spallation overcorrection.

High-Al basalt 14072 and its paired companion 14053 are the most reduced basalts retrieved from the Moon, demonstrated by the reduction of fayalite in the mesostasis and spinel minerals in the exterior portions of the rock (Taylor et al., 2004). It has been shown from textural evidence that this reduction proceeded continuously with crystallisation (Haggerty, 1977). Several mechanisms are suggested for sub-solidus reduction of lunar basalts (Brett, 1976; El Goresy, 1976), among which is the basalt extrusion over solar wind (H+ saturated regolith). Indeed, solar wind is considered as a substantial contributor of hydrogen and may be responsible for low-δD values recorded in various lunar samples, but in this case the starting composition for δD = +200‰ (also based on the average of δD from the H2O-rich MI from 10020 and 10058), as defined for diffusional H+ loss (Fig. 10A).

5. IMPLICATIONS FOR THE MOON

5.1. Estimation of the water content of the mare-basalt parental magmas

A common practice while studying the H2O content of MIs is to take the highest reported H2O to represent the pre-degassing H2O content of the melt (Saal et al., 2008; Hauri et al., 2011; Chen et al., 2015). However, an early-formed MI should contain less water than a later-formed MI as the melt gets enriched in H2O during fractional crystallisation, if no other process is involved. The variability in water contents of Apollo 12 MIs appears to be mainly controlled by fractional crystallisation (cf. Fig. 8), with few exceptions where H diffusion is also involved. As such, the MI entrapped in highest Mg# host should be the better proxy for estimating volatile signature of the parental melt. Based on the four MIs in Apollo 12 basalts that are hosted in silicates with Mg# > 70 (excluding MIs showing high H isotopic fractionation), we estimate an initial water content of the parental melt for Apollo 12 suite to be 10 ± 4 μg/g H2O. Interestingly, 12040 crystallised from a more evolved melt, as revealed by the lower Mg# of MI hosts. This observation is consistent with relatively H2O-rich nature of MIs in 12040 compared to the other samples from the Apollo 12 suite. The naturally glassy MI #4A is probably the most pristine MI in this sample and recorded the highest water content for this sample at 194 ± 51 μg/g H2O.

Because other samples do not show any correlation between the water content in MI and their hosts’ Mg#, we chose to use their highest water content (PEC corrected) as lower limit of the pre-eruptive abundance of their magma. Samples 14072 and 15016 are similar to 12040 in term of H2O-δD systematics of both MIs and apatites (Fig. 10C). Their highest MI water contents are 73 ± 44 and 135 ± 39 μg/g H2O, respectively. Finally, Apollo 11 samples 10020 and 10058 showed higher water contents in the early-formed MIs, i.e., 161 ± 65 and 212 ± 27 μg/g H2O. One should note here that we decide to report H2O/18O ratios measured in lunar MI into equivalent H2O concentrations, and therefore, it is possible that we might have overestimated H2O concentrations in the parent melts as some H might be speciated under other H forms. As such, these values should be seen as upper limits.

Water contents thus seem to be heterogeneous among mare parental magmas. While Apollo 10020, 10058, 12040, 14072 and 15016 parental magmas appears to have broadly similar range for their water contents (100–200 μg/g H2O), the Apollo 12 suite is highly depleted in water, with an estimated average of 10 μg/g H2O for the parental magmas. Assuming a range between 3 and 30% partial melting in the lunar mantle (Binder, 1982; Shearer and Papke, 1993; Hallis et al., 2014), we estimate a water content for the source region of most Apollo basalts studied.
here in the region of 3–60 μg/g H₂O, and lower than 3 μg/g H₂O for the Apollo 12 samples.

This lunar mantle water concentration estimate of ~3 to 60 μg/g H₂O is towards the lower range of estimates based on various lunar phases. Apatite from mare and KREEP-basalts tends to be water-rich (Boyce et al., 2010; McCubbin et al., 2010b; Greenwood et al., 2011; Tartèse et al., 2013, 2014) and the water content for their source regions has been estimated to be between 0.64 and 450 μg/g H₂O (McCubbin et al., 2010b; Tartèse et al., 2013), calculated for 3 and 30% partial melting of the lunar mantle. However, these estimates based on apatite volatile abundances need to be taken with caution (e.g., Boyce et al., 2014). Indeed, McCubbin et al. (2015) revised their previous estimate to 0.15 to 5.3 μg/g H₂O, arguing that higher estimates are biased towards wettest samples. Based on 74220 lunar volcanic glasses and their MI's, Hauri et al. (2011) estimated a water content for the lunar mantle of between 79 and 409 μg/g H₂O (calculated for 5 and 30% partial melting, resp.). This range was later revised between 133 and 292 μg/g H₂O (Hauri et al., 2015) based on ratios of volatile to non-volatile elements in Apollo 15 and 17 pyroclastic glasses (Saal et al., 2008). Despite the fact that the high-water concentration of the 74220 parental melt (~1410 μg/g H₂O) has been considered by some as a local anomaly (Albarede et al., 2015), the similarity between the volatile/refractory element ratios for MI's from 74220 and for MI's, glass beads, and mare basalts from other lunar samples suggests the opposite (Ni et al., 2019), indicating that these pyroclastic deposits are one of the best proxies to ascertain lunar mantle volatile concentrations. Füri et al. (2014) estimated a water concentration from 74002 LVG in the lower range of 74220 estimation, i.e., between 4 and 92 μg/g H₂O (for 3 and 30% partial melting, resp.). Similar to Hauri et al. (2015), Chen et al. (2015) estimated a lunar mantle with 111 ± 23 μg/g H₂O from mare basalt MI study, while Ni et al. (2019) estimated ~84 μg/g H₂O. Singer et al. (2017) also measured 740 μg/g H₂O in 12018 mare basalt MI's (Fig. 6), which can be converted into ~25–160 μg/g H₂O for its source region. All these sample-based estimates of bulk mantle appear higher, with the exception of McCubbin et al. (2015) estimate (i.e., 0.15 to 5.3 μg/g H₂O), than the estimate of Elkins-Tanton and Grove (2011) of <10 μg/g H₂O for the bulk lunar interior, which they derived from petrological and magma ocean modelling.

The relatively long cooling time, i.e., weeks to years, of mare basalts (Holness et al., 2012) compared to volcanic glasses, i.e., minutes, is the best explanation for the preservation of higher water concentration in Apollo 17 LVG and MI's (e.g., up to ~1410 μg/g; Hauri et al., 2015) compared to other lunar basaltic samples (e.g., Chen et al., 2015; Ni et al., 2019). Indeed, crystallised MI's may have undergone loss of hydrogen, either by trapping of a degassed melt, or during post-entrapment H diffusion. Similarly, apatite likely crystallised after intense H degassing from mare magmas (Greenwood et al., 2011; Tartèse and Anand, 2013; Tartèse et al., 2013). As such, our estimates of water concentration in mare source regions are likely to be towards the lower end of the actual range.

A lunar mantle water concentration of ~3–60 μg/g H₂O might seem high when considering (i) modelling of the crystallisation of the LMO that suggests a concentration of ~10 ppm H₂O (Elkins-Tanton and Grove, 2011), and (ii) the difficulty in water retention during the high-energy formation event of the Moon and the expected hydrodynamic escape of volatiles (Pahlevan and Stevenson, 2007; Canup, 2012). Hauri et al. (2015) suggested that either the Moon inherited its water solely from the Earth, or that only 25% of the water originated from proto Earth-derived material and the remaining came from highly degassed material from the protolunar disk. Recent studies show that indigenous lunar water may indeed be a complement of terrestrial water that survived the high-energy lunar formation event (Greenwood et al., 2018), along with some water that was delivered by carbonaceous chondrite-like material during late accretion (Tartèse and Anand, 2013; Barnes et al., 2016; Hauri et al., 2017).

5.2. Unravelling H isotope composition of the primordial lunar water

5.2.1. Multiple processes modifying MI hydrogen signature in lunar basalts

Melt inclusions in nominally anhydrous minerals are supposedly a good proxy to document the variety of magmatic and secondary processes that have affected their volatile inventory (Danyushevsky et al., 2002; Hauri, 2002; Massare et al., 2002; Severs et al., 2007; Steele-MacInnis et al., 2011; Gaetani et al., 2012; Bucholz and Gaetani, 2013). Lunar basaltic MI's have undergone H⁺ diffusion, and their parent melts experienced interaction with a D-poor reservoir (probably as a result of solar wind-rich regolith incorporation) prior to entrainment in MI's. Analyses of several (>5) MI's in a single sample is thus required in order to identify δD-H₂O trends and the associated process(es) to unravel the initial magmatic δD-H₂O values.

Melt inclusions in 10020 and 10058 high-Ti basalts show evidence of differential proton loss as well as evidence of mixing with a D-poor H₂O-poor reservoir, for which the initial value could have been as low as ~500‰. The parental melts of these two samples could have interacted with solar wind-rich regolith either by incorporation, metasomatism or sub-solidus reduction, as suggested for samples 12040, 14072 and 15016 (Taylor et al., 2004; Treiman et al., 2016; Barnes et al, in press). From modelling of these two processes (Fig. 10A), we estimated that the source-region water reservoir of these two samples had a δD of ~ +200 ± 100‰, even though these two samples represent separate igneous cooling units (Beatty and Albee, 1978). Interestingly, apatite from both 10058 and 10020 are in disequilibrium with this initial value, with average δD values of ~ +800‰ for 10058 apatite (Tartèse et al., 2013) and ~600‰ for 10020 apatite (Fig. 7). This suggests that apatite in 10058 and 10020 crystallised after significant H₂ degassing after entrapment of MI's (e.g., Tartèse et al., 2013).

The Apollo 12 basalt suite (excluding sample 12040) documents a different story. All of these basalts (i.e., 12002, 12004, 12008 and 12020) are relatively rapidly cooled (>1°C/h - Walker 1976). Their parental melts seem
to have been unaffected by magmatic and secondary processes. Water content in the MIs is dependent on the timing of MI entrapment. Considering all MIs located in silicates with Mg# > 70, the $\delta^D$ value for the parental melt of Apollo 12 suite is estimated to be $-157 \pm 65\%$, lower than what is estimated for Apollo 11 high-Ti basalts. This estimation is consistent with 12018 MIs previously measured with water contents up to $740 \pm 74 \mu g/g$. The $\delta^D$ values of apatite in Apollo 12002 and 12004 basalts are $>500\%$ (cf. Fig. 7). This is typical of mare basalt apatite, suggesting that these samples have undergone severe H$_2$ degassing prior to apatite formation, explaining this large discrepancy between MIs and apatite D/H ratios.

For samples 12040, 15016 and 14072, the only process that seems to have altered the initial $\delta^D$-H$_2$O signal is mixing with solar wind-implanted material. In these samples, the limited variation between $\delta^D$ values of MIs and apatite reveals that apatite are close to equilibrium with the melt, with $\delta^D$ values of apatite ranging between $-200$ and $+200\%$ for 12040 (Greenwood et al., 2011; Boyce et al., 2015; Singer et al., 2017; this study), between $-100$ and $+500\%$ for 15016 (Barnes et al, in press) and between 0 and $+400\%$ for 14072 (this study – cf. Fig. 7). These three samples thus seem to record a different volatile history than other mare basalts: their parent melts may have been affected by magmatic degassing of H-bearing species to a lesser extent than “typical” mare basalts, later overprinted by mixing with a solar wind-rich component, either by incorporation of solar wind-rich regolith material (Treiman et al., 2016), metasomatism (Rumpf et al., 2013; Potts et al., 2018) or due to sub-solidus reduction of the basalt (Haggerty, 1977; Taylor et al., 2004). Mare basalts 12040 and 15016 are both slowly cooled samples compared to other typical mare basalts (Walker et al., 1976; Tikoo et al., 2012). Singer et al. (2017) have interpreted the lower water abundance in slowly cooled sample 12040 as suggesting that slow cooling favour degassing. We do not see evidence suggesting that 12040 was affected by larger extent of H$_2$O or H$_2$ degassing in our dataset compared to data for more rapidly-cooled samples. Based on both the $\delta^D$ values of MIs with the highest water concentration in these samples and our solar wind implantation model, the $\delta^D$ of 12040, 15016 and 14072 initial reservoirs are estimated to be $\sim -200\%$.

Apollo 11 high-Ti basalts 10020 and 10058, Apollo 12 low-Ti basalts 12002, 12004, 12008, 12020 and 12040, Apollo 14 high-Al basalt 14072 and Apollo 15 low-Ti basalt 15016 were derived from distinct parental melts, due to the heterogeneity of the lunar mantle at the time of generation of mare magmas (Hallis et al., 2014). As revealed by the H$_2$O-$\delta^D$ systematics of their MIs, each of these parental melts also had different initial $\delta^D$ values, ranging between $-200\%$ and $+200\%$. Our findings are therefore consistent with the present understanding that the water in the Moon has a broadly chondritic origin (Saal et al., 2013; Tartese and Anand, 2013; Barnes et al., 2016).

5.2.2. Origin of the lunar hydrogen – a conundrum?

The inferred hydrogen isotopic composition for the lunar interior (i.e., $-200$ to $+200\%$) does not seem significantly higher compared to that of the Earth’s mantle (i.e., $-43 \pm 19\%$; Lécuyer et al., 1998). This appears to be in contrast with the isotopic signatures of lunar samples for moderately volatile elements such as chlorine (Sharp et al., 2010; Tartese et al., 2014; Treiman et al., 2014; Boyce et al., 2015; Barnes et al., 2016; Potts et al., 2018; Stephant et al., 2019; Wang et al., 2019), zinc (Moynier et al., 2006; Paniello et al., 2012; Kato et al., 2015), rubid-
ium (Pringle and Moynier, 2017), potassium (Wang and Jacobsen, 2016) and gallium (Kato and Moynier, 2017) (Fig. 11). However, heavier isotopic composition compared to the Earth for these volatiles and moderately volatile elements for the Moon are consistent with volatile loss of these elements either during the giant impact (Paniello et al., 2012; Wang and Jacobsen, 2016) or during the LMO differentiation (Day and Moynier, 2014; Kato et al., 2015; Barnes et al., 2016). At face value, lunar hydrogen isotopes are thus difficult to reconcile with existing lunar formation scenarios unless (i) the initial δD signature of indigenous lunar water was lighter than carbonaceous chondrite-like D/H values and increased because of H2 degassing from the LMO (Desch and Robinson, 2019), or, more likely, (ii) much of the lunar water was added late, after the main phase of LMO solidification, by carbonaceous-chondrite like material. This water was subsequently sampled by the younger mare basalts and pyroclastic deposits (Tartèse and Anand, 2013; Barnes et al., 2016; Hauri et al., 2017).

6. CONCLUSION

The abundance and origin of water in the lunar interior is crucial for our understanding of the Moon’s formation and magmatic differentiation processes. However, lunar samples have been affected by various magmatic and secondary processes that make estimating the initial H2O-δD systematics of basaltic parental melts challenging. In this study we have measured H 18O/16O (reported in terms of equivalent H2O concentration) and the H isotopic composition of 56 olivine- and pyroxene-hosted MIs, and 13apatites, from nine different mare basalts collected by four Apollo missions. Melt inclusions from mare basalts reveal that several magmatic and secondary processes have affected their original H2O contents and δD values, as well as that of their parental magmas. These processes include crystallisation, diffusional proton loss through the silicate hosts (olivine and pyroxene), mixing of solar wind-derived and indigenous water reservoirs, metasomatism, and sub-solidus reduction. Based on modelling for the effects of all these processes on our dataset of studied mare basalts, we estimate initial water abundances of ~10 µg/g H2O for parental magmas of Apollo 12 basaltic suite while between 100 and 200 µg/g H2O for Apollo 11 samples, and samples 12040, 14072 and 15016. Furthermore, the δD values of these basaltic parent melts (and that of their mantle source regions) ranged between −200‰ to +200‰, concordant with the hypothesis of a carbonaceous chondrite-like hydrogen isotopic signature for indigenous lunar water. This study highlights the fact that MIs are not a closed system with respect to hydrogen gain and/or loss and associated hydrogen 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. If possible, future studies should focus on samples with relatively short CRE ages to reduce the considerable uncertainties in determining the primary H isotopic signature of lunar water.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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