



# The origin of water in the primitive Moon as revealed by the lunar highlands samples



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## ABSTRACT

The recent discoveries of hydrogen (H) bearing species on the lunar surface and in samples derived from the lunar interior have necessitated a paradigm shift in our understanding of the water inventory of the Moon, which was previously considered to be a 'bone-dry' planetary body. Most sample-based studies have focused on assessing the water contents of the younger mare basalts and pyroclastic glasses, which are partial-melting products of the lunar mantle. In contrast, little attention has been paid to the inventory and source(s) of water in the lunar highlands rocks which are some of the oldest and most pristine materials available for laboratory investigations, and that have the potential to reveal the original history of water in the Earth–Moon system. Here, we report *in-situ* measurements of hydroxyl (OH) content and H isotopic composition of the mineral apatite from four lunar highlands samples (two norites, a troctolite, and a granite clast) collected during the Apollo missions. Apart from troctolite in which the measured OH contents in apatite are close to our analytical detection limit and its H isotopic composition appears to be severely compromised by secondary processes, we have measured up to ~2200 ppm OH in the granite clast with a weighted average  $\delta D$  of  $-105 \pm 130\%$ , and up to ~3400 ppm OH in the two norites (77215 and 78235) with weighted average  $\delta D$  values of  $-281 \pm 49\%$  and  $-27 \pm 98\%$ , respectively. The apatites in the granite clast and the norites are characterised by higher OH contents than have been reported so far for highlands samples, and have H isotopic compositions similar to those of terrestrial materials and some carbonaceous chondrites, providing one of the strongest pieces of evidence yet for a common origin for water in the Earth–Moon system. In addition, the presence of water, of terrestrial affinity, in some samples of the earliest-formed lunar crust suggests that either primordial terrestrial water survived the aftermath of the putative impact-origin of the Moon or water was added to the Earth–Moon system by a common source immediately after the accretion of the Moon.

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## 1. Introduction

The recent findings of 'water' in lunar materials have called into question mechanisms related to the retention of volatiles during accretion and have highlighted the possibility of late delivery of volatiles to the Moon (Barnes et al., 2013a; Boyce et al., 2010; Füri et al., 2014; Greenwood et al., 2011; Hauri et al., 2011; Hui et al., 2013; Liu et al., 2012; McCubbin et al., 2010a, 2010b, 2011; Saal et al., 2008, 2013; Tartèse et al., 2013). Apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})]$  is a common accessory mineral in

lunar rocks that forms late in the crystallisation history of mafic magmas (e.g., Sha, 2000); crucially apatite is the only hydrous mineral found in lunar rocks. Consequently, a number of recent investigations have focused on quantifying the amount of hydroxyl (OH) in apatites from mare basalts (Apollo samples and lunar basaltic meteorites), with reports of OH contents up to ~15 000 ppm, with H isotopic composition (reported as  $\delta D$ ) ranging between ~100 and 1100‰ (Barnes et al., 2013a; Boyce et al., 2010; Greenwood et al., 2011; McCubbin et al., 2010a, 2011; Tartèse et al., 2013). Partly because of the rarity of apatites in lunar highlands samples, reports of OH and  $\delta D$  from these apatites are very limited but indicate OH contents ranging from ~150 to 1000 ppm with associated  $\delta D$  values between ~200 and 800‰ (Barnes et al., 2013c; Boyce et al., 2013; Greenwood et al., 2011; McCubbin et al., 2010a; Robinson et al., 2012, 2013). Recently,

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Hui et al. (2013) measured the H<sub>2</sub>O content of nominally anhydrous minerals (NAMs) from two ferroan anorthosites (FAN) and a Mg-suite troctolite. Their results predict a relatively wet lunar mantle, with the late-stage residual melt, termed urKREEP (K – potassium, REE – rare earth elements, P – phosphorous), of the lunar magma ocean (LMO) containing up to 1.4 wt.% H<sub>2</sub>O. These predictions are in apparent disagreement with the measured water contents from KREEP-related alkali-suite and Mg-suite lunar highlands samples that seem to be characterised by moderate to low water contents (e.g., Boyce et al., 2013; Greenwood et al., 2011; McCubbin et al., 2010a; Robinson et al., 2012, 2013).

It is widely accepted that the mare basalts and pyroclastic lunar glasses (mostly <4 Ga in age) formed much later than products composing the lunar highlands, after the LMO crystallisation and subsequent overturn/hybridisation of the LMO cumulate pile (e.g., Grove and Krawczynski, 2009). Consequently, their sources may have potentially incorporated late-delivered components such as water (Tartèse and Anand, 2013) and highly siderophile elements (Bottke et al., 2010; Day et al., 2007). These samples, therefore, appear to be non-ideal for constraining the water inventory and isotopic composition of water in the primitive Moon. In contrast, the water inventory of some of the lunar highlands samples, such as those analysed in this study, was most likely inherited from the earliest products of LMO crystallisation (McCubbin et al., 2011) and consequently these rocks are better candidates to reveal the amount and origin of water at the time of the Moon's formation.

We have measured the OH contents and H isotopic compositions of apatite grains from four lunar highlands samples belonging to the alkali-suite and Mg-suite group of rocks, namely, granite 14303,205, troctolite 76535,51, norite 77215,202, and norite 78235,43. Based on their geochemical characteristics and crystallisation ages (~4.44 to 4.29 Ga), these rocks are considered to represent mixtures of some of the most primitive magmas that formed from the partial-melting of early LMO cumulates, which then assimilated urKREEP and crustal components (Shearer and Papike, 2005; Elardo et al., 2011). Therefore, the results presented in this study provide key insights into the history of water in the primitive Moon and help place constraints on the source of this water in the context of the evolution of the Earth–Moon system.

## 2. Samples studied

The four Apollo samples (14303,205, 76535,51, 77215,202, and 78235,43) studied are in the form of polished thin sections (~30 µm thickness), mounted in an epoxy resin and prepared in a water-free medium at the NASA Johnson Space Centre.

Sample 14303 was collected at the Apollo 14 site, and has been classified as a crystalline-matrix breccia. The rock is identified as a strongly annealed clast-rich breccia from Fra Mauro in the lunar highlands (Chao et al., 1972). It contains a large granite clast originally identified in section 14303,204 by Warren et al. (1983), which is also represented in our thin section of the sample (14303,205). Geochemically, the granite clast is pristine and mineralogically it is composed of ~33 vol.% plagioclase, 32 vol.% K-feldspar, ~23 vol.% silica, ~11 vol.% pyroxene, and <1 vol.% ilmenite, and trace amounts of apatite, zircon, Fe–Ni metal, troilite, and olivine (Warren et al., 1983). The coarseness of the graphic intergrowths and pyroxene exsolution lamellae supports an intrusive origin for the granite clast (e.g. Warren et al., 1983). Shih et al. (1993, 1994) dated the granite clast using the bulk-rock K–Ca and Rb–Sr methods and obtained a date of  $3.95 \pm 0.38$  Ga, initially interpreted as its crystallisation age. This age is similar to a bulk-rock <sup>40</sup>Ar/<sup>39</sup>Ar plateau age of  $3.91 \pm 0.04$  Ga obtained by Kirsten et al. (1972). However, Meyer et al. (1996) analysed zircons in the granite clast and found U–Pb dates as old as  $4.308 \pm 0.004$  Ga. This date therefore represents a minimum crystallisation age for the granite,

the younger K–Ca, Rb–Sr and <sup>40</sup>Ar/<sup>39</sup>Ar dates at ~3.9 Ga being considered as the age of an impact event that formed the breccia. This sample has a cosmic ray exposure (CRE) age of 29 Ma (Kirsten et al., 1972).

Troctolite 76535 was collected at Apollo 17 Station 6 as part of a rake sample. It is a chemically pristine, un-shocked, coarse-grained plutonic rock (Warren, 1993). It contains ~40 to 50 vol.% plagioclase, ~40 to 50 vol.% olivine, ~4 vol.% orthopyroxene, accessory minerals and mesostasis (Dymek et al., 1975; Gooley et al., 1974; McCallum and Schwartz, 2001; Warren, 1993). This rock has a cumulate texture thought to be a result of slow cooling in a plutonic environment. It subsequently underwent a long period of sub-solidus recrystallisation and annealing, during which it was possibly affected by melt metasomatism creating symplectite assemblages (Elardo et al., 2012; Neal and Taylor, 1991), before being excavated by an impact which brought it onto the lunar surface. Sample 76535 can be considered as an end-member of the Mg-suite plutonic rocks, and crystallised at ~4.35 Ga (Borg et al., 2013). This sample has CRE age of  $210 \pm 30$  Ma (Bogard et al., 1975; Crozaz et al., 1974; Lugmair et al., 1976).

The friable breccia 77215 was collected from a boulder at Apollo 17 Station 7. It is a highly brecciated rock with several remnant lithic clasts which retain their primary igneous textures. The brecciated norite investigated in the present study contains ~41 vol.% orthopyroxene, ~54 vol.% plagioclase and minor amounts of phosphates, ilmenite, spinel, and other minerals. Plagioclase in this sample has only partially been converted to maskelynite. 77215 also contains low abundances of Ir and Ni attesting to its pristine nature (Chao et al., 1976). Studies of pyroxene exsolution lamellae suggest that this rock crystallised at upper crustal levels (Huebner et al., 1975), equilibrating at temperatures of ~850 °C (Andersen and Lindsley, 1982). The <sup>40</sup>Ar/<sup>39</sup>Ar date of ~3.98 Ga (Stettler et al., 1974) is thought to represent an impact age, while older dates ranging from ~4.4 Ga (Rb–Sr) to ~4.3 Ga (Sm–Nd) (Nakamura et al., 1976; Carlson et al., 2013) likely represent the crystallisation age of the norite parental melt. This rock has a CRE age of ~27 Ma (Stettler et al., 1974).

Norite 78235 was chipped from a boulder at Apollo 17 Station 8, and it is a coarse-grained, heavily shocked rock being composed of ~51 vol.% orthopyroxene, ~48 vol.% plagioclase, and accessory phases including phosphates, glasses and glass veins (e.g., McCallum and Mathez, 1975). This is one of the most Mg-rich norites, also considered to be of cumulate origin crystallising at a depth between 8 and 30 km in the lunar crust (Jackson et al., 1975). Recent age determinations seem to indicate a crystallisation age around ~4.35–4.44 Ga (Andreassen et al., 2013; Edmunson et al., 2009), making 78235 one of the oldest lunar samples. One of the youngest dates for this sample comes from <sup>40</sup>Ar/<sup>39</sup>Ar dating, which yielded a date of  $4.11 \pm 0.02$  Ga (Aeschlimann et al., 1982). These results are consistent with work of Premo and Tatsumoto (1991) who reported a U–Pb crystallisation age of  $4.426 \pm 0.065$  Ga, with a disturbance event dated at  $3.93 \pm 0.21$  Ga. The younger <sup>40</sup>Ar/<sup>39</sup>Ar and U–Pb dates thus likely record one or several impact events that affected this sample. Indeed, 78235 has experienced extensive shock-induced deformation, mainly evident through the occurrence of maskelynite (Dymek et al., 1975), thought to have formed at pressures reaching up to ~50 GPa (e.g., Sclar and Bauer, 1975). This sample has a long CRE age of  $292 \pm 14$  Ma (Drozd et al., 1977).

## 3. Analytical protocol

A combination of Scanning Electron Microscopy (SEM) and Electron Probe Micro-Analysis (EPMA) was used to locate apatites in polished sections and obtain their qualitative and quantitative elemental composition, respectively (see Supplementary Material for

further details). We surveyed at least 25 different lunar highlands samples but only these four samples contained apatite grains that were suitable for ion-probe analysis. The Cameca NanoSIMS 50L at The Open University was used for determining the OH contents and H isotopic composition of apatites following the protocol described in Barnes et al. (2013a) and Tartèse et al. (2013). We analysed 12 apatite grains in total from the four samples. A Cs<sup>+</sup> primary beam of ~420 to 480 pA current was used and negative secondary ions of <sup>1</sup>H, D, <sup>12</sup>C, and <sup>18</sup>O were collected simultaneously on electron multipliers. Electronic gating was used to restrict counting secondary ions from the inner 25% of the sputtered area. Before analysis, pre-sputtering was performed over a 20 μm × 20 μm area using a ~850 pA primary beam for 1 min to clean the sample surface. An electron gun was used to provide charge compensation. Due to the variation of apatite grain size within and between samples, and the need to avoid cracks or inclusions, the analysis areas varied from 10 μm × 10 μm to 4 μm × 4 μm. Over the different analytical sessions (November–December 2012 and May 2013) the vacuum of the analysis chamber of the instrument ranged from 1.5 × 10<sup>-9</sup> to 7.0 × 10<sup>-10</sup> Torr. Real time isotope imaging was carried out during the pre-sputtering to monitor <sup>1</sup>H and <sup>12</sup>C in order to identify cracks and hotspots. Occasionally, during an analysis a crack or hotspot appeared; in such a case, only the signal corresponding to analysis of the pristine sample was considered. This signal was isolated using the NanoSIMS DataEditor, software developed by Frank Gyngard (Washington University). Data inclusion was based on the <sup>12</sup>C signal, which is very low in lunar apatites but is several orders of magnitude higher for material filling the cracks. It must be pointed out that no discernible differences in D/H and <sup>1</sup>H/<sup>18</sup>O ratios have been observed when isolating portions of the signals compared to the ~20 min integration for the reference apatites, which ensure that standardisation to ~20 min long analyses remained valid. D/H ratios are hence forth expressed as δD relative to standard mean ocean water (SMOW).

Three terrestrial apatite standards (Ap003, Ap004, and Ap018 described in McCubbin et al., 2012) pressed in indium were used for calibration along with a “dry” San Carlos olivine crystal. This dry olivine was used to monitor instrumental H background (reported as equivalent OH throughout this manuscript), which varied from ~20 to 50 ppm OH (equivalent to 1–3 ppm H, or 11–26 ppm H<sub>2</sub>O). To ensure that this measure is adequate for epoxy-mounted samples, analyses were also carried out under our routine analytical conditions in olivine and plagioclase in sample 76535. Both minerals yielded between 7 and 9 ppm OH which is considered background OH assuming that these minerals are indeed dry. Overall, the calculated background OH contents for indium-pressed dry olivine and epoxy-mounted nominally anhydrous minerals are similar (see Supplementary Material for further details). Background OH calculated for each analytical session was therefore subtracted from the measured values of the unknown apatites (background for the different analytical sessions are given in Table 1). In addition we have estimated the associated D/H ratio of the instrumental H background measured on the San Carlos olivine, which corresponds to a δD value of -212 ± 212‰. As background H represents ~30 to 80% of the bulk signals measured on apatite in troctolite 76535, it obviously has a strong effect on the measured D/H ratios (Table 1). In the case of sample 76535, the driest sample we have analysed, the corrections for background contribution of OH and spallogenic contribution of D and H proved problematic (Table 1), rendering this data unusable. Therefore, the data for apatite in 76535 will not be discussed further in this contribution but can be found in the accompanying Supplementary Material. In contrast, correcting the apatite δD values in the norite and the granite samples for background contribution OH and spallogenic contribution of H and D does not seem to have any significant effect.

#### 4. Results

The OH contents and H isotopic compositions of apatite grains measured in this study considerably expand the existing OH-δD database for lunar highlands samples. Although a few investigators have reported preliminary OH-δD data for apatites from lunar highlands samples in conference abstracts (e.g., Barnes et al., 2013b, 2013c; Boyce et al., 2013; Robinson et al., 2012, 2013), only two reliable OH-δD data points (acquired on a single apatite grain from an alkali-suite clast in sample 14305) exist in the current peer-reviewed literature (Greenwood et al., 2011). Naturally, this limited OH-δD dataset on apatites from lunar highlands samples has not provided any significant insights into the history of water in the lunar crust.

Furthermore, none of these previous studies made any corrections for spallogenic production of H and D to their OH-δD dataset, which in some cases do seem to have significant effects. Samples with relatively long cosmic ray exposure ages in which apatites contain <200 ppm OH are especially affected. The CRE ages used to correct the data for each sample are provided above together with sample descriptions. The production rates we used in our corrections for cosmogenic production of H and D were 2 × 10<sup>-10</sup> mol H<sub>2</sub>/g/Ma for H and 0.5 × 10<sup>-12</sup> mol D<sub>2</sub>/g/Ma for D (Merlivat et al., 1976). We also applied this spallation correction to the OH-δD results published by Greenwood et al. (2011) for sample 14305, using a CRE age of 27.6 ± 1.5 Ma (Eugster et al., 1984). The final total uncertainties for both δD and OH were calculated by propagating the uncertainties in H and D production rates (estimated at 50% at the 2σ level; see discussion in Saal et al., 2013) and taking into account the uncertainties associated with both the CRE ages and the analytical error on the measured OH-δD values. Fig. 1 shows Back Scatter Electron (BSE) images of areas containing some of the apatite grains analysed in this study. The measured OH contents and δD values are listed in Table 1 along with the calculated OH contents and δD values after correcting for background contribution and spallogenic production of H and D. In norite 77215, apatite OH contents ranged from ~430 to 3400 ppm, with homogeneous δD values defining a weighted average δD of -281 ± 49‰ (95% confidence level) (Fig. 2). The apatites in norite 78235 have a very similar range of OH contents, from ~400 to 3100 ppm, and are also characterised by homogeneous δD values defining a weighted average δD value of -27 ± 98‰ (95% confidence level) (Fig. 2). Finally, the OH contents of apatites in the granite clast 14303 display a range from ~130 to 2240 ppm with associated δD values ranging from 110 ± 295‰ to -321 ± 390‰, the weighted average δD value being -105 ± 130‰ (95% confidence level) (Fig. 2). This average value is consistent with the δD value of -139 ± 97‰ of the analysis with the highest OH content, which is the least affected by any instrumental correction procedure and cosmogenic production of H and D.

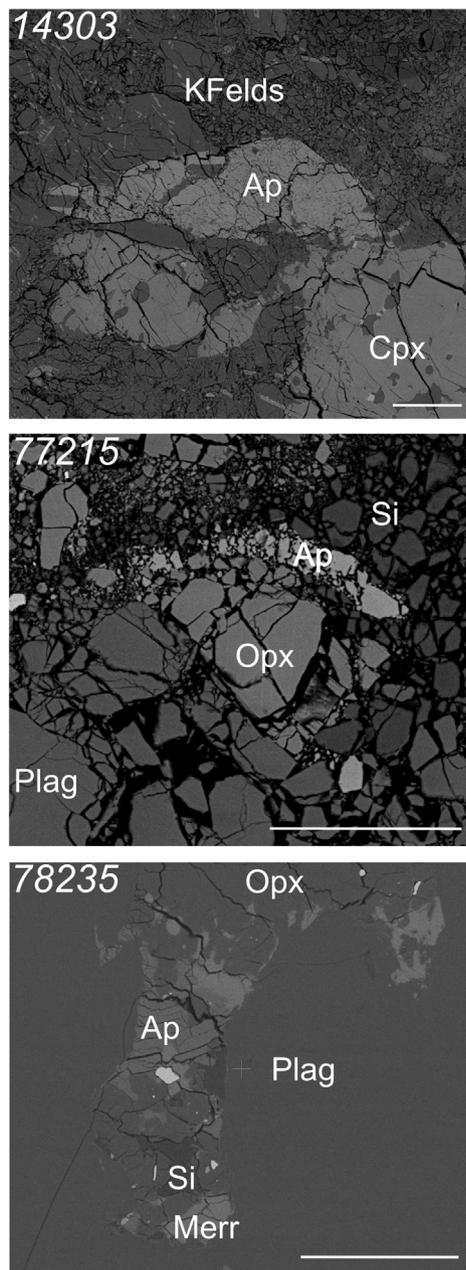
#### 5. Discussion

Compared to the data previously reported for apatites in highlands sample 14305 (Greenwood et al., 2011), only one data point from granite 14303 and one from norite 78235 fall within a similar range of OH content and δD (Fig. 2). The rest of the data for the granite clast and two norites display significantly elevated OH contents with lower δD values than have been reported previously. These new findings of elevated water contents in lunar highland samples suggest that appreciable amounts of water must have been present at the time of the LMO crystallisation, providing good consistency between our measurements and the predictions made by Hui et al. (2013). Also, the δD signatures of the two norites and the granite clast are clearly distinct from the Apollo

**Table 1**

Measured, background corrected, and spallation corrected OH- $\delta$ D data for apatites in the lunar highlands samples. The final column lists the spallation corrected uncertainties which are the total uncertainties including uncertainties in H and D spallogenic production rates ( $\pm 50\%$ ), uncertainties in cosmic ray exposure ages and the analytical uncertainties. Note: Data for sample 76535 (given in italics) are for information only and have not been used in making any scientific interpretations in the manuscript. However, a brief discussion about these data can be found in the Supplementary Material.

Filename	Measured				Background			Background corrected				Spallation corrected						
	OH (ppm)	$2\sigma$ (ppm)	$\delta$ D (‰)	$2\sigma$ (‰)	OH (ppm)	$\delta$ D (‰)	$2\sigma$ (‰)	%Bckg	OH (ppm)	$2\sigma$ (ppm)	$\delta$ D (‰)	$2\sigma$ (‰)	OH (ppm)	$2\sigma+$	$2\sigma-$	$\delta$ D (‰)	$2\sigma+$	$2\sigma-$
14303_Ap1_1	219	5	-177	372	49	-212.8	212.0	22	170	5	-167	375	170	5	5	-184	375	375
14303_Ap2a_1	1082	32	26	216	49	-212.8	212.0	5	1033	32	37	216	1033	32	32	35	216	216
14303_Ap2b_1	178	4	-274	385	49	-212.8	212.0	28	129	4	-297	390	129	4	4	-321	390	390
14303_Ap2c_1	2290	69	-139	97	49	-212.8	212.0	2	2241	69	-137	97	2241	69	69	-139	97	97
14303_Ap2d_1	257	7	60	292	49	-212.8	212.0	19	208	7	125	295	208	7	7	110	295	295
77215_Ap2_1	904	26	-203	163	49	-212.8	212.0	5	855	26	-202	163	855	26	26	-205	163	163
77215_Ap4_1	3451	105	-297	84	49	-212.8	212.0	1	3402	105	-298	84	3402	105	105	-299	84	84
77215_Ap5_1	478	13	-226	202	49	-212.8	212.0	10	429	13	-228	203	428	13	13	-234	203	203
77215_Ap6_1	2848	87	-269	95	49	-212.8	212.0	2	2799	87	-270	95	2799	87	87	-271	95	95
77215_Ap9_1	1757	53	-261	131	49	-212.8	212.0	3	1708	53	-262	132	1708	53	53	-264	132	132
77215_Ap8_1	1016	30	-373	174	49	-212.8	212.0	5	967	30	-381	175	967	30	30	-384	175	175
78235_Ap1#1_1	436	5	234	232	40	-212.8	212.0	9	396	5	279	233	395	5	5	203	237	238
78235_Ap1#1b_1	644	7	-109	156	40	-212.8	212.0	6	604	7	-102	156	603	7	7	-152	159	159
78235_Ap5_1	1084	12	37	105	40	-212.8	212.0	4	1044	12	46	106	1043	12	12	18	107	107
78235_Ap5#2_1	3132	35	-7	125	40	-212.8	212.0	1	3092	35	-5	125	3091	35	35	-14	125	125
78235_Ap5#4_1	2159	24	-41	78	40	-212.8	212.0	2	2119	24	-38	79	2118	24	24	-52	79	79
<i>76535_Ap1#1_1</i>	<i>46</i>	<i>0.3</i>	<i>1721</i>	<i>323</i>	<i>28</i>	<i>-212.8</i>	<i>212.0</i>	<i>61</i>	<i>18</i>	<i>0.3</i>	<i>4794</i>	<i>348</i>	<i>17</i>	<i>0.5</i>	<i>0.6</i>	<i>3720</i>	<i>1011</i>	<i>1131</i>
<i>76535_Ap1#2_1</i>	<i>54</i>	<i>0.4</i>	<i>1249</i>	<i>327</i>	<i>28</i>	<i>-212.8</i>	<i>212.0</i>	<i>52</i>	<i>26</i>	<i>0.4</i>	<i>2836</i>	<i>345</i>	<i>25</i>	<i>0.6</i>	<i>0.7</i>	<i>2055</i>	<i>689</i>	<i>783</i>
<i>76535_Ap1#3_1</i>	<i>45</i>	<i>0.3</i>	<i>1614</i>	<i>323</i>	<i>28</i>	<i>-212.8</i>	<i>212.0</i>	<i>62</i>	<i>17</i>	<i>0.3</i>	<i>4628</i>	<i>349</i>	<i>16</i>	<i>0.5</i>	<i>0.6</i>	<i>3503</i>	<i>1042</i>	<i>1166</i>
<i>76535_Ap3#1_1</i>	<i>82</i>	<i>0.8</i>	<i>687</i>	<i>345</i>	<i>28</i>	<i>-212.8</i>	<i>212.0</i>	<i>34</i>	<i>54</i>	<i>0.8</i>	<i>1150</i>	<i>353</i>	<i>54</i>	<i>0.9</i>	<i>1.0</i>	<i>763</i>	<i>440</i>	<i>477</i>
<i>76535_Ap3#2_1</i>	<i>38</i>	<i>0.2</i>	<i>987</i>	<i>428</i>	<i>28</i>	<i>-212.8</i>	<i>212.0</i>	<i>73</i>	<i>10</i>	<i>0.2</i>	<i>4312</i>	<i>456</i>	<i>9</i>	<i>0.4</i>	<i>0.6</i>	<i>2336</i>	<i>1733</i>	<i>1897</i>
<i>76535_Ap3#3_1</i>	<i>34</i>	<i>0.1</i>	<i>2243</i>	<i>367</i>	<i>28</i>	<i>-212.8</i>	<i>212.0</i>	<i>82</i>	<i>6</i>	<i>0.1</i>	<i>13305</i>	<i>406</i>	<i>5</i>	<i>0.4</i>	<i>0.5</i>	<i>11130</i>	<i>3953</i>	<i>3699</i>



**Fig. 1.** Back scatter electron (BSE) images of some of the apatite-bearing areas in the samples analysed in this study (14303, 77215, 78235). Ap = apatite, Merr = merrillite, Cpx = clinopyroxene, Opx = orthopyroxene, Si = silica, Plag = plagioclase, Kfelds = potassium feldspar. Scale bar in each image represents 100  $\mu\text{m}$ .

mare basalts in the OH– $\delta\text{D}$  space, being shifted towards lighter, Earth-like,  $\delta\text{D}$  values (Fig. 2).

### 5.1. Indigenous H isotopic composition of apatites in highland samples and petrological context

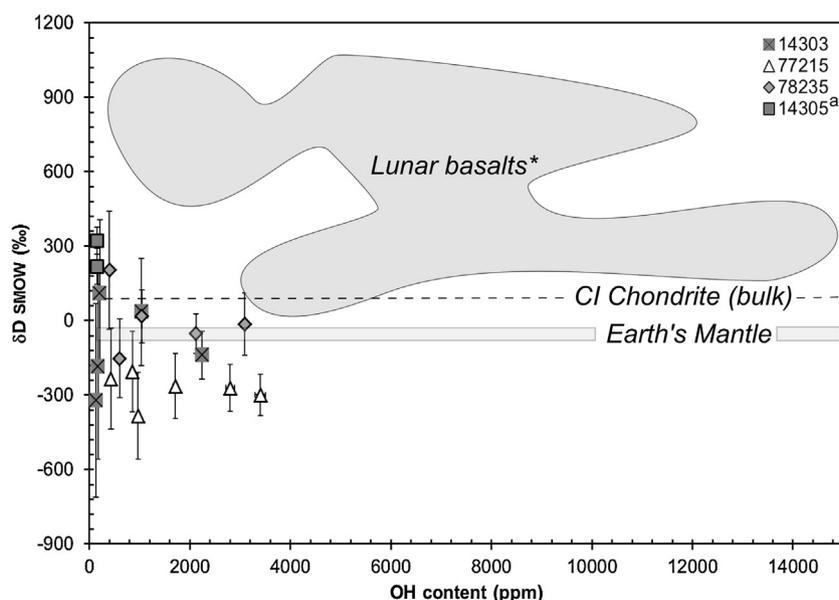
Firstly, it is important to note that the Earth-like D/H ratios measured in apatites in the norites and the granite clast are unlikely to result from cryptic terrestrial contamination as these are Apollo samples, which unlike lunar meteorites, have not been exposed to terrestrial weathering processes. Secondly, there appears to be no obvious effect of shock on the OH– $\delta\text{D}$  systematics of apatites when comparing data from highly-shocked lunar basaltic meteorites and those from Apollo mare basalts (Tartèse et al., 2013). Furthermore, Miniti et al. (2008) showed that hydrous am-

phibole exposed to shock pressures of  $\sim 32$  GPa, akin to impact shock pressures that may have been experienced by some of the lunar samples we have studied, devolatilises water and preferentially loses H over D, which resulted in an increase in  $\delta\text{D}$  by  $\sim 87\%$ . Therefore, if shock indeed plays a role in altering the original D/H ratio of apatite in the same manner as is observed for amphibole, which we do not know at present, then an increase of D/H ratios should be expected. In any case, such an increase in  $\delta\text{D}$  would not be resolvable in our analyses considering the uncertainties associated with the  $\delta\text{D}$  values.

In particular, examination of the shock related textural and mineralogical evidence suggests that of the three samples analysed 78235 is the most shocked, with 14303 being the least shocked. Despite the apparent differences in the levels of shock experienced by the three samples, there are no observable trends in their  $\delta\text{D}$ -OH systematics (Fig. 2). In fact, data for 14303 cover the entire range exhibited by the other two norite samples. Thus, it is unlikely that shock has played any significant role in altering the OH– $\delta\text{D}$  systematics of apatites in lunar highland samples investigated in this study. The matrix of the 14303 breccia is relatively fine grained (Chao et al., 1972), in comparison to the coarse-grained relict plutonic texture of the granite clast. Any extensive thermal annealing of the matrix after the impact event would have significantly affected the clast, by facilitating H diffusion, resulting in apatites with homogeneous OH– $\delta\text{D}$  signature in the granite. In contrast, this sample is the most heterogeneous in terms of its  $\delta\text{D}$  signature of the three samples that have been analysed in this study. Given the impact processing of all of the lunar highlands samples (all brecciated to a greater or lesser extent) it is worth considering the possibility of incorporation of solar wind H during formation of these breccia samples resulting in lowering of their  $\delta\text{D}$  values. However, for samples such as those analysed in this study in which the original igneous textural context for apatites is still preserved, and no impact melt occurs in the immediate vicinity of these grains, it is difficult to imagine a mechanism by which gaseous solar-wind H could have been introduced into crystalline structure of apatite. Incorporation of different amounts of solar-wind H also cannot be an explanation for the low- $\delta\text{D}$  signatures, especially for apatites in sample 77215, in which the measured OH content varies over a large range but  $\delta\text{D}$  values remain relatively constant. It is also worth noting that the effects of shock on the halogen content in apatite have not been well documented and virtually no such information exists in a lunar context. Hence, it is difficult to further quantify the shock effects. Nevertheless, based on the information we currently have, it seems justified to suggest that impact-induced shock effects are unlikely to account for the Earth-like D/H ratios observed, and as such we consider that apatites in these samples have preserved their indigenous magmatic  $\delta\text{D}$  signatures.

The plutonic nature of the studied samples implies that they crystallised at depth in the lunar crust (e.g. Jackson et al., 1975), and therefore likely did not experience volatile loss due to magmatic degassing of a vapour phase, which is known to be a process that can fractionate H from D isotopes, especially at the low  $f\text{O}_2$  that prevailed in the lunar interior as the major degassing H-bearing species is  $\text{H}_2$  (Füri et al., 2014; Sharp et al., 2013; Tartèse and Anand, 2013; Tartèse et al., 2013). The large range in OH contents measured in apatite grains characterised by relatively restricted  $\delta\text{D}$  variations, as observed in the two norites, is similar to what has been observed in low-Ti mare basalts and is consistent with protracted apatite crystallisation after variable degrees of crystallisation of the parental magma (Tartèse et al., 2013).

The fact that this pattern of large intra-sample and intra-grain OH variations is observed both in volcanic mare basalts that experienced little to moderate shock and in plutonic, heavily shocked, samples suggests that this observation is unlikely to be related to



**Fig. 2.** Plot comparing the spallation corrected values obtained in this study for two norite samples (77215, 78235) and a granite clast (14303) with literature data for Apollo mare basalts and lunar basaltic meteorites (Barnes et al., 2013a; Greenwood et al., 2011; Tartèse et al., 2013), and spallation corrected OH and  $\delta D$  of apatite in highlands rock 14305 (Greenwood et al., 2011). The black dashed line represents the approximate  $\delta D$  for CI – chondrites (Alexander et al., 2012), and the grey box indicates the range in estimates for the  $\delta D$  of the Earth's mantle (Lécuyer et al., 1998; McKeegan and Leshin, 2001). Uncertainties are reported at the  $2\sigma$  level.

a shock-related feature. For the plutonic norites 77215 and 78235, the variability of OH content within individual apatite grains might result from slow cooling of grains in isolated melt pockets, in which growing apatites are in contact with melts that become progressively more and more enriched in OH, as OH is incompatible in all the possible crystallising phases. This is in contrast to some known terrestrial examples whereby the intercumulus melt remains connected throughout the cumulate mush following slow solidification, allowing open diffusion and re-equilibration to occur (e.g. Wager et al., 1960). It appears that in the present case the slow crystallisation of isolated pockets of intercumulus melt with a lack of diffusion, has preserved the original cumulate textures (i.e. 78235) and produced the OH heterogeneities observed in the apatites. Thus the OH contents and the H isotopic composition of apatites in the two norites analysed in this study likely reflect their true lunar geochemical signatures. Whether the magma from which apatites crystallised in the granitic clast suffered degassing or not is less clear given the limited available dataset. Additionally, the granitic clast is considered to have formed from a highly evolved liquid which is thought to have undergone silicate liquid immiscibility (SLI) (e.g., Rutherford et al., 1974; Neal and Taylor, 1989; Snyder et al., 1995). In its simplest form, SLI is an igneous fractionation process by which the K-rich fraction (i.e. granitic composition) and REEP-rich fraction (i.e. ferrobasic composition) of a previously evolved basaltic liquid are separated (Rutherford et al., 1974). It is likely that SLI occurred prior to the crystallisation of apatite in the granitic melt, which could have affected the OH– $\delta D$  systematics of this sample. The similarities in the OH– $\delta D$  systematics of the granite (alkali suite) and that of the norites (Mg-suite) may indicate a potential petrogenetic link between the two suites. However, at this stage, we do not have sufficient understanding of the D/H fractionation in a highly fractionated magmatic system which has undergone SLI to merit any further discussion.

## 5.2. Water content of the norite parental melts

Among the samples we have analysed, the two norites are the best candidates to investigate the history of water in the lunar crust and to understand the origin of water in the primitive Moon. From the OH concentrations measured in apatite grains, it

is possible to estimate the minimum concentration of dissolved OH in the melt at the time of apatite crystallisation, provided accurate apatite–silicate melt partitioning data for OH are known. Unfortunately this information is not available for (1) lunar noritic compositions and (2) for typical conditions ( $P$ ,  $T$ ,  $fO_2$ ) under which lunar magmas crystallised. Nonetheless, two previous studies have investigated the apatite–melt partitioning behaviour of F, Cl, and OH in terrestrial and martian basaltic systems (Mathez and Webster, 2005; Vander Kaaden et al., 2012). The  $D^{OH}_{\text{apatite/melt}}$  determined by Vander Kaaden et al. (2012) ranges from 0.05 to 0.3. To estimate the minimum OH content of the melts at the time of apatite crystallisation, the larger value of 0.3 has been used as it provides the most conservative estimate of the OH content in the melt. On this basis, we calculated that at the time of apatite crystallisation the norite melt contained between  $\sim 1300$  and  $12000$  ppm OH. The cumulate nature of the norites and other Mg-suite rocks make calculation of parental melt water contents from apatite difficult given the paucity of information available on the major-element bulk-compositions of the norite parental melts. At a minimum, the bulk  $P_2O_5$  contents of the norite parental melt are needed to make estimates of parental-melt  $H_2O$  abundances from apatite. If we consider the range in  $P_2O_5$  abundances for all known lunar liquids, we can construct a possible range for parental melt  $H_2O$  abundances of the norites using existing phosphate saturation models (Tollari et al., 2006; Watson, 1979). In combining the phosphate saturation models with bulk-rock  $P_2O_5$  abundances from mare basalts (300–900 ppm) and KREEP basalts (4000–7000 ppm), apatite crystallisation can occur in lunar magmas as early as 88% crystallisation and as late as 99.5% crystallisation (e.g., Sha, 2000). Based on this range and on the effect of prior crystallisation of nominally anhydrous minerals (plagioclase and pyroxene), the parental melt of the norites could have contained between 3.6 to 785 ppm  $H_2O$ . It is important to note that these estimates are constructed primarily to illustrate the possible ranges in water contents in the absence of any better constraints on  $P_2O_5$  abundances in norite parental melts. Regardless of the actual value, the OH abundances of the apatite in the norites are strong evidence that the magmas involved in secondary crust production on the Moon were hydrated, and it is not only the lunar mantle that hosts water in the lunar interior. These observations

are also consistent with recent findings of water in lunar ferroan anorthosites (Hui et al., 2013), thought to represent the primary lunar crust.

### 5.3. Potential sources for lunar water

A number of sources potentially contributed to the overall inventory of lunar water, including primary indigenous water acquired during lunar accretion (Elkins-Tanton and Grove, 2011; Hui et al., 2013; McCubbin et al., 2010a; Saal et al., 2013), late addition of water through asteroidal and cometary impacts (Greenwood et al., 2011; Tartèse and Anand, 2013), and solar wind implanted H in lunar soils (Liu et al., 2012). The average D/H ratio of apatite in norite 78235 and in the granite clast in sample 14303 are consistent with estimates for the H isotopic composition of the present-day bulk-Earth and terrestrial mantle ( $\sim -40$  to  $-80\%$ ; Lécuyer et al., 1998, and references therein). In contrast, the average H isotopic composition of apatites in norite 77215 ( $\delta D = -280 \pm 50\%$ ) is lower. Such a value is comparable to reports of the  $\delta D$  of some CM chondrites and may be comparable to the  $\delta D$  values of pre-altered/metamorphosed primitive chondrites (Alexander et al., 2012 and references therein). Also, Sharp et al. (2013) recently suggested that the  $\delta D$  value of the proto-Earth mantle could have been lower by  $\sim 100$ – $200\%$  compared to its present-day value, yielding  $\delta D$  values of  $\sim -200 \pm 50\%$ . In such a case, the H isotopic composition measured in apatite in norite 77215 would be consistent with the H isotopic composition of the proto-Earth mantle.

Since we consider that the OH and D/H systematics in apatite in the noritic and granitic samples have not been significantly affected by degassing or impact processes, we ascertain that these samples retain their original  $\delta D$  signatures. In the Apollo collection, the norites are among the oldest and most pristine samples from the Moon and they have the potential to record the water signature of the Moon just after its formation. Petrogenetically, the Mg-suite is proposed to have formed from melt mixtures of some of the most primitive magmas that were derived from the partial-melting of early LMO cumulates and assimilated urKREEP and crustal components (Shearer and Papike, 2005). Therefore, these samples offer an excellent opportunity to investigate the primordial  $H_2O$  content and D/H ratio of the lunar interior. Our measurements indicate a range in OH contents in the noritic apatites overlapping those reported for apatite in an alkali-suite clast in sample 15404 (McCubbin et al., 2010a). The apatite  $\delta D$  values in the granite clast, especially those associated with higher OH contents, show some overlap with the norite data which is consistent with a petrogenetic link between the alkali-suite and Mg-suite rocks comprising the lunar highlands (e.g., Snyder et al., 1995). The range of  $\delta D$  values of apatites in norites and the granite, between  $\sim -300$  and  $100\%$ , is similar to those found in terrestrial and carbonaceous chondritic materials, as are D/H ratios of primitive melt inclusions trapped in high-Ti lunar pyroclastic glasses (Saal et al., 2013). This strongly suggests that there is a common origin for the water in the Earth–Moon system. Despite the similarity between the Earth and the Moon in terms of H isotopic composition (as well as other isotopic systems such as Si, W, O, and Ti; Fitoussi and Bourdon, 2012; Touboul et al., 2007; Wiechert et al., 2001; Zhang et al., 2012), it remains unclear if the volatiles were delivered before, during or soon after the Moon accreted. It is possible that the Earth–Moon system accreted volatiles from the same source (e.g., carbonaceous chondrites; Marty, 2012) and then subsequently differentiated such that their interiors were characterised by water with similar H isotopic composition. In a less cumbersome scenario, the Moon-forming material was derived from the proto-Earth, which would readily explain why both bodies share the same H isotopic composition. However, as pointed out by Saal et al. (2013), it is debated whether volatiles could

have been equilibrated between the vapour-silicate portions of the proto-lunar disk and the Earth's magma ocean (e.g., Pahlevan and Stevenson, 2007), or if a lunar embryo made of solid or partially molten Earth material could have cooled quickly in Earth orbit to later receive addition of disk material, including volatiles (Solomon and Chaiken, 1976). In addition, a new impact-generated silicate melt–vapour model from Visscher and Fegley (2013) may actually negate the dominating effect of hydrodynamic escape as a mechanism to lose H from the proto-lunar disk (e.g., Pahlevan and Stevenson, 2007) given the highly oxidising nature of the silicate material which likely comprised the disc. Their model indicates that H may not have been lost, and by extension, lends itself to the possibility that at least some Earth- $H_2O$  may have actually survived the Moon-forming impact (Füri et al., 2014; Visscher and Fegley, 2013).

Our study has investigated rocks belonging to the highlands magnesian suite (norites) and alkali suite (the granite clast) both of which are believed to be products of secondary crust production on the Moon. The presence of water in the magmas parental to the norites imply that their source regions in the lunar interior contained water. Therefore, regardless of how the volatiles were delivered into the accreted Moon, water had to be present early in the Moon's history, prior to the onset of crystallisation of the LMO, for water to be present in the source regions of the Mg-suite magmas (and incidentally the source regions of the mare basalts). Estimates of the timing of LMO crystallisation suggest that the entire LMO can solidify within the first 10 Ma and up to 200 Ma after the Moon formation (Elkins-Tanton et al., 2011). This implies that volatiles must have been present or delivered within this time frame to the lunar interior. The growing evidence for the presence of water (and other volatiles) in the lunar interior with similar composition to water found in the Earth suggests that the water was present at the time of the Moon-forming impact and may actually have survived this event.

## 6. Conclusions

- This study has highlighted the significance of the rare but crucially important hydrous-mineral, apatite, in lunar highlands samples for investigating the amount and sources of water in the primitive Moon.
- This work considerably expands the existing dataset for OH– $\delta D$  systematics for apatites in lunar highlands samples and is consistent with a petrogenetic link between the Mg-suite and alkali-suite rocks.
- A first order estimate for the water content of the norite parental melts provide strong evidence that the magmas involved in secondary crust production on the Moon were hydrated, in agreement with recent findings of water in lunar ferroan anorthosites.
- The analysis of some of the most primordial samples that we have from the Moon show that the water they contain, locked in the crystalline structure of apatite, is characterised by a H isotopic composition similar to that of the Earth and some carbonaceous chondrites.
- This remarkable consistency between the H isotopic composition of crustal samples from the lunar highlands and water-reservoirs of the Earth strongly argues for a common origin for water in the Earth–Moon system.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2014.01.015>.

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