The abundance, distribution, and isotopic composition of Hydrogen in the Moon as revealed by basaltic lunar samples: Implications for the volatile inventory of the Moon

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Abstract

In this study we have measured the OH contents and D/H ratios in apatite grains in lunar basalts. These new data considerably expand the limited dataset published so far. The data presented in this study also show that there is a major difference between high- and low-Ti mare basalts in terms of their OH and D/H systematics. Apatites in high-Ti basaltic samples display a relatively restricted range in OH contents (~1500–3000 ppm) with large δD variations (~600–1000‰) whereas apatites in low-Ti Apollo basalts and lunar meteorites display a comparatively larger range in OH contents (~500–15000 ppm), each sample displaying relatively restricted variations in their D/H ratios. Analyses of apatites in basaltic meteorites Miller Range 05035 and LaPaz Icefield 04841 substantially expand the lower bound for δD values measured in apatites from Apollo mare basalts, down to δD values of ~100‰. In these meteorites, high resolution mapping of the distribution of secondary ions of H and C was used to avoid cracks and hotspots. Together with mixing calculations for terrestrial contamination, this analytical protocol ensured that most of the values reported for MIL 05035 and LAP 04841 correspond to their actual lunar signatures. We interpret the large variations of apatite δD values in mare basalts between ~200‰ and 1000‰ as a result of different amounts of degassing of H-bearing species initially dissolved in the basaltic parental melts. Indeed, the average δD values measured in different low-Ti basalts are consistent with ~85–99% degassing of H as H2, starting from a δD value of 100‰. Degassing of H-bearing species essentially as H2 was favoured by the reduced nature of lunar magmas. In low-Ti mare basalts, apatite crystallisation occurred after degassing of the H-bearing species and the OH variations reflect different degrees of fractional crystallisation. In high-Ti mare basalts, large δD variations with relatively restricted range in OH contents imply that apatite crystallisation and degassing of H-bearing species were mostly coeval. Geochemical modelling integrating corrections for degassing and fractional crystallisation suggests that the mantle source regions of the different low-Ti mare basalts could have contained ~5–50 ppm H (equivalent to ~45–450 ppm H2O), which are similar to the estimated range of ~60–350 ppm water for the Earth’s upper mantle. Finally, the H isotopic composition of pre-degassed lunar hydrogen in mare basalts is consistent with a CI-chondrite-type value of ~100‰, which is consistent with the increasing evidence suggesting that the Earth, Mars and the Moon might have accreted similar water of chondritic origin.

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1. INTRODUCTION

Analytical advancements in recent years have permitted the successful detection of H-bearing species in lunar volcanic glasses, in olivine-hosted melt inclusions in these volcanic glasses (Hauri et al., 2011; Saal et al., 2008, 2013), in nominally anhydrous minerals from the lunar highlands (Hui et al., 2013), and in the mineral apatite present in both lunar basalts and magmatic rocks comprising the lunar highlands (Boyce et al., 2010, 2013; McCubbin et al., 2010b, 2010c, 2011; Greenwood et al., 2011, 2012; Barnes et al., 2013). To date, water has been detected and measured in apatite grains, structurally bound in its hydroxyl form (the structural formula of apatite is \([\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})]\)), in mare basalts from Apollo missions 11, 12, 14, 15 and 17 and from basaltic lunar meteorites (Boyce et al., 2010, 2013; McCubbin et al., 2010b, 2010c, 2011; Greenwood et al., 2011, 2012; Barnes et al., 2013). Clues to understanding the origin of lunar water lie in its isotopic composition. For example, the H isotopic composition of OH in olivine-hosted melt inclusions in volcanic glass beads is indistinguishable from the bulk D/H ratios of Cl-chondrites, and only marginally heavier than the D/H ratios of terrestrial materials (Saal et al., 2013). On the other hand, H isotopic composition of OH in agglutinates found in the lunar regolith suggests that H is in part derived from solar wind sources on the lunar surface (Liu et al., 2012). Hydrogen isotopic compositions of OH bound in apatite have been measured in mare basalts collected from all Apollo missions except from Apollo 15 collections (Greenwood et al., 2011, 2012; Barnes et al., 2013; Boyce et al., 2013). The high δD values that most mare basalts exhibit (≈600–1000‰) led Greenwood et al. (2011) to propose the existence of a high δD water reservoir in the Moon, arguing for its exotic cometary origin. In contrast, lunar water may be of chondritic origin, with high δD values in mare basalts reflecting intense H₂ degassing during magma ascent and emplacement (e.g. Sharp et al., 2012; Tartèse and Anand, 2013) or a result of spallogenic production of D on the lunar surface as in the case of pyroclastic glasses (Saal et al., 2013). In certain respects, samples brought back by the Apollo and Luna missions provided unrepresentative sampling of the lunar surface. Additional data from samples collected from other geographical locations are required to refine our models and to fully understand the origin, abundance and distribution of water inside the Moon.

Lunar meteorites arguably provide a random but wider and more representative sampling of the lunar surface compared to the samples collected during the Apollo and Luna Missions. Extending the database for the OH contents and the H isotopic composition of apatites in lunar rocks by including meteorites data allows additional constraints to be placed on lunar magmatic processes (e.g. Korotev, 2005). Among all lunar meteorites found on the Earth to date, there are ~10 distinct basaltic stones including LaPaz Icefield 04841 and Miller Range 05035, which are part of this study. The crystallisation ages of basaltic lunar meteorites have also expanded the age range for mare volcanism from as old as 4.35 Ga (Terada et al., 2007; Sokol et al., 2008) to as young as ~2.90 Ga (e.g. Fernandes et al., 2003; Borg et al., 2009). Among these basaltic meteorites, Yamato-793169, Asuka-881757, MIL 05035 and basaltic clasts in MET 01210 are thought to be paired (Joy et al., 2008; Liu et al., 2009; Arai et al., 2010) forming the Y/A/M/M group of meteorites. These stones are considered to be sourced from a region outside the Procellarum-KREEP Terrane (PKT) and provide, therefore, a unique view on a non-PKT-like mantle (Joy et al., 2008, 2010; Arai et al., 2010) as all the Apollo landing sites are within or in close proximity to the PKT.

In this study, we report the OH contents and H isotopic compositions of apatite grains from four mare basalts collected during the Apollo missions and from two lunar basaltic meteorites, MIL 05035 and LAP 04841. These new data include the first report of D/H ratio ofapatites from Apollo 15 mare basalts in peer-reviewed literature.

2. STUDIED SAMPLES

In this study, we have investigated 30 μm thick polished sections 10058,46, 12039,44, 15058,20 and 15555,991 from the Apollo collections, a 30 μm polished section (LAP 04841,19) of the meteorite LAP 04841, and two polished sections of the meteorite MIL 05035 (MIL 05035,37; 30 μm thickness and MIL 05035,30; ~150 μm thickness). Representative back-scattered electron (BSE) images highlighting textural features, and, bulk-rock chemical compositions of each sample are provided in Supplementary Fig. SM1 and Supplementary Table SM1, respectively. For the sake of completeness and to facilitate discussion, we have included data for samples 10044 and 12064 that have been previously studied by Barnes et al. (2013), as they have been analysed in the same lab following the same analytical protocol.

Sample 10058 is a high-Ti, low-K type basalt, and belongs to the B1 group of Apollo 11 basalts together with samples 10044 and 10047 (Beaty and Albee, 1978). It is a coarse-grained subophitic ilmenite basalt mainly composed of pyroxene, plagioclase, ilmenite and interstitial silica (e.g., Beaty and Albee, 1978). Sample 12039 is a low-Ti, coarse-grained pigeonite basalt mostly composed of pyroxene and plagioclase and accessory ilmenite (e.g., Neal et al., 1994). Sample 15058 is a coarse-grained low-Ti quartz-normative basalt that contains pyroxene and plagioclase with trace amounts of ilmenite and silica, whereas sample 15555 is a coarse-grained low-Ti olivine-normative basalt composed of olivine, pyroxene and plagioclase with trace amounts of ilmenite and silica, whereas sample 15555 is a coarse-grained low-Ti olivine-normative basalt composed of olivine, pyroxene and plagioclase with trace amounts of ilmenite and silica (Rhodes and Hubbard, 1973). In all of these samples, apatite is commonly found in late-stage mesostasis areas where it is associated with fayalite, K–Si-rich glass, FeNi grains, ulvöspinel, troilite, Zr-rich minerals and merrillite. LAP 04841 is the sixth stone comprising the LAP basaltic suite recovered in Antarctica (Hill et al., 2009). LAP stones are coarse-grained, holocrystalline basalts mainly consisting of pyroxene and plagioclase with interstitial ilmenite, and minor amounts of olivine and silica (Righter et al., 2005; Anand et al., 2006; Day et al., 2006; Joy et al., 2006; Hill et al., 2009). Late-stage mesostasis areas are abundant in LAP (~1–5 modal%) and mostly consist of fayalite, silica, K–Si-rich glass, FeNi grains, troilite,
baddeleyite, and phosphates (Anand et al., 2006; Day et al., 2006; Joy et al., 2006; Hill et al., 2009). Chemically, LAP basalts are low-Ti, low-Al and low-K basalts similar to Apollo 12 and 15 basalts. However, they are significantly more ferroan and enriched in REEs compared to Apollo 12 and 15 low-Ti basalts (Anand et al., 2006; Day et al., 2006; Joy et al., 2006). The MIL 05035 sections investigated are very similar to sections 31 and 34 described by Joy et al. (2008), displaying a coarse-grained texture consisting mainly of phenocrysts of pyroxene and plagioclase. One distinctive petrographic feature of MIL 05035 is the even larger abundance of late-stage mesostasis areas (~3–7% modal abundance in the two sections studied by Joy et al., 2008) that also contain silica, fayalite, FeNi grains, troilite, phosphates and K-rich glass (see for example Fig. 4g and h in Joy et al., 2008). Chemically, MIL 05035 is low- to very-low-Ti (hereafter grouped with the low-Ti basalts), low-Al and low-K basalt depleted in incompatible trace elements (ITE) compared to other basaltic meteorites and Apollo low-Ti basalts (Joy et al., 2008; Liu et al., 2009).

Our sample suite records approximately 1 billion years of the volcanic history of the Moon. MIL 05035 is the oldest basalt in our sample suite. For this sample, Nyquist et al. (2007) have reported Rb–Sr and Sm–Nd internal isochron ages of 3.90 ± 0.04 Ga and 3.80 ± 0.05 Ga, respectively. Fernandes et al. (2009) and Zhang et al. (2010), using 40Ar/39Ar dating and 206Pb/206Pb dating of zirconolite, respectively, reported an identical age of 3.85 ± 0.01 Ga. All the ages are therefore in good agreement and define a weighted mean age of 3.85 ± 0.02 Ga for MIL 05035, which likely corresponds to its crystallisation age. The crystallisation ages of the Apollo 11 B1 basalts (10044, 10047 and 10058) have been precisely constrained at 3.710 ± 0.004 Ga (Rasmussen et al., 2008; Tartèse et al., 2013).

Rb–Sr and Ar/Ar dating studies carried out on Apollo 15 sample 15058 suggest a crystallisation age of ~3.40 ± 0.05 Ga (Husain, 1974; Birck et al., 1975). More than 10 age-dating studies, mostly using Rb–Sr and Ar/Ar dating, have been carried out on sample 15555, suggesting a crystallisation age of ~3.35 ± 0.05 Ga, indistinguishable from the crystallisation age of 15058 (e.g., Papanastassiou and Wasserburg, 1973; Husain, 1974; Nyquist et al., 1991, and references therein). Apollo 12 samples 12064 and 12039 also define indistinguishable Rb–Sr isochron ages of 3.16 ± 0.07 Ga and 3.14 ± 0.08 Ga, respectively (Papanastassiou and Wasserburg, 1971; Nyquist et al., 1977). Finally, the LAP mare basalt is the youngest in the suite of samples studied here. Most of the ages obtained on LAP samples are in the range 3.04–2.93 Ga: the LAP mare-basalt meteorites. It should also be acknowledged that older 206Pb/206Pb dates have been reported in two baddeleyite grains (3351 ± 62–3614 ± 62 Ma in one grain analysed by Wang and Hsu, 2010; 3109 ± 29–3547 ± 21 Ma in another grain analysed by Zhang et al., 2010). These older dates might correspond to inherited baddeleyite grains entrained in the magma that formed the LAP mare basalt. Critical assessment and implications of these older dates recorded in LAP baddeleyite are beyond the scope of the current study and, therefore, are not discussed further.

3. ANALYTICAL TECHNIQUES

Polished sections were prepared at NASA Johnson Space Center in a water-free medium (see Supplementary material for details), mounted onto a glass plate using araldite epoxy. Each polished section was carbon coated and examined using a Quanta 3D Focused Ion Beam Scanning Electron Microscope (FIB SEM) at the Open University, fitted with an Oxford Instruments INCA energy dispersive X-ray detector. An electron beam with an acceleration voltage of 20 kV was used. To locate phosphate grains in these sections, BSE images and X-ray maps of the whole sections were obtained by energy dispersive spectroscopy (EDS). Phosphates were located using P X-ray maps of the sections. High magnification BSE imaging and quick acquisition of X-ray spectra for ~15 s permitted distinction betweenapatite and merrillite. We have previously tested the possibility of electron beam-induced volatile mobility inapatites during this mapping stage, and did not observe any adverse effects using such short exposures at light analytical conditions (Barnes et al., 2013). Isopropanol was subsequently used for removing carbon coating from the samples in preparation for ion-probe work.

The OH content and H isotope composition were measured in apatite grains using the Cameca NanoSIMS 50L at the Open University, following the protocol detailed in Barnes et al. (2013). In brief, a large Cs⁺ primary beam of ~250 pA current with an accelerating voltage of 16 kV was rastered on the sample surface over a 12 μm × 12 μm area during a 3 min pre-sputter to eliminate any remaining surface contamination. For the analysis, secondary ions of 1H, 2H, 13C and 18O were collected simultaneously from the central 5 μm × 5 μm area, of a 10 μm × 10 μm raster, on electron multipliers for ~20 min. In lunar meteorites, smaller raster areas were chosen depending on the sizes of the crack-free areas (Fig. 1). An electron gun was used for charge compensation and tuned to minimise its contribution to the background. The mass resolving power was set to ~4000, more than sufficient to readily resolve 3H⁺ from H₂⁺. For analysis, clean and crack-free areas within each apatite grain were first selected on the basis of BSE images. This was a straightforward task in Apollo samples but was complicated in lunar meteorites. For the latter, secondary ion images of 1H and 12C were monitored during pre-sputtering to further ensure that the analysed areas were free of any surficial contamination, cracks or hotspots. Unfortunately, hidden cracks often appeared during analyses ofapatites in lunar meteorites. In such cases, only portions of the secondary ion signal corresponding to analysis of pristine
material were considered and further processing was performed using the NanoSIMS DataEditor software developed by Frank Gyngard (Washington University). Data inclusion was based on the $^{13}$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 $^{13}$H/$^{18}$O ratios have been observed when partitioning portions of the signals compared to the ~20 min integration for the reference apatites, which ensure that standardisation to ~20 min long analyses remains valid. The OH contents were calibrated using the measured $^{13}$H/$^{18}$O ratio and the calibrations derived using reference apatites with known OH contents. Until May 2012, calibrations were based on repeated analyses of two apatite standards, Morocco (8600 ± 600 ppm OH) and Imaichi (400 ± 80 ppm OH) (as detailed in Barnes et al., 2013). Since May 2012, calibrations are made using a new set of reference apatites provided by Francis McCubbin and comprising Ap003 (1130 ± 750 ppm OH), Ap004 (10390 ± 940 ppm OH), Ap005 (7000 ± 570 ppm OH) and Ap018 (3780 ± 750 ppm OH) (McCubbin et al., 2012). Over the ~12 month period of analyses, standard errors on the slopes of the calibration lines used to calculate OH contents ranged from 0.5% to 5%, with an average value of 1.7% ($n = 19$). To correct measured D/H ratios from instrumental mass fractionation (IMF), two reference apatites were used, Morocco ($\delta D = -80 ± 3^\circ_{\text{off}}$, Barnes et al., 2013) until May 2012 and Ap004 ($\delta D = -45 ± 5^\circ_{\text{off}}$, McCubbin et al., 2012) since May 2012. For Morocco and Ap004 reference apatites, IMF (defined as $[1000 \times (D/H_{\text{measured}}/D/H_{\text{true}} - 1)]$) are 312 ± 69$^\circ_{\text{off}}$ ($n = 43$) and 299 ± 26$^\circ_{\text{off}}$ ($n = 15$), respectively. IMF is similar for these two reference apatites, which is consistent with these having similar OH contents (e.g., Hauri et al., 2006). The overall reproducibility of the D/H ratios measured on the reference apatites varied between 10 and 51$^\circ_{\text{off}}$ with an average of 29$^\circ_{\text{off}}$ (2σ standard deviation). For unknowns, the OH contents and D/H ratios, given using standard delta ($\delta$) notation with respect to the D/H ratio of the Vienna Standard Mean Ocean Water (VSMOW), and corrected for IMF effects based on repeated measurements of reference apatites, are reported with their 2σ uncertainties derived from the reproducibility of associated sets of standard analyses and the internal precision of each analysis in Table 1.

Finally, electron microprobe analysis of apatites was carried out at the Open University using a Cameca SX100 electron microprobe, following a slightly modified procedure described in Goldoff et al. (2012). The following analytical routine was used: Condition 1: F (PCO, 60s, no time zero correction) using beam conditions of 10 kV, 4 nA, and 5 μm spot size; and Condition 2: Na Kα (LTAP, 30s), Mg Kα (LTAP, 30s), Si Kα (LTAP, 30s), Fe Kα (LLIF, 30s), Mn Kα (30s), Cl Kα (LPET, 30s), Y Kα (LPET, 25s), Ce Kα (LPET, 25s), Ca Kα (PET, 25s), P Kα (PET, 25s), S Kα (PET, 30s) using beam conditions of 20 kV, 20 nA, and 5 μm spot size. Standardisation of F was performed using a SrF₂ crystal, and of Cl using a tugtuptite crystal, and were carefully checked against secondary apatite standards Ap003, Ap004, Ap018 (McCubbin et al., 2012).

4. RESULTS

4.1. F and Cl contents in apatites

After NanoSIMS analyses, we carried out electron microprobe analyses of apatites in all the samples in which OH contents and D/H ratios were measured except 10058 and MIL 05035 (Supplementary Table SM2). The F and Cl contents of apatites in the studied samples are plotted in Fig. 2. In sample 10044, apatite grains appear homogeneous and contain >3.0 wt.% F and <0.1 wt.% Cl. In sample 12039, apatite composition is much more variable with ~2.0–3.4 wt.% F and ~0.05–0.25 wt.% Cl. The measured F and Cl contents of apatites in sample 12064 range from ~2.0 to 2.8 wt.% and from 0.1 to 0.5 wt.%, respectively. In apatite grains from sample 15058, McCubbin et al. (2010b) measured F and Cl contents of ~3.0–3.6 wt.% and ~0.1–0.5 wt.%, respectively. This is consistent with our analyses of apatites in this sample that yielded ~3.0–3.8 wt.% F and ~0.2–0.3 wt.% Cl. In sample 15555, only two analyses were possible yielding ~2.0–2.6 wt.% F and ~0.2–0.3 wt.% Cl. Apatites in the two lunar meteorites have lower F contents. Analyses of apatites in LAP 04841 yielded F and Cl contents of ~0.7–1.7 wt.% and ~0.15–0.75 wt.%, respectively. F and Cl contents of 1.4–1.9 wt.% and 0.6–1.1 wt.%, respectively, were measured in apatite grains in MIL 05035 (Joy et al., 2008).
4.2. The OH contents and H isotopic composition of apatites

In Apollo mare-basalts, all the apatites analyzed display elevated \( \delta D \) values above \( /C24 \), which is consistent with previous investigations (Greenwood et al., 2011, 2012; Barnes et al., 2013). The heaviest \( \delta D \) values measured is \( /C24 \) in sample 10058 (Fig. 3), which is also in line with the heaviest \( \delta D \) values reported in case of lunar basalts by Barnes et al. (2013) and Greenwood et al. (2011, 2012). The OH content of apatites covers a wide range, from \( /C24 \) ppm up to \( /C24 \) ppm, which is comparable to OH contents reported by Greenwood et al. (2011, 2012) for apatites in Apollo 11 and 17 high-Ti basalts and in low-Ti basalt 12039. It is worth noting that Greenwood et al. (2011) reported even higher OH contents for some apatites in 12039 compared to this study (Fig. 3). Apatites in Apollo 12 and 15 low-Ti mare basalts are characterized by a large range of OH contents at relatively restricted \( \delta D \) values. In Apollo 11 high-Ti mare basalts, apatites display a comparatively restricted range of OH contents with highly variable \( \delta D \) values (Fig. 3). In samples 10044 and 10058, average OH contents and \( \delta D \) values are very similar (OH = 2401 ± 422 ppm and \( \delta D = 756 ± 131 \) ppm), respectively. In Apollo 15 samples 15058 and 15555, the average...

| Sample | OH (ppm) | 2σ (ppm) | \( \delta D \) (%o) | 2σ (%o) |
|--------|----------|----------|------------------|---------|
| 10058,46 |
| Ap1#1  | 3012 | 17 | 724 | 74 |
| Ap1#2  | 2318 | 15 | 949 | 80 |
| Ap1#3  | 2112 | 14 | 1098 | 79 |
| Ap4#1  | 2619 | 16 | 678 | 84 |
| Ap4#2  | 3115 | 18 | 648 | 82 |
| Ap7#1  | 2098 | 14 | 735 | 86 |
| Ap3#1  | 2128 | 14 | 965 | 84 |
| Ap2#1  | 2528 | 15 | 929 | 79 |
| Ap2#2  | 2431 | 15 | 884 | 85 |
| Ap5#1  | 2962 | 17 | 618 | 77 |
| Sample 12039,44 |
| Ap2#1  | 3932 | 26 | 904 | 67 |
| Ap2#2  | 4552 | 30 | 967 | 65 |
| Ap1#1  | 4189 | 28 | 880 | 66 |
| Ap1#2  | 5607 | 35 | 767 | 63 |
| Ap1#3  | 3764 | 25 | 785 | 68 |
| Ap1#4  | 7174 | 44 | 812 | 60 |
| Ap1#5  | 3154 | 22 | 860 | 69 |
| Ap3#1  | 3646 | 24 | 889 | 67 |
| Ap3#2  | 2773 | 20 | 875 | 72 |
| Ap5#1  | 4492 | 29 | 822 | 65 |
| Ap6#1  | 1992 | 15 | 882 | 79 |
| Ap6#2  | 6006 | 38 | 991 | 61 |
| Ap8#1  | 5672 | 36 | 915 | 62 |
| Sample 15058,20 |
| Ap1#1  | 895  | 94  | 565 | 73 |
| Ap1#2  | 877  | 94  | 637 | 73 |
| Ap1#3  | 410  | 84  | 637 | 103 |
| Ap1#4  | 382  | 84  | 611 | 109 |
| Ap1#5  | 504  | 86  | 483 | 125 |
| Ap7#1  | 439  | 85  | 556 | 106 |
| Ap4#1  | 712  | 90  | 647 | 87 |
| Ap3#1  | 1418 | 105 | 510 | 69 |
| Sample 15355,991 |
| Ap5#1  | 2271 | 107 | 454 | 145 |
| Ap5#2  | 2653 | 113 | 682 | 115 |
| Ap2#1  | 6836 | 189 | 520 | 76 |
| Ap1#1  | 6022 | 174 | 578 | 56 |
| Ap1#2  | 5945 | 173 | 715 | 102 |
| Ap1#3  | 3665 | 132 | 632 | 63 |
| Sample MIL 05035,37 |
| Ap7#1  | 14222 | 372 | 317 | 29 |
| Ap7#2  | 6304  | 207 | 443 | 32 |
| Ap3#1  | 8676  | 256 | 574 | 47 |
| Ap3#2  | 11449 | 314 | 341 | 49 |
| Sample MIL 05035,30 |
| Ap11#1 | 9244  | 75  | 237 | 39 |
| Ap11#3 | 7693  | 64  | 388 | 71 |
| Ap11#4 | 5135  | 45  | 417 | 99 |
| Ap1#1  | 5684  | 50  | 283 | 117 |
| Ap1#2  | 5868  | 50  | 157 | 47 |
| Ap1#3  | 4799  | 42  | 93  | 75 |
| Ap1#4  | 3861  | 35  | 157 | 101 |
| Sample LAP 04841,19 |
| Ap1#1  | 10799 | 370  | 340 | 40 |
| Ap1#2  | 13909 | 474  | 278 | 72 |
| Ap1#3  | 14427 | 491  | 485 | 46 |

* Analyses that were truncated due to crack contamination (see text for details).
OH contents are 705 ± 354 ppm and 4565 ± 1945 ppm, also with very similar average δD values of 581 ± 62‰ and 597 ± 99‰, respectively. On average, δD values in apatites in Apollo 12 low-Ti mare basalts are ~300‰ heavier than those in apatites in Apollo 15 low-Ti mare basalts (Fig. 3). In MIL 05035, the OH contents and H isotope compositions obtained from 11 analyses, carried out on 4 separate apatite grains, range from ~3800 to 14200 ppm and ~100 to 570‰, respectively (Fig. 3). For LAP 04841, the OH contents and H isotope composition obtained from 10 analyses, carried out on 5 separate apatite grains, range from ~6600 to 14400 ppm and ~280 to 560‰, respectively (Fig. 3). For MIL 05035, our apatite δD measurements are consistent with the average δD value of ~400 ± 80‰ reported by Wang et al. (2012). The OH contents in apatites in LAP 04841 are also consistent with elevated OH contents reported by McCubbin et al. (2011) for apatites in the paired stone LAP 02205. It is interesting to note that apatites in both MIL 05035 and LAP 04841 display large variations in OH contents at relatively restricted δD values; a characteristic shared by Apollo 12 and 15 low-Ti mare basalts (Fig. 3). Notably, the δD values measured in apatites in these two lunar meteorites are outside the terrestrial range (Fig. 3). A few analyses show some overlap with data from Apollo 15 low-Ti mare basalts but, overall, the range in δD values of apatites in lunar meteorites MIL 05035 and LAP 04841 considerably expand the lower bound for δD values recorded in apatites from Apollo mare basalts. Also, apatites from MIL 05035 and LAP 04841 have higher OH contents than those in Apollo mare basalts. Finally, the δD values measured in apatites in MIL 05035 and LAP 04841 are comparable with the few δD values reported for apatites in an alkali anorthosite clast and in felsites (Greenwood et al., 2011, 2012; Robinson et al., 2012) suggesting the existence of reservoirs with low-δD signatures in the lunar interior.

5. DISCUSSION

5.1. Does the OH/δD systematics of apatites in lunar meteorite correspond to indigenous lunar water signatures?

5.1.1. Shock-induced effects

H isotope analyses carried out on apatites in Martian meteorites (Watson et al., 1994; Leshin, 2000; Boctor et al., 2003; Greenwood et al., 2008; Hallis et al., 2012) provide a good starting point to evaluate potential effects of impacts on the H isotope systematics in apatites. The high pressures and temperatures reached during a shock event can indeed volatilise hydrogen from hydrous minerals.
During such a process, the lighter isotope, H, is much more susceptible to mobilisation compared to the heavier isotope, D. For example, experiments conducted on kaersutite at a pressure of \(~32\) GPa have shown that impact shock can induce an increase of H\(_2\)O contents by \(2500–9000\) ppm together with an increase in \(\delta D\) values by \(70–90\%\) (Mnitti et al., 2008). Shock-induced volatilisation is also likely accompanied by implantation of hydrogen from the surrounding atmosphere. For Martian meteorites, such a process might indeed in part explain the very high \(\delta D\) values \((\sim1000–4000\%o)\) recorded in several minerals, as the Martian atmosphere is heavily enriched in D \((\delta D \sim 5000–7000\%o)\). Since the Moon has virtually no atmosphere, shock-induced implantation of hydrogen intoapatites from the surrounding atmosphere could not have altered their OH contents and H isotopic compositions. Finally, Greenwood et al. (2011) have proposed that some low \(\delta D\) values measured inapatites in sample 14053 could result from interaction with solar wind-implanted hydrogen in the lunar regolith during an impact-heating event. As stated by these authors, rock 14053 has a unique petrologic history (Greenwood et al., 2011). It is known to be the most reduced rock from the Moon, as exemplified by mesostasis fayalite and spinels being extensively reduced in the exterior portions of this rock (Taylor et al., 2005). Numerous sections of MIL 05035 and of the different paired LAP lunar meteorites have been studied in detail (Righter et al., 2005; Anand et al., 2006; Day et al., 2006; Joy et al., 2006, 2008; Hill et al., 2009; Liu et al., 2009). But such textural observations have never been reported. We, therefore, believe that it is unlikely that \(\delta D\) values inapatites in MIL 05035 and LAP 04841 were altered due to interaction with solar wind-implanted hydrogen in the lunar regolith during a metamorphic event.

5.1.2. Terrestrial contamination

LAP 04841 and MIL 05035 meteorites are finds that were inevitably subjected to terrestrial weathering. Based on a detailed petrological study, Joy et al. (2008) argued that fractures in the two sections of MIL 05035 they studied were not filled with terrestrial alteration products. However, Liu et al. (2009) reported terrestrial weathering products, characterised by the presence of clay minerals and a reddish-brown coloration, in one of the two sections they studied. These weathering products are limited to a restricted region in the section MIL 05035.6 studied by Liu et al. (2009), along cracks cutting through the fusion crust. Terrestrial weathering features are also minimal in the LAP mare-basalt meteorites (Anand et al., 2006; Day et al., 2006). In this study the NanoSIMS analyses were carried out in areas of theapatites that initially appeared to be devoid of cracks and hotspots. However, cracks originally hidden underneath the surface were often encountered during the course of the analyses, as evidenced by a sudden spike in \(^{13}C\) count rates. In these cases we used the NanoSIMS DataEditor software developed by Frank Gyngard (Washington University) to select only initial parts of the secondary ions signals that corresponded to analysis of pristine apatite. For the sake of completeness and cross-checking, we also carried out a few analyses in large fractures to ascertain the chemical and isotopic makeup of the infilling material. We measured D/H and \(^1H/^{12}C\) ratios of \(\sim 1.4 \times 10^{-4}\) and \(\sim 1.3 \times 10^{-1}\), respectively, which is consistent with measurements made on the Araldite resin surrounding the MIL 05035 section \((D/H \sim 1.3 \times 10^{-4}\) and \(^{1}H/^{12}C \sim 1.5 \times 10^{-1}\)). These results indicate that cracks and fractures have been filled by the Araldite resin used for sample preparation.

The residence of MIL 05035 and LAP 04841 in the Antarctic ice may have caused cryptic alteration ofapatite grains, although the cold temperatures of Antarctica would have significantly decreased the efficiency of any exchange between hydrogen isotopes in crystalline minerals and the Antarctic water. To test this hypothesis, we have calculated and plotted mixing trends between theoretical primary unaltered lunar apatite compositions and Antarctic water in a \(\delta D\) vs. OH binary diagram (Fig. 3). Unaltered apatite compositions have been selected to represent typical OH-\(\delta D\) compositions of Apollo 12 and 15 low-Ti mare basalts. A \(\delta D\) value of \(\sim 300\%o\) has been selected for Antarctic water, according to the data reported by Masson-Delmotte et al. (2008) for Antarctic ice in the regions from where MIL 05035 and LAP 04841 have been recovered. Fig. 3 shows that most of the apatite data from both meteorites are inconsistent with such a mixing between moderate OH contents/elevated \(\delta D\) values typical of Apollo mare basalts and \(\delta D\) value for Antarctic ice. In someapatites, in LAP 04841 for example, OH contents increase from \(\sim 9000\) ppm to \(\sim 15000\) ppm without any change in their \(\delta D\) values, which remain constant at \(300–400\%o\) (Fig. 3). At most, a few data points for apatites in MIL 05035 with OH contents below 6000 ppm and \(\delta D\) values of \(100–200\%o\) (Fig. 3) might represent contamination by Antarctic ice. Finally, apatites in some lunar meteorites have among the highest \(\delta^{37}Cl\) values reported for lunar samples \((\sim 20\%o\) in NWA 2977 and \(\sim 75\%o\) in Dhofar 458; Wang et al., 2012; Boyce et al., 2013). \(\delta^{37}Cl\) values of terrestrial materials do not depart greatly from \(0 \pm 2\%o\) (e.g., Sharp et al., 2013). It seems, therefore, unlikely that apatites in these lunar meteorites would have preserved some of the heaviest Cl isotope ratios among lunar samples if they had been compromised by weathering on Earth. From all the above lines of evidence, we believe that most of the apatite grains we have analysed in basaltic meteorites LAP 04841 and MIL 05035 are likely to have retained their original lunar H isotopic composition.

5.2. Differences between high- and low-Ti mare basalts

5.2.1. F, Cl and OH systematics

Firstly, it is important to assess whether OH contents measured by SIMS are consistent with OH contents calculated from electron microprobe measurements of F and Cl contents (this assumes that all of the missing component in apatite volatile sites corresponds to structurally bound OH; see for example McCubbin et al., 2010b). Fig. 4a shows that there is good general agreement between OH contents calculated from electron microprobe analyses (given as atom per formula unit (apfu) in Fig. 4a) and those directly measured by SIMS. The OH variations measured in apatite
and low-Ti mare basalts in terms of their OH content and D/H signatures. The high-Ti mare basalts display a restricted range in OH contents (~1500–3000 ppm) with large δD variations (~600–1000‰) whereas the existing dataset for low-Ti mare basalts displays a large range in OH contents (~500–15000 ppm), as shown in Fig. 3. Moreover, individual low-Ti samples display relatively restricted δD ranges (~800–1000‰ for Apollo 12 basalts, ~500–700‰ for Apollo 15 samples, ~300–500‰ for LAP 04841 and ~200–400‰ for MIL 05035; Fig. 3).

During magma cooling and crystallisation, there are two processes which have opposite effects on the concentration of the total H-component (including H, OH and H₂O) in the melt: the progressive crystallisation of nominally anhydrous phases such as pyroxene and plagioclase will lead to enrichment of the total H-component in the melt, because H behaves incompatibly during crystallisation of magmas (e.g., Aubaud et al., 2004), whereas magma degassing of H-bearing species leads to a decrease in the total H-component. The OH contents measured in apatites in mare basalts are thus likely a net result of the complex interplay between crystallisation and degassing processes. These two processes have distinct effects on D/H ratios of the remaining melt. Crystallisation of nominally anhydrous phases has only a limited effect on fractionation of H and D isotopes; of the order of a few tens of permil (e.g., Bindeman et al., 2012). Degassing of OH/H₂O also results in very limited D/H frctionations of the order of a few tens of permil (e.g., Taylor et al., 1983; Kyser and O’Neill, 1984). However, degassing of H-bearing species such as H₂, CH₄ or HCl, for example, strongly fractionates H from D (Richet et al., 1977), leaving a D-enriched residual total H-component in the melt. The large δD variations and limited range of OH contents recorded in high-Ti Apollo mare basalts thus suggest that the crystallisation of apatite grains and the degassing of H-bearing species were two processes that occurred simultaneously. In contrast, the large OH variations with a narrow range of δD values characterising the low-Ti mare basalts imply that apatite started to crystallise after degassing of H-bearing species, such that the large ranges in apatite OH contents recorded in most of the low-Ti mare basalts reflect protracted crystallisation during slow cooling following the main phase of degassing. This major difference between high- and low-Ti mare basalts may be related to fundamental differences in their petrogenesis. This suggests that degassing occurred very late in high-Ti mare-basalt evolution, during apatite crystallisation, whereas magma degassing had already occurred in low-Ti mare basalts by the time apatite started to crystallise. This might be related to differences in several parameters, which are all interlinked but poorly understood for lunar conditions, such as magma ascent rate, emplacement temperature, viscosity and chemical composition.

5.3. Elevated D/H ratios and magma degassing

To account for the elevated δD values measured in most of the Apollo mare basalts they studied, Greenwood et al. (2011) proposed the existence of a D-enriched reservoir of cometary origin trapped in the lunar interior. Tartèse and
Anand (2013) proposed an alternative hypothesis to account for these elevated $\delta^D$ values involving D/H fractionation during degassing of molecular $H_2$ from lunar basaltic magmas. At the low oxygen fugacity that prevailed in lunar magmas, about 1–2 log units below the iron-wüstite buffer (hereafter denoted as IW; Sato et al., 1973; Sato, 1976; Wadhwa, 2008), the total H-component is likely to be a mixture of molecular $H_2$ and of the hydrous species $H_2O$ and OH, hereafter referred as $H_2Ot$ (e.g., Elkins-Tanton and Grove, 2011; Hirschmann et al., 2012; Zhang, 2012). In lunar magmas, the $H_2/(H_2+H_2Ot)$ ratio varies with the total H content, the temperature, the pressure and the oxygen fugacity (Hirschmann et al., 2012). The total H-component that can be dissolved in the melt and its $H_2/(H_2+H_2Ot)$ ratio both decrease with decreasing P, and at the low pressures that prevailed during mare basalt eruptions, $H_2Ot$ likely dominated the total budget of dissolved H-bearing species (Hirschmann et al., 2012). However, speciation of these species in the degassed phase would have been different. Indeed, the gas phase will behave more ideally than the melt during degassing, and the $H_2/(H_2+H_2Ot)$ ratio in the gas phase will be $>1$ at IW–2 to IW–1.

As a result, the vapour always has a higher $H_2/H_2Ot$ ratio than the melt at given T, P and $fO_2$ conditions (e.g., Zhang and Ni, 2010 and references therein). Thus, degassing processes have redox implications, as degassing converts some dissolved $H_2Ot$ to $H_2$ vapour. Also, other volatile species such as C, S, F and Cl were probably dissolved in lunar magmas. Indeed, mare basalts contain $\sim$10–50 ppm C, $\sim$500–2000 ppm S, $\sim$50 ppm F and $\sim$5 ppm Cl (e.g., Fegley and Swindle, 1993). We have used the GFluid package (Zhang and Duan, 2010) to compute the composition of the gas phase in the C–O–H system, at 1200 °C and for different pressures and $fO_2$ (Fig. 5). At high pressures above 5 kbar and $fO_2<1W$, CH$_4$ is by far the dominant C species. At $fO_2<1W–0.5$, $H_2$ dominates over $H_2O$, the $H_2/(H_2+H_2Ot)$ ratio reaching $\sim$0.9 at $fO_2=1W–2$. When the pressure decreases to about 1 kbar, CO and CO$_2$ species become important constituents of the gas phase at $fO_2>1W$. Finally, at 100 bar, the C–O–H system is only stable at $fO_2<1W–1.2$ and the $H_2–H_2O$ inventory is largely dominated by $H_2$. Degassing of mare magmas likely occurred at low pressures, upon arrival closer to the surface, and at low $fO_2(<IW–1; e.g., Wadhwa, 2008). Under such conditions, CH$_4$ appears to be a very minor constituent of the degassed phase. S-bearing species might be important constituents of the gas phase but unfortunately S is not included in the GFluid package. However, S is much more stable in the melt than in the gas phase for oxygen fugacity below 1W+1 (O’Neill and Mavrogenes, 2002; Gaillard and Scaillet, 2009), and degassing of S-bearing species might have thus been very limited. Finally, little is known on the partitioning behaviour of F and Cl between vapour and basaltic melts for terrestrial systems but it appears that the relatively high Cl and F solubility in mafic silicate melts make them unlikely to be major constituents of magmatic vapours produced by decompression-driven degassing of deep-ascending magmas (e.g., Webster et al., 1999; Aiuppa et al., 2009; Edmonds et al., 2009). Our knowledge of F and Cl behaviour is even more limited at reducing conditions. Ustunisik et al. (2011) have recently investigated the behaviour of these species during degassing (H, F, Cl and S) by simulating low-P crystallisation of a lunar-type magma under vacuum conditions. Their experiment suggests that extensive degassing occurred very quickly, with more than 85% of H, Cl and S and $\sim$60% of F lost. The degassed phase was constituted by

![Fig. 5. Vapour-phase compositions at 1200 °C, expressed in mole fraction, as a function of oxygen fugacity. The four panels show results at different pressures of 10000, 5000, 1000 and 100 bar. Calculations have been carried out with the GFluid package (Zhang and Duan, 2010).](image-url)
at which causes a smaller increase of at 1100–1300 °C than displayed in (1977) between the different H-bearing species and H₂ at 900 °C. In Apollo 15 low-Ti mare basalts, ~97–98% degassing at 1100–1300 °C was required to reach δD values of ~600‰ (Fig. 6). In Apollo 12 low-Ti mare basalts, the elevated δD values of ~900‰ can be accounted for by 99% degassing at ~1100 °C (Fig. 6). Finally, the highest δD values of ~1000‰ recorded in Apollo 11 high-Ti can only be reached after ~98.5% degassing at relatively lower temperatures of ~900 °C (Fig. 6). This “low-T” degassing for high-Ti mare basalts is consistent with our observation that degassing occurred very late in these high-Ti magmas, during apatite crystallisation.

5.4. Implications for the hydrogen content of the lunar interior

As first highlighted by Boyce et al. (2010), apatites in lunar basalt 14053, have volatile abundances comparable to terrestrial apatites. Over the last few years, several groups have reported hydroxyl contents of apatite grains from mare basalts (McCubbin et al., 2010c; Greenwood et al., 2011, 2012; Barnes et al., 2013) expanding the existing dataset and confirming the elevated volatile abundances in lunar apatites. These recent findings are also consistent with measurements made on volcanic glass beads and their melt inclusions by Saal et al. (2008, 2013) and Hauri et al. (2011), suggesting that mare magmas contained as much H (in terms of mass equivalence) as terrestrial basalts. Our current study significantly expands the database of apatite OH contents in mare basalts by adding 58 new measurements from samples collected during the Apollo missions and from two lunar meteorites. Overall, the OH content of apatites analysed in this study range between ~0 and 1.5 wt.% (Fig. 7). This range is similar to the range of OH contents recorded in terrestrial apatites from mafic magmas (Fig. 7). The distribution of OH contents in lunar apatites is also similar to the distribution in terrestrial apatites from mafic rocks, with a majority of analyses yielding between ~0 and 0.5 wt.% OH (Fig. 7). Our new measurements on apatites coupled with the existing dataset on apatites, glass beads and melt inclusions, provide the strongest evidence yet of the existence of at least some portions of the lunar mantle with as much hydrogen as the terrestrial upper mantle.

From the OH concentrations measured in apatite grains, it is possible to estimate the concentration of dissolved OH present in the melt when apatite crystallised, provided adequate apatite–silicate melt partitioning data for OH are known. Unfortunately these are not known for (1) typical lunar basalt compositions and (2) for typical conditions (P, T, fO₂) under which mare magmas crystallised. Two studies have determined 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 experimental martian basaltic melts of Vander Kaaden et al. (2012) simulate the composition of the basaltic shergottite QUE 94201, which represents a relatively good analogue for low-Ti mare basalt compositions.
The $D_{\text{OH}}^{\text{apatite/basalt}}$ determined by Vander Kaaden et al. (2012) range from 0.05 to 0.3. To estimate the OH content of the melts at the time ofapatite crystallisation, the larger value of 0.3 has been used as it provides the most conservative estimate of the OH content in the melt. This value is also consistent with the value of 0.25 for $D_{\text{OH}}^{\text{apatite/basalt}}$ estimated by McCubbin et al. (2011) based on the experimental work of Mathez and Webster (2005). Overall, OH contents in the basaltic melts at the time ofapatite crystallisation range between 0.54 and 1.09 wt.% for the Apollo high-Ti basalts and from 0.13 to 2.28 wt.% for the Apollo low-Ti mare basalts (Table 2). Melts parental to basaltic meteorites were richer in OH (1.29–4.81 wt.% OH), compared to parental melts for Apollo mare basalts (Table 2). For low-Ti mare basalts, this corresponds to approximately an order of magnitude variation in terms of maximum H contents in the melts (278–2829 ppm, Fig. 8a and Table 2). To try to constrain the H content in the mantle source regions of lunar basalts, we need to take into account both the crystallisation of nominally anhydrous minerals (NAM) such as pyroxenes and plagioclases, which increased the total H-component in the melt, and the magmatic degassing that decreased it. In low-Ti mare basalts, apatite crystallisation occurred after volatile degassing. In the following calculation, we thus consider that degassing occurred early during magma ascent towards the surface, followed by lava crystallisation on the lunar surface.

In mare basalts, apatite crystallises very late, from residual or immiscible melts produced by extreme crystal fractionation (e.g., Hess et al., 1990). Experiments conducted by Sha (2000) have shown that phosphate saturation is reached after more than 96% fractional crystallisation in both high- and low-Ti mare basalts. The calculation made by Tartèse and Anand (2013), using the few reports of the Th contents in phosphates, also suggest that phosphates crystallise after 97–99.5% fractional crystallisation. Considering that the highest H contents were measured in the last-forming apatite areas that crystallised, after 99.5% fractional crystallisation, we calculate that the low-Ti melts contained between ~1.5 and 15 ppm H after degassing of H-bearing species, and that overall, apatite crystallisation occurred after 98% fractional crystallisation (Fig. 8a and Table 2). As detailed in the previous section, the $\delta D$ values measured in apatites allow us to estimate the amount of H that has been degassed from the magmas. Taking into account that ~85–99% of H had been lost through degassing, depending on the samples, we can calculate that the different low-Ti basaltic melts contained between ~74 and 620 ppm H before degassing (Fig. 8a and Table 2). As detailed above, apatite crystallisation and degassing occurred simultaneously in high-Ti mare basalts. It is therefore complicated to estimate their pre-eruptive H content. Fig. 8b illustrates a simplified model that could account qualitatively for the OH contents and $\delta D$ values measured in apatites in high-Ti mare basalts. These OH contents and $\delta D$ values can be modelled starting from a melt containing ~100 ppm H. This melt underwent 98% of crystallisation of NAMs, which raised the H content in the melt to ~5000 ppm (~4.5 wt.% H$_2$O). This melt then started degassing. Degassing of ~96% of H increased the $\delta D$ value of the remaining H-bearing species in the melt to ~600$^{\text{ppm}}$. Crystallisation of NAMs continued to take place, and ~70% crystallisation of the remaining melt raised the total H content from ~250 to 1200 ppm. Further degassing of H and concomitant crystallisation of NAMs adequately model the melt H contents (~300–600 ppm) and $\delta D$ values (~600–1000$^{\text{ppm}}$) corresponding to analyses of apatites in high-Ti mare basalts (Fig. 8b). This model is non-unique and only provides qualitative estimates of the possible H contents of the undegassed high-Ti melts. Hence, these samples won’t be considered further when discussing the H budget of the lunar mantle. The low-Ti basalts are thought to be produced by 5–10% partial melting of their source regions (e.g., Shearer and Papike, 1993). This would imply that the source regions of Apollo 15 mare basalts contained ~5–40 ppm H, the source region of Apollo 12 mare basalts contained ~30–65 ppm H and the source regions of MIL 05035 and LAP 04841 contained ~5–20 ppm H (Fig. 9 and Table 2). Apollo mare-basalt source regions thus appear to be slightly enriched in H compared to the source regions of the basaltic meteorites, especially for Apollo 12 mare basalts. Overall, the range of H contents in the mantle source regions of different samples studied here is consistent with estimates made by Hauri et al. (2011) of ~9–45 ppm H for the lunar mantle (Fig. 9). These values are also similar to the range of ~7–40 ppm H estimated for the terrestrial mantle (e.g., Saal et al., 2002; Albarède, 2009) and with
the estimates proposed by McCubbin et al. (2010a, 2012) of ~10–30 ppm H for the martian mantle although others have proposed lower H contents for the martian mantle below 5 ppm (Mysen et al., 1998; Wänke and Dreibus, 1994; Usui et al., 2012). The fact that apatites in both the terrestrial and lunar mafic rocks and their respective mantle source regions are characterised by similar OH contents may suggest that the petrogenesis of mafic rocks in these two planetary bodies adhered to very similar processes.

5.5. On the source of lunar hydrogen

Petrologic modelling of the crystallisation of the Lunar Magma Ocean (LMO) suggests that the lunar mantle may contain a maximum of 10 ppm water, which corresponds to about 1 ppm H (Elkins-Tanton and Grove, 2011). Indeed, apatites in KREEP-rich samples are mostly dry (McCubbin et al., 2011; Robinson et al., 2012). It is possible that the Moon initially accreted largely dry with most of the
volatiles likely being lost in the aftermath of a giant impact that led to its formation (e.g., Pahlevan and Stevenson, 2007). On the other hand, Hui et al. (2013) have measured the H$_2$O content of nominally anhydrous minerals from two ferroan anorthosites (FAN) and a Mg-suite troctolite. Their results predict a relatively wet lunar mantle, with mantle cumulates formed before the formation of the FAN flotation crust containing $\sim$1–10 ppm H$_2$O and a late-stage urKREEP residue containing up to 1.4 wt.% H$_2$O. Our petrologic modelling suggests that the source regions of different lunar basalts contained between 5 and 50 ppm H, which corresponds to $\sim$45–450 ppm H$_2$O in terms of mass equivalence. Such H abundances imply the addition of H into the lunar interior after the LMO crystallisation, consistent with the hypothesis put forward by Tarte`se and Anand (2013). To account for the elevated $\delta^D$ values measured in apatites in most of the Apollo mare basalts they studied, Greenwood et al. (2011) proposed the existence of a D-enriched reservoir in the lunar interior. As Oort cloud comets generally have elevated D/H ratio similar to those measured in some basaltic lunar apatites (Fig. 10), Greenwood et al. (2011) argued that delivery of cometary water was responsible for this D-enriched reservoir. However, as pointed out by Alexander et al. (2012), accretion of cometary material would not only have included cometary ices but also organic material, which is also D-rich. Hence, the bulk H isotopic composition of comets is likely to be even more D-rich than its water, which would not fit with the $\delta^D$ values measured in lunar basalts. Tarte`se and Anand (2013) proposed that late accretion of water-rich carbonaceous chondritic material was the source of H in the lunar interior. This has been recently backed up by the study carried out by Saal et al. (2013) on olivine-hosted melt inclusions in pyroclastic glasses. From the H isotopic composition of these melts inclusions these authors reached the same conclusion that lunar indigenous water has an isotopic composition indistinguishable to that of carbonaceous chondrites. As argued above, the degassing of H from basaltic melts, largely as molecular H$_2$, which is feasible at the very low lunar $f_{O_2}$, could adequately account for the elevated $\delta^D$ values up to $\sim$1000‰, starting with an initial $\delta^D$ typical of CI-type carbonaceous chondrites of 100‰ (Fig. 10). Accretion of chondritic material to the Earth–Moon system agrees well with direct observations made in ancient lunar regolith (e.g., Joy et al., 2012) and impact melt breccia (Steele et al., 2010), and numerous geochemical data such as different stable isotope ratios (Robert, 2001; Alexander et al., 2012; Marty, 2012), chondritic abundances of highly siderophile elements (Day et al., 2007; Bottke et al., 2010; Dale et al., 2012) and Hf–W systematics (Willbold et al., 2011). Interestingly, Usui et al. (2012) measured $\delta^D$ values of $\sim$275‰ in melt inclusions in the shergottite Yamato 980459 (Fig. 10), implying that the initial H isotope composition of the primordial water retained in the martian depleted-mantle source-region was lower than 275‰. This is in good agreement with the H isotopic composition of apatites in the martian meteorite Nakhla, reported by Hallis et al. (2012). These authors suggested a maximum $\delta^D$ value of $\sim$–110‰ for the martian mantle. There are growing pieces of evidence suggesting that the Earth, Mars and the Moon might therefore have accreted similar water of chondritic origin. The new data presented in this study on

Fig. 9. Calculated H contents of the mantle source regions for the different basalts studied here, as a function of the amount of partial melting of each mantle source region. Ranges in H contents for (a) the Moon is from Hauri et al. (2011) and (b) the Earth is from Albare`de (2009) and Saal et al. (2002).

Fig. 10. H isotopic composition of several Solar System objects. Data taken from Alexander et al. (2012), Bockelée-Morvan et al. (2012), Hartogh et al. (2011) and Usui et al. (2012).
Apollo mare basalts and basaltic lunar meteorites suggest heterogeneous and elevated H contents of ~5–50 ppm in the lunar mantle. This is also in line with the 25 ppm H estimate made by Tartèse and Anand (2013) for the mantle source regions of the samples analysed by Greenwood et al. (2011, 2012). Considering the uncertainties associated with the OH partitioning data between apatite and melts under lunar conditions, and the degree of partial-melting required to generate lunar magmas of specific compositions, it is remarkable to achieve a broad consistency with the estimate of ~9–45 ppm H made by Hauri et al. (2011) for the lunar mantle. This could indicate that late accretion to the Moon was dominated by a few very large impactors (e.g., Bottke et al., 2010), which were able to breach the early crystallised lithosphere and subsequent efficient mixing of H into the lunar mantle, as has been suggested for the Earth (e.g., Albarède, 2009; Willbold et al., 2011).

6. SUMMARY

The main findings from the present study are summarised below:

- The high spatial resolution afforded by the NanoSIMS 50L allowed the measurement of OH contents and D/H ratios in apatite grains in highly-fractured lunar meteorites. These data considerably expand the D/H ratios measured in Apollo mare basalts down to δD values of about 100‰.
- Apatites in high-Ti mare basalts are characterised by large D/H variations with relatively restricted OH variations, whereas apatites in low-Ti mare basalts display large OH variations with relatively little D/H variations.
- The overall large range in apatite δD values between ~100 and 1000‰ is well explained by different amount of degassing of H-bearing species initially dissolved in the basaltic melts. The average δD values measured in the different low-Ti basalts are consistent with ~85–99‰ degassing of H as H₂, starting from a δD value of 100‰. Degassing of H-bearing species essentially as H₂ was favoured by the reduced nature of lunar volcanism.
- In low-Ti mare basalts, apatite crystallised after degassing of the H-bearing species; the OH variations resulting from different degrees of fractional crystallisation afterwards. In high-Ti mare basalts, large δD variations with relatively restricted OH variations imply that apatite crystallisation and degassing of H-bearing species were mostly coeval.
- Geochemical modelling integrating corrections for degassing and fractional crystallisation suggests that the mantle source regions of the different low-Ti mare basalts were heterogeneous and contained ~5–50 ppm H (equivalent to ~45–450 ppm H₂O), which is similar to the range estimated for the Earth’s upper mantle.
- The D/H ratio of lunar hydrogen in undegassed mare basalt is consistent with a CI-chondrite-type value of ~100 ‰. Results from this study are thus in agreement with the growing pieces of evidence that suggest that the Earth, Mars and the Moon might have accreted similar water of chondritic origin.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.08.014.

REFERENCES

Aiuppa A., Baker D. R. and Webster J. D. (2009) Halogens in volcanic systems. Chem. Geol. 263, 1–18.
Albarède F. (2009) Volatile accretion history of the terrestrial planets and dynamic implications. Nature 461, 1227–1233.
Alexander C. M. O’., Bowden R., Fogel M. L., Howard K. T., Herd C. D. K. and Nittler L. R. (2012) The provenances of asteroids, and their contributions to the volatile inventories of the terrestrial planets. Science 337, 721–723.
Anand M., Taylor L. A., Floss C., Neal C. R., Terada K. and Tanikawa S. (2006) Petrology and geochemistry of LaPazPicefield 02205: a new unique low-Ti mare-basalt meteorite. Geochim. Cosmochim. Acta 70, 246–264.
Arai T., Hawke B. R., Giguere T. A., Misawa K., Miyamoto M. and Kojima H. (2010) Antarctic lunar meteorites Yamato-793169, Asuka-801757, MIL 05035, and MET 01210 (YAMM): launch pairing and possible cryptomare origin. Geochim. Cosmochim. Acta 74, 2231–2248.
Aubaud C., Hauri E. H. and Hirschmann M. M. (2004) Hydrogen partition coefficients between nominally anhydrous minerals and basaltic melts. Geophys. Res. Lett. 31, L20611. http://dx.doi.org/10.1029/2004GL021341.
Barnes J. J., Franchi I. A., Anand M., Tartèse R., Starkey N. A., Koike M., Sano Y. and Russell S. S. (2013) Accurate and precise measurements of the D/H ratio and hydroxyl content in lunar apatites using NanoSIMS. Chem. Geol. 337–338, 48–55.
Beatty D. W. and Albee A. L. (1978) Comparative petrology and possible genetic relations among the Apollo 11 basalts. Lunar Planet. Sci. IX. Lunar Planet. Inst., Houston. pp. 359–463.
Bindeman I. N., Kamenetsky V. S., Palandrini J. and Vennemann T. (2012) Hydrogen and oxygen isotope behaviors during variable degrees of upper mantle melting: example from the basaltic glasses from Macquarie Island. Chem. Geol. 310–311, 126–136.
Birck J. L., Fourcade S. and Allegre C. J. (1975) 87Rb/86Sr age of rocks from the Apollo 15 landing site and significance of internal isochron. Earth Planet. Sci. Lett. 26, 29–35.
Bockelé-Morvan D., Biver N., Swinyard B., de Val-Borro M., Crovisier J., Hartog P., Lis D. C., Moreno R., Szutowicz S., Lellouch E., Empeigne M., Blake G. A., Courtin R., Jarchow C., Kidger M., Küssers M., Rengel M., Davis G. R., Fulton T., Naylor D., Sidher S. and Walker H. (2012) Herschel measurements of the D/H and 18O/16O ratios in water in the Oort-cloud comet C/2009 P1 (Garradd). Astron. Astrophys. 544, L15.

Boctor N. Z., Alexander C. M. O. D., Wang J. and Hauri E. H. (2003) The sources of water in martian meteorites: clues from hydrogen isotopes. Geochim. Cosmochim. Acta 67, 3971–3986.

Borg L. E., Gaffney A. M., Shearer C. K., DePaolo D. J., Hutcheon I. D., Owens T. L., Ramon E. and Brennecka G. (2009) Mechanisms for incompatible-element enrichment on the Moon deduced from the lunar basaltic meteorite Northwest Africa 032. Geochim. Cosmochim. Acta 73, 3963–3980.

Boudreau A. and Simon A. (2007) Crystallization and degassing in the basement Sill, McMurdo Dry Valleys, Antarctica. J. Petrol. 48, 1369–1386.

Bottke W. F., Walker R. J., Day J. M. D., Nesvorny D. and Elkins-Tanton L. T. (2010) Stochastic late accretion to Earth, the Moon and Mars. Science 330, 1527–1530.

Boye J. W., Liu Y., Rossman G. R., Guan Y., Eiler J. M., Stolper E. M. and Taylor L. A. (2010) Lunar apatite with terrestrial volatile abundances. Nature 466, 466–469.

Boye J. W., Guan Y., Treiman A. H., Greenwood J. P., Eiler J. M. and Ma C. (2013) Volatile components in the moon: Abundances and isotope ratios of Cl and H in lunar apatites. Lunar Planet. Sci. XLIV. Lunar Planet. Inst., Houston. #28511 (abstr.).

Chu M. F., Wang K. L., Griffin W. L., Chung S. L., O’Reilly S. Y., Pearson N. J. and Izuka Y. (2009) Apatite composition: tracing petrogenetic processes in Transhimalayan granitoids. J. Petrol. 50, 1829–1855.

Dale C. W., Burton K. W., Greenwood R. C., Gannoun A., Wade J., Wood B. J. and Pearson D. G. (2012) Late accretion on the earliest planetesimal tracks revealed by the highly siderophile elements. Science 336, 72–75.

Day J. M. D., Pearson D. G. and Taylor L. A. (2007) Highly siderophile elements constraints on accretion and differentiation of the Earth-Moon system. Science 315, 217–219.

Day J. M. Taylor L. A., Floss C., Patchen A. D., Schnare D. and Pearson D. G. (2006) Comparative petrology, geochemistry and petrogenesis of evolved, low-Ti lunar mare basalt meteorites from the LaPaz icefield, Antarctica. Geochim. Cosmochim. Acta 70, 1581–1600.

Drinkwater J. L., Czamanske G. K. and Ford A. B. (1990) Apatite of the Dufek intrusion: distribution, paragenesis and chemistry. Can. Mineral. 28, 835–854.

Edmonds M., Gerlach T. M. and Herd R. A. (2009) Halogen degassing during ascent and eruption of water-poor basaltic magma. Chem. Geol. 263, 122–130.

Eiler J. M. and Kitchen N. (2004) Hydrogen isotope evidence for the origin and evolution of the carbonaceous chondrites. Geochim. Cosmochim. Acta 68, 1395–1411.

Elkins-Tanton L. T. and Grove T. L. (2011) Water (hydrogen) in the lunar mantle: results from petrology and magma ocean modeling. Earth Planet. Sci. Lett. 307, 173–179.

Fegley, Jr., B. and Swindle T. D. (1993) Lunar volatiles: implications for lunar resource utilization. In Resources of Near-Earth Space (eds. J. S. Lewis, M. S. Matthews and M. L. Guerrieri). Univ. of Arizona Press, Tucson, AZ, pp. 367–426.

Fernandes V. A., Burgess R. and Morris A. (2009) 39Ar/39Ar age determinations of lunar basalt meteorites Asuka 881757, Yamato 793169, Miller Range 05035, La Paz Icefield 02205, Northwest Africa 479, and basaltic breccia Elephant Moraine 96008. Meteorit. Planet. Sci. 44, 805–821.

Fernandes V. A., Burgess R. and Turner G. (2003) 39Ar–39Ar chronology of lunar meteorites Northwest Africa 032 and 773. Meteorit. Planet. Sci. 38, 555–564.

Guillard F. and Scaillet B. (2009) The sulfur content of volcanic gases on Mars. Earth Planet. Sci. Lett. 279, 34–43.

Goldoff B., Webster J. D. and Harlov D. E. (2012) Characterization of fluor-chlorapatites by electron probe microanalysis with a focus on time-dependent intensity variation of halogenes. Am. Mineral. 97, 1103–1115.

Greenwood J. P., Ioth S., Sakamoto N., Vicenzi E. P. and Yurimoto H. (2008) Hydrogen isotope evidence for loss of water from Mars through time. Geophys. Res. Lett. 35, L05203.

Greenwood J. P., Ioth S., Sakamoto N., Warren P., Taylor L. and Yurimoto H. (2011) Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. Nat. Geosci. 4, 79–82.

Greenwood J. P., Ioth S., Sakamoto N., Warren P., Taylor L. and Yurimoto H. (2012) Towards a wetter Moon: Implications of high volatile abundances in lunar apatite. Lunar Planet. Sci. XXXIII. Lunar Planet. Inst., Houston. #2089 (abstr.).

Hallis L. J., Taylor G. J., Nagashima K. and Huss G. R. (2012) Magmatic water in the martian meteorite Nakhl. Earth Planet. Sci. Lett. 359–360, 84–92.

Hartogh P., Lis D. C., Bockelé-Morvan D., de Val-Borro M., Biver N., Küppers M., Empeigne M., Bergin E. A., Crovisier J., Rengel M., Moreno R., Szutowicz S. and Blake G. A. (2011) Ocean-like water in the Jupiter-family comet 103P/Hartley 2. Nature 478, 218–220.

Hauri E. H., Shaw A. M., Wang J., Dixon J. E., King P. L. and Mandeville C. (2006) Matrix effects in hydrogen isotope analysis of silicate glasses by SIMS. Chem. Geol. 235, 352–365.

Hauri E. H., Weinreich T., Saal A. E., Rutherford M. C. and Van Orman J. A. (2011) High pre-eruptive water contents preserved in lunar melt inclusions. Science 333, 213–215.

Hess P. C., Horzempa P., Rutherford M. J. and Devine J. (1990) Phosphate equilibria in lunar basalts. Lunar Planet. Sci. XXXVIII. Lunar Planet. Inst., Houston. pp. 505–506.

Hill E., Taylor L. A., Floss C. and Liu Y. (2009) Lunar meteorite LaPazIcefield 04641: petrology, texture, and impact-shock effects of a low-Ti mare basalt. Meteorit. Planet. Sci. 44, 87–94.

Hirschmann M. M., Withers A. C., Ardia P. and Foley N. T. (2012) Solubility of molecular hydrogen in silicate melts and consequences for volatile evolution of terrestrial planets. Earth Planet. Sci. Lett. 345–348, 38–48.

Hui H., Peslier A. H., Zhang Y. and Neal C. R. (2013) Water in lunar anorthosites and evidence for a wet early Moon. Nat. Geosci. 6, 177–180.

Husain L. (1974) 39Ar–39Ar chronology and cosmic ray exposure ages of the Apollo 15 samples. J. Geophys. Res. 79, 2588–2606.

Joy K. H., Crawford I. A., Downes H., Russell S. S. and Kearsley I. A. (2008) The petrology and geochemistry of the lunar mare basalt meteorite Northwest Africa 032 and 773. Meteorit. Planet. Sci. 44, 1003–1025.

Joy K. H., Crawford I. A., Anand M., Greenwood R. C. and Franchi I. A. and Russell S. S. (2008) The petrology and geochemistry of Miller Range 05035: a new lunar gabbroic meteorite. Geochim. Cosmochim. Acta 72, 3822–3844.

Joy K. H., Crawford I. A., Russell S. S. and Kearsley A. T. (2010) Lunar meteorite regolith breccias: An in situ study of impact melt composition using LA-ICP-MS with implications for the composition of the lunar crust. Meteorit. Planet. Sci. 45, 917–946.

Joy K. H., Zolensky M. E., Nagashima K., Huss G. R., Ross D. K., McKay D. S. and Kring D. A. (2012) Direct detection of projectile relics from the end of the lunar basin-forming epoch. Science 336, 1426–1429.
Kerridge J. F. (1985) Carbon, hydrogen and nitrogen in carbonaceous chondrites: Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta* 49, 1707–1714.

Korotev R. L. (2005) Lunar geochemistry as told by lunar meteorites. *Chem. Erde-Ergeochem.* 65, 297–346.

Kyser T. K. and O’Neill J. R. (1984) Hydrogen isotope systematics of submarine basalts. *Geochim. Cosmochim. Acta* 48, 2123–2133.

Leshin L. A. (2000) Insights into martian water reservoirs from analyses of martian meteorite QUE 94201. *Geophys. Res. Lett.* 27, 2017–2020.

Liu Y., Floss C., Day J. M. D., Hill E. and Taylor L. A. (2009) A review of Antarctic surface snow isotopic composition: Observations, atmospheric circulation, and isotopic modeling. *J. Climate* 21, 3359–3387.

Mathez E. A. and Webster J. D. (2005) Partitioning behavior of chlorine and fluorine in the systemapatite-silicate-melt-fluid. *Geochim. Cosmochim. Acta* 69, 1275–1286.

McCubbins F. M., Elardo S. M., Shearer, Jr., C. K., Smirnov A., Mathez E. A. and Webster J. D. (2010) Petrogenesis of lunar mare basalt meteorite Miller Range 05095. *Meteorit. Planet. Sci.* 44, 261–284.

McCubbin F. M., Hauri E. H., Elardo S. M. and Taylor L. A. (2012) Direct measurement of hydroxyl in the lunar regolith and the origin of lunar surface water. *Nat. Geosci.* 5, 779–782.

Marty B. (2012) The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. *Earth Planet. Sci. Lett.* 313–314, 56–66.

Masson-Delmotte V., Hou S., Ekaykin A., Jouzel J., Arstariain A., Bernardo R. T., Bronwich D., Cattani O., Delmotte M., Faloud S., Frezzotti M., Gallée H., Genoni L., Isaksen E., Lantais A., Helsen M. M., Hofmann G., Lopez J., Morgan V., Motoyama H., Noone D., Oerter H., Petit J. R., Roayer A., Uemura R., Schmidt G. A., Schlosser E., Simões J. C., Steig E. J., Stenni B., Stevenard M., van den Brooere M. R., van de Wal S. R. W., van de Berg W. J., Vimeux F. and White J. W. C. (2008) A review of Antarctic surface snow isotopic composition: Observations, atmospheric circulation, and isotopic modeling. *J. Climate* 21, 3359–3387.

Nyquist L. E., Shih C. Y., Reese Y. and Bogard D. D. (2005) Age of lunar meteorite LAP 02205 and implications for impact-sampling of planetary surfaces. *Lunar Planet. Sci. XXXVI*. Lunar Planet. Inst., Houston. #1374 (abstr.).

O’Neill H. S. C. and Mavrogenes J. (2002) The sulfide saturation capacity and the sulphur content at sulfide saturation of silicate melts at 1400 °C and 1 bar. *J. Petrol.* 43, 1049–1087.

Pahlevan K. and Stevenson D. J. (2007) Equilibration in the aftermath of the lunar-forming giant impact. *Earth Planet. Sci. Lett.* 262, 438–449.

Papanastassiou D. A. and Wasserburg G. J. (1971) Lunar chronology and evolution from Rs-Rs studies of Apollo 11 and 12 samples. *Earth Planet. Sci. Lett.* 11, 37–62.

Papanastassiou D. A. and Wasserburg G. J. (1973) Rs-Rs ages and initial strontium in basalts from Apollo 15. *Earth Planet. Sci. Lett.* 17, 324–337.

Rasmussen B., Fletcher I. R. and Muhling J. R. (2008) Pb/Pb geochronology, petrography and chemistry of Zr-rich accessory minerals (zirconolite, tranquillityite and baddeleyite) in mare basalts. *Lunar Sci. VIII*. Lunar Sci. VIII, 288–302.

Rasmussen B., Fletcher I. R. and Muhling J. R. (2008) Pb/Pb geochronology, petrography and chemistry of Zr-rich accessory minerals (zirconolite, tranquillityite and baddeleyite) in mare basalts. *Lunar Sci. VIII*. Lunar Sci. VIII, 288–302.

Rasmussen B., Fletcher I. R. and Muhling J. R. (2008) Pb/Pb geochronology, petrography and chemistry of Zr-rich accessory minerals (zirconolite, tranquillityite and baddeleyite) in mare basalts. *Lunar Sci. VIII*. Lunar Sci. VIII, 288–302.

Rhodes J. M. and Hubbard N. J. (1973) Chemistry, classification, and petrogenesis of Apollo 15 mare basalts. *Lunar Planet. Sci.* 4, 1141–1140.

Saal A. E., Hauri E. H., Langmuir C. H. and Perfit M. R. (2002) Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth’s upper mantle. *Nature* 419, 451–455.
Sala A. E., Hauri E. H., Lo Cascio M., Van Orman J. A., Rutherford M. C. and Cooper R. F. (2008) Volatile content of lunar volcanic glasses and the presence of water in the Moon’s interior. *Nature* **454**, 192–196.

Sala A. E., Hauri E. H., Van Orman J. A. and Rutherford M. J. (2013) Hydrogen isotopes in lunar volcanic glasses and melt inclusions reveal a carbonaceous chondrite heritage. *Science* **340**, 1317–1320.

Sato M. (1976) Oxygen fugacity and other thermochemical parameters of Apollo 17 high-Ti basalts and their implications on the reduction mechanism. *Lunar. Sci. VII.* Lunar Planet. Inst., Houston. pp. 1323–1344.

Sato M., Hickling N. L. and Mclane J. E. (1973) Oxygen fugacity of Apollo 12.14 and 15 lunar samples and reduced state of lunar magmas. *Lunar Sci. IV.* Lunar Planet. Inst., Houston. pp. 1061–1079.

Sha L. K. (2000) Whitelocke solubility in silicate melts: some insights into lunar and planetary evolution. *Geochim. Cosmochim. Acta* **64**, 3217–3236.

Sharp Z. D., McCubbin F. M. and Shearer C. K. (2012) A unifying theory for H-bearing volatiles on the Moon. *Lunar Planet. Sci. XLIII.* Lunar Planet. Inst., Houston. #2751 (abstr.).

Sharp Z. D., Mercer J. A., Jones J. H., Brearley A. J., Silverstone J., Bekker A. and Stachel T. (2013) The chlorine isotope composition of chondrites and Earth. *Geochim. Cosmochim. Acta* **107**, 189–204.

Shearer C. K. and Papike J. J. (1993) Basaltic magmatism on the Moon: a perspective from volcanic picritic glass beads. *Geochim. Cosmochim. Acta* **57**, 4785–4812.

Sokol A. K., Fernandes V. A., Schulz T., Bischoff A., Burgess R., Sharp Z. D., McCubbin F. M. and Shearer C. K. (2012) A unifying theory for H-bearing volatiles on the Moon. *Lunar Planet. Sci. XLIII.* Lunar Planet. Inst., Houston. #2751 (abstr.).

Webster C. R., Mahaffy P. R., Leshin L. A., Atreya S. K., Flesch G. J., Stern J., Christensen L. E., Vasavada A. R., Owen T., Niles P. B., Jones J. H., Franz H. and the MSL Science Team (2013) Mars atmospheric escape recorded by H, C and O isotope ratios in carbon dioxide and water measured by the SAM tunable laser spectrometer on the Curiosity rover. *Lunar Planet. Sci. XLIV.* Lunar Planet. Inst., Houston. #1365 (abstr.).

Webster J. D., Kinzer J. R. and Mathez A. (1999) Chloride and water solubility in basalt and andesite melts and implications for magmatic degassing. *Geochim. Cosmochim. Acta* **63**, 729–738.

Willbold M., Elliott T. and Moorbath S. (2011) The tungsten isotopic composition of the Earth’s mantle before the terminal bombardment. *Nature* **477**, 195–198.

Zhang C. and Duan Z. (2010) GFluid: An Excel spreadsheet for investigating C-O-H fluid composition under high temperatures and pressures. *Comput. Geosci.* **36**, 569–572.

Zhang C., Holtz F., Ma C., Wolf P. E. and Li X. (2012) Tracing the evolution and distribution of F and Cl in plutonic systems from volatile-bearing minerals: a case study from the Liujiawa pluton (Dabie orogen, China). *Contrib. Mineral. Petrol.* **165**, 859–879.

Zhang Y. (2012) “Water” in lunar basalts: the role of molecular hydrogen (H₂), especially in the diffusion of the H component. *Lunar Planet. Sci. XLIII.* Lunar Planet. Inst., Houston. #1957 (abstr.).