H and Cl isotope systematics of apatite in brecciated lunar meteorites Northwest Africa 4472, Northwest Africa 773, Sayh al Uhaymir 169, and Kalahari 009

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Abstract—We have investigated the H and Cl systematics in apatite from four brecciated lunar meteorites. In Northwest Africa (NWA) 4472, most of the apatites contain ~2000–6000 ppm H2O with δD between ~200 and 0‰, except for one grain isolated in the matrix, which contains ~6000 ppm H2O with δD of ~500–900‰. This low-δD apatite contains ~2500–7500 ppm Cl associated with δ37Cl of ~15–20‰, while the high-δD grain contains ~2500 ppm Cl with δ37Cl of ~7–15‰. In NWA 773, apatites in a first group contain ~700–2500 ppm H2O with δD values averaging around ~0 ± 100‰, while apatites in a second group contain ~5500–16500 ppm H2O with δD ~250 ± 50‰. In Sayh al Uhaymir (SaU) 169 and Kalahari (Kal) 009, apatites are similar in terms of their H2O contents (~600–3000 ppm) and δD values (~100 to 200‰). In SaU 169, apatites contain ~6000–10,000 ppm Cl, characterized by δ37Cl of ~5–12‰. Overall, most of the analyzed apatite grains have δD within the range reported for carbonaceous chondrites, similar to apatite analyzed in ancient (>3.9 Ga) lunar magmatic. One grain in NWA 4472 has H and Cl isotope compositions similar to apatite from mare basalts. With an age of 4.35 Ga, this grain could be a representative of the oldest known lunar volcanic activity. Finally, since numerous evolved clasts in NWA 773 formed through silicate liquid immiscibility, the apatite grains with extremely high H2O contents, reaching pure hydroxylapatite composition, could provide insights into the effects of such process on the evolution of volatiles in lunar magmas.

INTRODUCTION

Over the past decade, the long-standing paradigm of an anhydrous Moon has been challenged based on new measurements on lunar samples utilizing recent analytical developments. These measurements have revealed significant quantities of water, tens to thousands of parts per million (ppm) equivalent H2O, in lunar volcanic glasses, in olivine-hosted melt inclusions within these glasses (Saal et al. 2008, 2013; Hauri et al. 2011), in nominally anhydrous minerals from the lunar highlands (Hui et al. 2013), and in the mineral apatite from nearly all type of lunar lithologies (Boyce et al. 2010; McCubbin et al. 2010a, 2010b, 2011; Greenwood et al. 2011; Barnes et al. 2013, 2014; Tartèse et al. 2013, 2014a, 2014b).

Although the utility of abundance measurements for OH, F, and Cl in lunar apatite for constraining the volatile abundances in their parental magmas is currently debated (e.g., Boyce et al. 2014), the H and Cl isotope compositions of apatite still provide clues regarding the origin of lunar volatiles and the influence of any petrogenetic processes in modifying the original signatures. Therefore, a significant database for the H isotopic composition of lunar apatite has emerged recently (Greenwood et al. 2011; Barnes et al. 2013, 2014; Tartèse et al. 2013, 2014a, 2014b), and a few studies have also initiated investigations of Cl isotope composition of lunar apatite (e.g., Sharp et al. 2010a; Boyce et al. 2013; Treiman et al. 2014). Based on data available so far, the combined H and Cl isotope compositions of lunar...
apatite indicate that apatite in mare basalts generally show $\delta^{18}O \approx 500_{\text{oo}}$ and $\delta^{37}Cl \approx 0\sim 15_{\text{oo}}$, while apatite from the KREEP-rich Mg- and alkali-suite lithologies from the lunar highlands have comparatively lower $\delta^{18}O$ values ($<300_{\text{oo}}$), but elevated $\delta^{37}Cl$ values ($>25_{\text{oo}}$).

Phosphates, especially apatite, have also been a target for U-Pb and Pb/Pb geochronological investigations in lunar meteorites, notably to constrain the crystallization ages of basaltic meteorites, where apatite is a common late-stage phase (Anand et al. 2003, 2006; Terada et al. 2005, 2007a, 2007b, 2008; Joy et al. 2011, 2014). The wide range of crystallization ages, from approximately 4.35 Ga to approximately 2.9 Ga, obtained for lunar basaltic meteorites has expanded the range for the timing of basaltic volcanism on the Moon as previously determined on basaltic samples from the Apollo collection (approximately 4.2–3.1 Ga; see the review of Shearer et al. [2006] and references therein). Yet interpretation of apatite U-Pb and Pb/Pb dates can be equivocal; Pb isotopes can be disturbed in apatite at moderate temperatures of approximately 500°C (Cherniak et al. 1991), which makes the apatite U-Pb and Pb/Pb chronometers highly sensitive to reheating during impact events. As a result, the interpretation of dates obtained on isolated apatite grains found in the matrix of breccias might sometimes be complex (e.g., Joy et al. 2011, 2014) as they lack petrological context. In such cases, additional constraints are required to decipher the source lithology and the petrogenetic history of the dated mineral grains.

In this study, we have investigated the H isotope systematics of apatite from four hot desert lunar meteorites (NWA 4472, NWA 773, SaU 169, and Kal 009). We have also measured the Cl isotopic composition of apatite from two of these meteorites (NWA 4472 and SaU 169). Two of these meteorites are regolith breccias (NWA 4472 and NWA 773), one is an impact-melt breccia (SaU 169), and the fourth one is a fragmental basaltic breccia (Kalahari 009). Geochronological data obtained on these meteorites cover the entire range of crystallization ages of basaltic meteorites (Fernandes et al. 2003; Gnios et al. 2004; Terada et al. 2007a; Sokol et al. 2008; Borg et al. 2009; Joy et al. 2011; Liu et al. 2012). Most of the studied apatite grains lack a full petrographic context (i.e., they are not associated with any other minerals), preventing us from relating them to different lithologies observed in these breccias. This study, therefore, aims to investigate how volatile abundances and the H and Cl isotope characteristics of apatite grains lacking petrographic context can be used to further decipher their source lithology. This approach has only become feasible because of the availability of a wealth of recent H and Cl data obtained on various lithologies represented in the Apollo sample collection (i.e., high- and low-Ti mare basalts, KREEP basalts, Mg- and alkali-suite magmatic rocks). We also use the volatile abundances of the studied apatite grains, and their isotopic characteristics, to investigate the petrogenetic processes that could have affected their parental melt evolution (e.g., degassing of volatiles from magmas, silicate liquid immiscibility).

**LUNAR METEORITES**

The lunar meteorites investigated in this work have been described for their mineralogical and petrological characteristics in sufficient detail in several previous studies. Therefore, the following sections summarize their main petrographic and geochronological characteristics and refer to relevant previous work as appropriate.

**Northwest Africa 4472**

Northwest Africa 4472 is a ~65 g polymict lunar meteorite paired with NWA 4485 (Connolly et al. 2007; Arai et al. 2009, 2010; Korotev et al. 2009). In this study we have investigated a 7.1 × 7.5 mm polished section of NWA 4472 (Figs. 1a and 2a; see also Figs. S1 and S2), which is part of the larger slab studied by Joy et al. (2011). These authors described the mineralogical, petrographic, geochemical, and geochronological characteristics of NWA 4472. The sample is a KREEP-rich regolith breccia comprising heterogeneous lithic clasts, mineral fragments, and spherules of impact glass, which have been linked to various lunar lithologies such as the Mg-suite, the alkali-suite, KREEP basalts, and mare basalts. Based on the elevated bulk-KREEP content of NWA 4472 and orbital remote sensing data obtained by the Lunar Prospector gamma-ray instrument, Joy et al. (2011) proposed that NWA 4472 was derived from the lunar regolith on the nearside of the Moon, in the vicinity of the Imbrium impact basin in the Procellarum KREEP Terrane (PKT).

Based on U-Pb and Pb/Pb dating of phosphates and zircons in NWA 4472 and NWA 4485 that yielded some old Pre-Nectarian (4.35 Ga) dates, it has been suggested that some fragments in this breccia could be related to early episodes of KREEP-driven magmatism, while younger U-Pb and Pb/Pb dates around 3.9–4.0 Ga could either date younger episodes of KREEPy magmatism or represent resetting dates related to impact events (Arai et al. 2010; Joy et al. 2011), possibly the Imbrium basin-forming event itself.

**Sayh al Uhaymir 169**

Sayh al Uhaymir 169 is a ~206 g lunar meteorite composed of two main lithologies; a regolith breccia...
Fig. 1. Montaged backscattered electron (BSE) images of the whole sections of the lunar meteorites investigated in this study: NWA 4472 (a), Sayh al Uhaymir (SaU) 169 (b), olivine-cumulate (OC) lithology of NWA 773 (c), brecciated lithology of NWA 773 (d), and Kalahari 009 (e–f). Scale bars are indicated on each image. See Fig. 2 for corresponding false-colored X-ray element maps of these samples.
Fig. 2. Composite X-ray element maps of the studied lunar meteorites. Color scheme: Al = white; Mg = green; Fe = red; Si = blue; Ca = yellow; Ti = pink; K = cyan. Generally, Mg-rich olivine and pyroxene appear green-brown, Fe-rich olivine appears red, plagioclase appears white, K-feldspar and K-rich glass appears cyan, silica appears blue, ilmenite appears pink, and Ca-phosphates appear yellow. Fractures also often appear yellow due to terrestrial filling by calcite. (see online version for color figure.)
Fagan et al. 2003, 2014; Jolliff et al. 2003). In a lithology, which is likely a large clast in the breccia regolith breccia and a greenish-olivine cumulate (OC) meteorite composed of two main lithologies; a dark mafic lunar meteorites (Sokol et al. 2008; Korotev et al. 2009). Lin et al. (2012) have recently described a new type of lithic clast in SaU 169 IMB that they termed VHK (very high potassium) KREEP, which comprises Ca-poor and Ca-rich pyroxenes, Ba-rich K-feldspar, phosphates (merrillite and apatite), ilmenite, and zircon. Together with the Apollo 12 high-Th IMB fragments described by Korotev et al. (2011), this VHK KREEP lithology in SaU 169 is the most ITE-rich lunar mafic lithology identified to date, being 2–3 times more enriched in KREEP component compared to the bulk IMB of SaU 169 (Lin et al. 2012). VHK KREEP clasts are easily identified in the section we investigated, as they appear as K-enriched cyan colored pixels (Fig. 2b). The SaU 169 IMB is also characterized by Th/REE and U/REE ratios of about 0.9 times those measured in the mafic Apollo 14 high-K KREEP IMB, and by Eu/Sm and Ba/Sm ratios of only approximately 0.8 and 0.6 times those of Apollo 14 high-K KREEP IMB (Korotev et al. 2009). According to Korotev et al. (2009), such differences indicate that the IMB in SaU 169 lacks granite/felsite components (high Th/REE and Ba/REE compared to KREEP) and alkali anorthosite components (high Eu/Sm compared to KREEP) that are found in Apollo 12 and 14 IMBs (e.g., Jolliff et al. 1991; Jolliff 1998).

Zircon U-Pb and Pb/Pb dating in the IMB of SaU 169 yielded a major age peak at ~3.91–3.92 Ga (Gnos et al. 2004; Lin et al. 2012; Liu et al. 2012) that has been interpreted as the likely age of the Imbrium basin-forming impact event (Gnos et al. 2004; Liu et al. 2012).

Northwest Africa 773

Northwest Africa 773 is a ~633 g mafic lunar meteorite composed of two main lithologies; a dark regolith breccia and a greenish-olivine cumulate (OC) lithology, which is likely a large clast in the breccia (Fagan et al. 2003, 2014; Jolliff et al. 2003). In a previous study, we have investigated volatiles (H2O, F, Cl) and the H isotopic composition of apatite in the OC lithology (Tartèse et al. 2014a) by studying a 4.3 × 6.4 mm polished section of NWA 773 (Figs. 1c and 2c; see also Figs. S5 and S6). In this study, we have investigated a 5.9 × 7.7 mm polished section of NWA 773 mostly composed of the brecciated lithology (Figs. 1d and 2d; see also Figs. S7 and S8). The OC lithology of NWA 773 displays coarse-grained (mm sized) olivine crystals, low- and high-Ca pyroxene, and plagioclase with minor amounts of ilmenite (Figs. 1c and 2c). Apatite grains analyzed by Tartèse et al. (2014a) were found in intercumulus pockets of late-stage melt trapped between major mineral phases, easily identified in Fig. 2c by the ubiquitous presence of late-crystallized K-feldspar. The OC lithology also constitutes the top and bottom edges of the polished section of the brecciated part of NWA 773 that we have studied (Figs. 1d and 2d). The polymict breccia lithology contains mineral and lithic clasts (Fig. 2d) and tends to be much more ferroan than the OC lithology. In addition to smaller OC clasts, the main lithic clasts contained within the brecciated lithology have been classified as pyroxene-gabbro clasts (PG), symplectite (hedenbergite + fayalite + SiO2) clasts (S) and alkali-phase-ferroan clasts (AF) by Fagan et al. (2014), who have argued that these four types of clasts (OC, PG, S, and AF) are co-genetic, and that S and AF clasts could correspond to the Fe-rich and Si-rich liquid fractions, respectively, that formed after silicate liquid immiscibility (SLI). In addition, some exotic clasts have also been observed by Fagan et al. (2003, 2014). The OC and the breccia lithology of NWA 773 are reported to be moderately enriched in ITE and display Apollo KREEP-like REE patterns, with La abundances of approximately 30–70 × CI chondrites (Fagan et al. 2003).

While a precise crystallization age is still unclear, the OC lithology within NWA 773 is young. Ar-Ar dating indicated closure to most Ar diffusion at ~2.9 Ga (Fernandes et al. 2003). Subsequent Sm-Nd dating yielded a whole-rock and mineral separate date of ~3.0 Ga (Borg et al. 2009), and more recent in-situ Pb/Pb dating of baddeleyite yielded dates of ~3.1 Ga (Zhang et al. 2010; Shaulis et al. 2013).

Kalahari 009

Kalahari (Kal) 009 is an enormous (~13.5 kg) monomict basaltic breccia, and is unique among the basaltic lunar meteorites (Sokol et al. 2008; Korotev et al. 2009). In this study, we have investigated two polished sections (7.1 × 5.3 mm for section 1, and 17 × 3 mm for section 2; Figs. 1e, 1f, 2e, and 2f; see
Kal 009 is classified as a very low-Ti basalt (~0.5 wt% TiO₂) that has low bulk rock FeO (~16 wt%) compared with the range for mare basalts, and ~13 wt% Al₂O₃, which is comparable to those of high-Al Apollo 14 mare basalts. Kal 009 contains basaltic fragments embedded within a fine-grained matrix, composed of mineral fragments occasionally found cemented by impact melt. The basaltic clasts display a coarse-grained subophitic texture and comprise pyroxene, plagioclase, and olivine with minor amounts of ilmenite, chromite, troilite, baddeleyite, phosphates, and Fe-Ni metal (Sokol et al. 2008). Similar mineral fragments constitute the matrix, and symplectic assemblages (hedenbergite + fayalite + silica) are commonly observed.

Phosphate U-Pb dating and Lu-Hf dating yielded dates of approximately 4.3 Ga, interpreted as the crystallization age of the basaltic component of Kal 009 (Terada et al. 2007a; Sokol et al. 2008), making Kal 009 one of the oldest known products of basaltic volcanism from the Moon.

**ANALYTICAL TECHNIQUES**

**Scanning Electron Microscopy and Electron Probe Micro-Analysis**

In brief, analyses were carried out using a Cameca SX100 electron microprobe using a 10 kV accelerating voltage, a 4 nA beam current, and a 5 μm focused beam for 60 s for F analysis and 20 kV accelerating voltage, a 20 nA beam current, and a 5 μm focused beam for 25–30 s for all other elements. Standardization of F and Cl were performed using a SrF₂ crystal and a tugtupite crystal, respectively, and were carefully checked against well-calibrated secondary apatite standards (see details in Barnes et al. [2014] and Tartèse et al. [2013]). At the NHM, apatite analyses were carried out using a Cameca SX100 electron microprobe using a 15 kV accelerating voltage, a 20 nA beam current, and a 5 μm focused beam for 10–30 s per element, and 60 s for the REE analyses. The instrument was calibrated using well-characterized mineral standards (see details in Joy et al. 2011), and F and Cl were standardized using apatite and halite crystals, respectively. Isopropanol was subsequently used to remove carbon coating from the samples in preparation for ion-probe work.

**Secondary Ion Mass Spectrometry**

**H Isotope Analysis**

The H₂O content and H isotopic composition of apatite grains were measured using the Cameca NanoSIMS 50L at the Open University, following a well-established protocol described in detail in Barnes et al. (2013, 2014) and Tartèse et al. (2013), during different analytical sessions between October 2012 and April 2014 (analytical conditions are given in Table S2). In brief, analyses were carried out with large Cs⁺ primary beams of approximately 260–400 pA current, with an accelerating voltage of 16 kV, after a 3 min presputtering during which the beam is rastered on the sample surface over 12 × 12 μm areas to eliminate any surface contamination. Secondary ions of ₁H, ₂H, ¹²C, and ¹⁸O were collected simultaneously on electron multipliers for 2000 cycles (approximately 20 min) from the inner 25% area, using electronic gating, of 7 × 7 μm to 10 × 10 μm raster sizes, depending on the size of the crack-free areas suitable for analysis. An electron gun was used for charge compensation and tuned to minimize its contribution to the H background. The mass resolving power was set to approximately 4000 ( Cameca definition), more than sufficient to readily resolve ²H⁺ from the interfering H₂⁺ species. Secondary ion images of ¹H and ¹²C were monitored in real time during presputtering to ensure that the analyzed areas were free of any surficial contamination, cracks, or hotspots. Unfortunately, cracks hidden underneath the sample surface appeared during some analyses. In such cases, only portions of the secondary ion signals 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 $^{12}$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 $^1$H/$^1$H ratios have been observed when isolating portions of the signals compared to the approximately 20 min integration for the reference apatite, which ensure that the standardization to approximately 20 min long analyses remains valid. Further details, such as calculations of H$_2$O contents, or correction of δD values for instrumental mass fractionation, can be found in the Supporting Information file.

**Cl Isotope Analysis**

The Cl content and Cl isotopic composition of apatite grains were also measured using the Cameca NanoSIMS 50L at the Open University. As for H isotopes, analyses were carried out with a Cs$^+$ primary beam, albeit at a lower current of approximately 40 pA, with an accelerating voltage of 16 kV. Each analysis was preceded by a 3 min presputter using a 150 pA primary beam rastered on the sample over 10 × 10 µm areas to eliminate any surface contamination. Secondary ions of $^{16}$O$^1$H, $^{35}$Cl, and $^{37}$Cl were collected simultaneously on five electron multipliers for 500–1500 cycles (approximately 5–15 min) from the inner 25% area, using electronic gating, of 6 × 6 µm to 8 × 8 µm area rasters. An electron gun was used for charge compensation. The mass resolving power was set to approximately 10,000 (Cameca definition) in order to readily resolve isobaric interferences such as $^{17}$O on the $^{16}$O$^1$H peak and $^{35}$Cl, and $^{37}$Cl peak. Secondary ion images of $^{16}$O$^1$H were monitored in real time during presputtering to ensure that the analyzed areas were free of any surficial contamination, cracks, or hotspots. The vacuum in the analysis chamber remained constant around 5 × 10$^{-10}$ torr.

Apatite Cl contents were calibrated using the measured $^{35}$Cl/$^{18}$O ratios and the calibrations derived using terrestrial apatite standards (Durango, Crystal Lode Pegmatite Mine, and Lake Baikal apatites described in McCubbin et al. 2012), pressed in indium along with a dry San Carlos olivine crystal. The slopes of the calibration lines defined by apatite standards with varying Cl contents were used to calculate the Cl contents of apatites in NWA 4472 and SaU 169 (see Fig. S13). The reported uncertainties on the Cl contents of apatite combine the 2σ uncertainty associated with the calibrations and the analytical uncertainties associated with each individual measurement. The dry San Carlos olivine was used to calculate the instrument background for Cl, which remained very low at approximately 0.1 ppm. To insure that this measure was adequate for epoxy-mounted samples such as SaU 169, analyses were also carried out under these analytical conditions on a plagioclase in an epoxy-mounted polished section of the meteorite Graves Nunataks 06128 that we also analyzed during the same analytical session. These analyses yielded approximately 0.05 ± 0.01 ppm Cl, which is consistent with the background Cl content determined on the indium-mounted San Carlos olivine. This background Cl was subtracted from the abundances measured in unknown apatites. Finally, reference apatite Ap005 was used to correct the measured $^{37}$Cl/$^{35}$Cl ratios for instrumental mass fractionation. The accuracy of our δ$^{37}$Cl measurements was checked by repeat measurements on a second reference apatite, the Durango apatite, Ap003, which yielded a weighted average δ$^{37}$Cl value of −0.6 ± 0.6 $\%$ (2σ; MSWD = 0.99; n = 18), consistent with the weighted average δ$^{37}$Cl value of 0.4 ± 0.6 $\%$ (2σ; MSWD = 0.95; n = 12) reported by Treiman et al. (2014). Cl isotopic composition is reported using the standard delta (δ) notation with respect to the $^{37}$Cl/$^{35}$Cl ratio of the standard mean ocean chloride (SMOC). δ$^{37}$Cl values are reported with their associated 2σ uncertainties, which combine the reproducibility of $^{35}$Cl/$^{35}$Cl measurements on the reference apatite Ap005 and the internal precision of each analysis.

**RESULTS**

**Petrographic Context of the Analyzed Apatites**

**NWA 4472**

Numerous analyses were carried out on large apatite grains that are part of a large lithic clast, which Joy et al. (2011) interpreted as a KREEP basalt assemblage (Fig. 3a). Apatite in this KREEP clast is associated with an intergrowth of coarse-grained ilmenite and hedenbergitic pyroxene (En$_{10}$Fs$_{50}$Wo$_{40}$, Mg#15–20; Fig. 4a). Pyroxene in this clast is highly ferroan and similar in composition to those in a silica and fayalite-rich clast (Fig. 4a). The other apatite grains investigated in this sample were isolated grains located throughout the matrix of NWA 4472 (Figs. 3b and 3c). They are generally surrounded by small grains of pyroxene and plagioclase. The composition of these pyroxene grains in the matrix ranges from $\sim$En$_{0.5}$Fs$_{30}$Wo$_{5}$ to $\sim$En$_{45}$Fs$_{45}$Wo$_{10}$ (Mg#50–70), similar to the compositions of low-Ca pyroxene in an alkali-suite (HAS) granulite clast and numerous matrix pyroxene analyzed by Joy et al. (2011) (Fig. 4a). Plagioclase in the matrix of NWA 4472 is generally Ca-rich (An$_{85.95}$).
Fig. 3. Detailed backscattered electron images displaying petrographic contexts of some of the apatites analyzed in this study in brecciated meteorites NWA 4472 (a–c), SaU 169 (d–f), NWA 773 (g–i), and Kal 009 (j–l). “ROI” refers to the different regions of interest. Red and cyan squares indicate the location where H isotope and Cl isotope analyses were carried out, respectively (with analysis numbers corresponding to those given in Tables 2 and 3). Mineral abbreviations: a = apatite; f = fayalite; i = ilmenite; k = K-feldspar; kg = K-rich glass; o = olivine; m = merrillite; p = pyroxene; pl = plagioclase; s = silica.
In SaU 169, several analyses were carried out on a large apatite grain present in a lithic fragment located toward the edge of the investigated polished section (approximately 2 mm × 2.5 mm; Figs. 1b and 2b). Apatite is intergrown with merrillite and this assemblage is surrounded by large grains of pyroxene, plagioclase, ilmenite, and K-feldspar (Fig. 3d). Low-Ca (En50–54Fs35–39Wo8–15) and high-Ca (En 40–45Fs17–20Wo36–40) pyroxenes coexist (Fig. 4b); plagioclase compositions are highly variable (An 64–81), consistent with the data reported by Lin et al. (2012); and K-feldspar contains 89–94 mol% of orthoclase component. The other apatite grains analyzed are associated with VHK KREEP clasts, which are easily recognizable in the composite X-ray element map of SaU 169 as patches enriched in K (Fig. 2b). The mineralogy of these VHK KREEP clasts is similar, containing assemblages of apatite and merrillite, low- and high-Ca pyroxenes, plagioclase, K-feldspar, and ilmenite (Figs. 3e and 3f). Mineral compositions are consistent with those in the large lithic clast; both low-Ca (En60–62Fs33–36Wo4–6) and high-Ca (En41–44Fs16–20Wo35–42) pyroxenes coexist (Fig. 4b), and plagioclase (An68–93) and K-feldspar (Or70–89) compositions are highly variable, which is again consistent with mineral compositions reported by Lin et al. (2012) for VHK KREEP clasts in SaU 169.

**NWA 773 (breccia)**

Apatite analyzed in the breccia lithology of NWA 773 occurs in a variety of settings, either as isolated grains in a fine-grained matrix or part of larger lithic clasts. Apatite in the region of interest (ROI) 3 is one such example of an isolated grain. It is surrounded by pyroxene displaying a large range of compositions, from low-Ca pyroxene (En61–66Fs25–26Wo25–30) typical of those found in the OC lithology of NWA 773 (Fig. 4c; Fagan et al. 2003, 2014), to ferroan compositions (En7–20 Fs51–66Wo25–30) more akin to some of the highly evolved clasts described by Fagan et al. (2003, 2014) (Fig. 4c). A couple of olivine analyses in ROI3 confirm their Mg-rich (Mg #63–68) nature compared with those in the ferroan lithologies (Fagan et al. 2003, 2014) and plagioclase is approximately An95; these compositions are consistent with those of mineral phases in the OC lithology (Fagan et al. 2003). A few grains of silica and small patches of K-rich glass (SiO2 ~ 70 wt%, Al2O3 ~ 15 wt%, and K2O ~ 11 wt%) were also observed. The petrographic context in which apatite in ROI13 occurs is very similar; it is surrounded by pyroxene, olivine, plagioclase, and tiny silica fragments (Fig. 3g). Matrix pyroxene compositions...
in ROI13 display large variations from magnesian to ferroan (En_{7.67Fs_{24.70}Wo_{6.32}}) (Fig. 4c), while olivine (approximately Mg#71) and plagioclase (An_{83.95}) display relatively restricted compositions similar to those in the OC lithology of NWA 773 (Fagan et al. 2003). In ROI17, apatite grains are associated with a plagioclase + silica assemblage surrounded by pyroxene and a few olivine grains (Fig. 3h). A large pyroxene grain below the plagioclase + silica assemblage (Fig. 3h) displays a homogeneous composition (En_{15.20Fs_{50.58}Wo_{27.30}}) while the smaller grains are characterized by a greater range of compositions (En_{6.57Fs_{32.56}Wo_{11.43}}) extending up toward the alkali-ferroan field defined by Fagan et al. (2014). The two olivine grains analyzed have different compositions (Mg#54 and Mg#71). Plagioclase composition within the plagioclase + silica assemblage seems to be quite variable and moderately Ca-rich (An_{77.90}) while the large plagioclase outside the assemblage is much more Ca-rich (An_{96}). Finally, apatite in ROI22 is associated with a large fayalitic olivine grain (Mg#3) enclosing large inclusions of K-rich glass (SiO_{2~78 wt%}, Al_{2}O_{3~11.5 wt%}, and K_{2}O~7 wt%) (Fig. 3i). Once again, compositions of pyroxene grains dispersed around the fayalite + apatite assemblage show very large variations (En_{3.62Fs_{14.78}Wo_{39}}) from low- and high-Ca magnesian compositions typical of those of the OC lithology to highly ferroan compositions (Fig. 4c; Fagan et al. 2003, 2014). ROI12 also contains a large symplectite assemblage composed of hedenbergite + fayalite + silica and isolated olivine grains (Mg#62-71) typical of olivine composition of the OC lithology (Fagan et al. 2003) (Fig. 3i).

**Kalahari 009**

In Kal 009, apatite grains occur mostly as tiny fragments, approximately 10–20 μm large, associated with olivine, pyroxene, and plagioclase with minor amounts of ilmenite, K-feldspar, and glass (Figs. 3j–l). Pyroxene compositions range from magnesian, low-Ca (approximately En_{60.65Fs_{35.36}Wo_{10}}) to ferroan, high-Ca (approximately En_{10Fs_{55.05}Wo_{15.40}}) varieties, consistent with the compositions reported by Sokol et al. (2008) (Fig. 4d). Olivines are Fe-rich (Mg#4.28) and plagioclases are Ca-rich (An_{48.97}), consistent with the data reported by Sokol et al. (2008). One of the features of these assemblages is the presence of small patches of glass (Figs. 3k and 3l) characterized by a wide range of compositions (SiO_{2~56–70 wt%}, Al_{2}O_{3~18–30 wt%}, K_{2}O~1.2–6.1 wt%, Na_{2}O~1.5–7.0 wt%, CaO~1–7 wt%, MgO~1–7 wt%, FeO~0.1–4.1 wt%).

**Volatile Inventory of Apatites**

All theapatite grains analyzed by EPMA in samples NWA 4472, NWA 773, and SaU 169 have less than 20 mol% Cl (equivalent to approximately 1.35 wt% Cl) in their volatile-bearing crystallographic X-site (Fig. 5), consistent with the Cl-poor nature of lunar apatites (e.g., Gancarz et al. 1971; Beaty et al. 1979; Taylor et al. 2004; Boyce et al. 2010; McCubbin et al. 2010a, 2010b, 2011; Tartese et al. 2013). In NWA 4472, apatite analyses in the KREEP clast (Fig. 3a) cluster toward the F-apex of the F-Cl-OH ternary diagram (Fig. 5), containing ~3.3 wt% F and ~0.6 wt% Cl (Table 1; see also Table S3). Assuming that the crystallographic X-site only contains F, Cl, and OH (e.g., McCubbin et al. 2010a, 2011), apatite grains in the KREEP clast (ROI1) in NWA 4472 could contain up to ~0.25 wt% H_{2}O. In NWA 4472, Matrix 1 apatite grain (Fig. 3c) contains ~2.9 wt% F and ~0.45 wt% Cl and up to ~0.5 wt% H_{2}O (Fig. 5), while other apatite grains in the matrix tend to contain more Cl (0.6–1.0 wt%) and up to approximately 0.6 wt% H_{2}O (Fig. 5). Overall, H_{2}O-poor and F-rich apatite grains in NWA 4472 appear to be similar to those in the crystalline impact-melt lithology 1 in other KREEP-rich lunar meteorites Dhofar (Dho) 925/961, all of them plotting within or close to the overlapping fields for apatites in KREEP basalts and mare basalts (Fig. 5).
Several analyses carried out in apatite grains in the matrix of NWA 4472 extend toward H₂O-rich compositions more typical of mare-basalt apatites (Fig. 5). Analyses of apatite grains in the breccia lithology of NWA 773 cover the whole field defined by mare basalt apatite, yielding homogeneous Cl contents of around 0.4 wt% but highly variable F and H₂O contents of ~1.0–2.7 wt% and ~0.35–1.25 wt%, respectively (Fig. 5). The few analyses of apatite from the OC lithology also seem to plot in the same field (Fig. 5). Finally, analyses of apatite in the IMB lithology of SaU 169 carried out by McCubbin et al. (2011) are characterized by relatively homogeneous volatile contents, with ~3.1 wt% F, ~1.1 wt Cl, and up to 0.2 wt% H₂O (Fig. 5), consistent with the volatile contents of apatite in KREEP-rich Apollo 12 and 14 crystalline impact-melt breccia (McCubbin et al. 2011).

### Water Content and H Isotope Systematics of Apatite

In NWA 4472, six analyses were carried out in the large apatite grains that occur in the KREEP clast (Fig. 3a). These apatite display variable H₂O contents between ~2850 and 5450 ppm associated with δD...
values ranging between $-103 \pm 91_{\%}$ and $9 \pm 92_{\%}$ (weighted average $\delta D$ is $-74 \pm 33_{\%}$, 2SD; Fig. 6; Table 2). These H$_2$O abundances appear to be higher compared to those estimated from the F and Cl contents measured by EPMA (detection limits for F and Cl by EPMA dictates that the H$_2$O contents, calculated by difference, are only reliable estimates for values greater than approximately 1400 ppm). In Matrix 2 apatite (Fig. 3b), an isolated grain lacking petrogenetic context, the measured H$_2$O contents and D/H ratios are similar, ranging from $\sim 3400$–$5300$ ppm H$_2$O with $\delta D$ values between $-243 \pm 150_{\%}$. $-12 \pm 84_{\%}$ (Fig. 6; Table 2). Another isolated apatite grain in the matrix of NWA 4472, Matrix 3, is also characterized by similar $\delta D$ values (weighted average $\delta D$ is $-35 \pm 81_{\%}$, 2SD) but slightly lower H$_2$O contents of $\sim 1800$–$2300$ ppm (Fig. 6; Table 2). However, Matrix 1 apatite, which also occurs as an isolated grain (Fig. 3c), has a very different $\delta D$ signature with values ranging between $486 \pm 62_{\%}$ and $904 \pm 44_{\%}$, for a narrow range (approximately 5300 to 6400 ppm) of H$_2$O contents (Fig. 6; Table 2). H$_2$O abundances determined by SIMS for matrix apatites are slightly higher compared to those calculated by difference from F and Cl abundances measured by EPMA (see the Volatile Inventory of Apatites section).

In the brecciated lithology of NWA 773, we have carried out fourteen analyses in seven apatite grains (some of these are shown in Figs. 3g–i). The H$_2$O contents and D/H characteristics of these apatite grains define two groups; the first group comprises analyses from three apatite grains (Ap#2, Ap#8, and Ap#13), which display moderate amounts of H$_2$O between $700$ and $2500$ ppm and relatively restricted range in $\delta D$ values between $-105 \pm 79_{\%}$ and $104 \pm 148_{\%}$ (weighted average $\delta D$ is $-54 \pm 82_{\%}$, 2SD; Fig. 6; Table 2). Four other apatite grains (Ap#3, Ap#17, Ap#21, and Ap#22) constitute a second group, characterized by high to extremely-high H$_2$O contents between $\sim 700$ and $2500$ ppm and comparatively elevated $\delta D$ values ranging between $144 \pm 63_{\%}$ and $319 \pm 64_{\%}$ (weighted average $\delta D$ is $255 \pm 46_{\%}$, 2SD; Fig. 6; Table 2). The H$_2$O contents for apatite of the second group are consistent with those estimated from the F and Cl contents measured by EPMA.

In SaU 169, six analyses were performed on four apatite grains (Figs. 3d–f). These yielded relatively narrow ranges in H$_2$O contents and D/H ratios, as H$_2$O

Fig. 6. H$_2$O contents and associated $\delta D$ values measured in apatite in brecciated lunar meteorites NWA 4472, NWA 773, SaU 169, and Kal 009. Data for KREEP basalts 15386, 72275, and the OC lithology of NWA 773 are from Tartèse et al. (2014a). Data for high-Al basalts 14072 and 14321 are from Tartèse et al. (2014b) and for 14053 from Greenwood et al. (2011). The colored fields illustrate literature data from Greenwood et al. (2011) and Tartèse et al. (2013) for high- and low-Ti Apollo basalts, from Tartèse et al. (2013) for low-Ti basaltic meteorites, and from Barnes et al. (2014) for the Mg- and alkali-suite rocks. The $\delta D$ range for terrestrial mantle ($\sim 60 \pm 20_{\%}$) is from Lécuyer et al. (1998), and the range for bulk CI, CM, CV, and CO chondrites is from Alexander et al. (2012).
content varies between ~1650 and 3420 ppm and δD values between ~148 ± 91‰ and 201 ± 156‰ (Fig. 6; Table 2). The results obtained for six apatite grains in Kal 009 (Figs. 3j–l) are comparable, as they gave 710–2390 ppm H2O with associated δD values ranging from 95 ± 118‰ to 149 ± 360‰, except one analysis performed in Ap#4 in section 1 that yielded ~530 ppm H2O with a slightly heavier δD value of 451 ± 213‰ (Figs. 6; Table 2).

Chlorine Content and Cl Isotope Systematics of Apatite

We have measured Cl contents and the associated Cl isotopic compositions of several apatite grains from two meteorites, NWA 4472 and SaU 169. Literature data for lunar apatite are from Sharp et al. (2010a) and Boyce et al. (2013).

Fig. 7. Cl contents and associated δ37Cl values measured in apatite in brecciated lunar meteorites NWA 4472 and SaU 169. Literature data for lunar apatite are from Sharp et al. (2010a) and Boyce et al. (2013).
which likely explains why the SIMS H2O contents are slightly lower than those measured by EPMA (approximately 4400 ppm; Table 3). The three other apatite grains analyzed are associated with two VHK KREEP clasts. They gave a similar range of Cl contents between ~7480 and 10,010 ppm, with $\delta^{37}$Cl values averaging ~11.4 ± 1.2‰ (2SD; Fig. 7; Table 3). For SaU 169, Cl contents measured by SIMS and EPMA are in better agreement than for NWA 4472.

**DISCUSSION**

Are Measured Apatite H and Cl Isotopic Compositions Indigenous Lunar Signatures?

Several secondary processes could have potentially modified the original isotopic compositions of lunar apatite after their magmatic crystallization. Two obvious processes affecting the material present at or near the surface of the Moon are the implantation of solar wind (SW) hydrogen and spallation from galactic cosmic ray (GCR). The H2O and H measured in lunar samples have long been interpreted as produced by either terrestrial contamination or SW implantation of hydrogen in the outer part of regolith grains (e.g., Epstein and Taylor 1973). In-situ analyses have subsequently demonstrated that SW implantation of Li, H, N, or C indeed occurred on the lunar surface, and could reach a depth of approximately 100 nm from the surface of the grains for H (e.g., Chaussidon and Robert 1999; Hashizume et al. 2000, 2004; Stéphant and Robert 2014). The depth over which SW hydrogen can be implanted in samples residing on the lunar surface is so small that it is unlikely to have affected the H2O contents and D/H ratios measured in apatite in the investigated lunar meteorites (contamination by SW hydrogen could only have occurred in apatites if they directly crystallized from an impact melt which itself had inherited a SW-hydrogen component from the regolith).

Spallation processes induced by exposure to GCR can greatly affect the H2O contents and D/H ratios measured in lunar samples, especially at low H2O contents (e.g., Saal et al. 2013; Barnes et al. 2014), as cosmic ray spallation can affect materials residing at much deeper levels (down to approximately 1–2 m depth; e.g., Williams and Gold 1975) than SW implantation. H and D are produced on the Moon by cosmic ray spallation (Merlivat et al. 1976), their amount depending on the cosmic ray exposure (CRE) time in the lunar regolith and the shielding depth of a given rock. For meteorites, it is generally assumed that CRE starts when they are ejected from their parent body, meteorites being buried at least several meters deep into their parent body before ejection (Eugster 2003). However, the meteorites investigated here are breccias and their constituent clasts could have been exposed to cosmic rays in the lunar regolith for prolonged periods of time during their geological history on the Moon. Lorenzetti et al. (2005) have discussed how...

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**Table 3. Apatite Cl contents and Cl isotope compositions.**

| Analysis # | Cl (ppm) | 2σ (ppm) | $\delta^{37}$Cl (%oo) | 2σ (%) |
|------------|----------|----------|-----------------------|--------|
| Sayh al Uhaymir 169 | | | | |
| SaU169_ROI7_Ap1#1 2May | 8078 | 118 | 8.4 | 2.4 |
| SaU169_ROI7_Ap1#2 2May | 6268 | 91 | 9.2 | 2.5 |
| SaU169_ROI7_Ap1#3 2May | 7687 | 112 | 8.9 | 2.5 |
| SaU169_ROI7_Ap1#4 3May | 10051 | 129 | 5.3 | 2.2 |
| SaU169_ROI7_Ap1#5 3May | 6464 | 83 | 6.6 | 2.4 |
| SaU169_ROI14_Ap1#1 2May | 9842 | 143 | 10.9 | 2.4 |
| SaU169_ROI14_Ap1#2 3May | 9828 | 126 | 11.5 | 2.3 |
| SaU169_ROI14_Ap1#3 2May | 10014 | 146 | 10.9 | 2.4 |
| SaU169_ROI21_Ap1#1 2May | 7476 | 109 | 12.2 | 2.5 |
| Northwest Africa 4472 | | | | |
| KREEP clast | | | | |
| 4472_ROI1_Ap1#1 3May | 3939 | 50 | 19.7 | 2.5 |
| 4472_ROI1_Ap1#2 3May | 4166 | 53 | 17.2 | 2.4 |
| 4472_ROI1_Ap1#3 3May | 2509 | 33 | 19.3 | 3.5 |
| 4472_ROI1_Ap1#4 7May | 4017 | 68 | 18.1 | 3.2 |
| 4472_ROI1_Ap1#5 7May | 3597 | 60 | 18.8 | 3.0 |
| 4472_ROI1_Ap2#1 3May | 2946 | 38 | 18.5 | 3.1 |
| Matrix 1 | | | | |
| 4472_ROI6_Ap1#1 3May | 2280 | 29 | 15.3 | 3.3 |
| 4472_ROI6_Ap1#2 3May | 2420 | 31 | 7.1 | 3.1 |
| 4472_ROI6_Ap1#3 7May | 2992 | 50 | 6.8 | 3.3 |
| 4472_ROI6_Ap1#4 7May | 2848 | 48 | 12.5 | 3.5 |
| Matrix 3 | | | | |
| 4472_ROI11_Ap1#1 3May | 5451 | 70 | 15.4 | 2.4 |

(Table 3). One analysis carried out in an isolated apatite grain in the matrix yielded ~5450 ppm Cl with a $\delta^{37}$Cl value of 15.4 ± 2.4‰ (Fig. 7; Table 3). Finally, four analyses were performed in the high-$\delta$D Matrix 1 apatite grain (Fig. 3c). These analyses yielded Cl contents of ~2280–2990 ppm associated with highly variable $\delta^{37}$Cl values ranging from 6.8 ± 3.3‰ up to 15.3 ± 3.3‰ (Fig. 7; Table 3). Once again these Cl contents are slightly lower than those measured by EPMA (approximately 4400 ± 200 ppm; Table 1), which likely explains why the SIMS H2O contents measured in Matrix 1 apatite are slightly higher than those calculated by difference based on EPMA analyses of F and Cl.

In SaU 169, four apatite grains were analyzed for their Cl contents and Cl isotopic compositions (Figs. 3d–f). Analyses carried out in the large apatite in ROI7 (Fig. 3d) show a relatively wide range of Cl contents between ~6270 and 10050 ppm with $\delta^{37}$Cl values ranging from 5.3 ± 2.2‰ to 9.2 ± 2.5‰ (weighted average $\delta^{37}$Cl is 7.6 ± 2.1‰, 2SD; Fig. 7; Table 3). The three other apatite grains analyzed are associated with two VHK KREEP clasts. They gave a similar range of Cl contents between ~7480 and 10,010 ppm, with $\delta^{37}$Cl values averaging ~11.4 ± 1.2‰ (2SD;...
determined CRE ages of several lunar meteorites, including SaU 169 and NWA 773. For the IMB lithology in SaU 169, they reported a residence time in the lunar regolith of 216 ± 45 Ma. For NWA 773, large discrepancies exist between different studies. Lorenzetti et al. (2005) reported that the brecciated lithology contains approximately 10 times more cosmogenic Ne than the OC lithology, and calculated residence times in the lunar regolith of approximately 100 ± 20 Myr for the OC lithology, while the brecciated lithology was exposed to GCR for about 1 Ga in the lunar regolith. On the other hand, Fernandes et al. (2003) have reported much younger exposure ages of 73 ± 2 Ma and 154 ± 3 Ma for the OC and brecciated lithologies of NWA 773, respectively, based on measurements of released cosmogenic \(^{38}\)Ar. For the basaltic breccia Kal 009, the concentrations of cosmogenic nuclides (\(^{10}\)Be, \(^{26}\)Al, \(^{36}\)Cl, \(^{41}\)Ca) are the lowest ever measured in a stony meteorite and suggest extremely short exposure time to GCR, <1 Ma (Sokol et al. 2008). We, thus, did not correct the measured D/H ratios in apatites in Kal 009 for spallation effects. Finally, no regolith exposure age has been reported for NWA 4472 so far. We have investigated the possible effect of spallation by GCR on the D/H systematics of apatites in NWA 4472 using the oldest known exposure age reported for lunar regolith breccias, which is around 2000 ± 200 Ma (Lorenzetti et al. 2005). Corrected H\(_2\)O-D/H data therefore likely represent an upper limit for the effect of spallogenic production of H and D in this meteorite. Similarly, we used the oldest exposure age of approximately 1000 ± 200 Ma for the corrected data presented in Fig. 8 for the brecciated lithology of NWA 773. We used the production rates for H (2 × 10^{-10} mol H\(_2\) g\(^{-1}\) Ma\(^{-1}\)) and D (0.5 × 10^{-12} mol D\(_2\) g\(^{-1}\) Ma\(^{-1}\)) determined by Merlivat et al. (1976) and assigned them a 50% uncertainty (see detailed discussion in Saal et al. 2013).

With these production rates, exposure to GCR for 1 Ga results in the production of approximately 2 ppm H\(_2\)O and approximately 4.6 × 10^{-3} ppm D\(_2\)O. Correction of the measured D/H ratios for spallation production of H and D resulted in a maximum decrease of \(\delta D\) by \(\sim 60\%\) for the driest apatite analysis (~1775 ppm H\(_2\)O) from NWA 4472, by \(\sim 75\%\) for the driest apatite analysis (~720 ppm H\(_2\)O) from NWA 773, and by \(\sim 7\%\) for the driest apatite analysis (~1600 ppm H\(_2\)O) from SaU 169 (Fig. 8). After correction for H and D production by GCR, all the data remain largely within uncertainties of the original measurements (Fig. 8). As a result, and considering the large uncertainties associated with CRE ages for samples such as NWA 773, or the lack of CRE age for NWA 4472, only the measured H\(_2\)O contents and \(\delta D\) values are eventually considered in this contribution.

Finally, alteration of the isotopic characteristics of apatite by terrestrial weathering processes must also be addressed, as the four samples investigated are all hot desert finds and, therefore, have resided for prolonged periods of time on Earth (e.g., ~10 ka and ~17 ka for SaU 169 and NWA 773, respectively; Gnos et al. 2004;
Nishiizumi et al. 2004). The majority of the apatite grains analyzed have δD values ranging between −200‰ and 100‰ (weighted average δD is −42 ± 37‰, 2σ—n = 30), with Matrix 1 grain in NWA 4472 and the high-H₂O group of apatites in NWA 773 having higher δD values (Fig. 6). The H isotopic composition of meteoric water and groundwater in the central Saharan region varies between −70‰ and 20‰ (Saighi et al. 2001), which is close to the D/H ratios measured in the majority of apatites. Thus, in the absence of any other independent constraints, it could be argued that most of the analyses reflect cryptic alteration of original H₂O contents and D/H signature by interaction with terrestrial waters. Yet, several features are clearly inconsistent with such a possibility. First, apatite in NWA 4472 and NWA 773 contain water with both high-δD as well as Earth-like δD values (Fig. 6). There are no a priori reasons for terrestrial waters to have altered the D/H systematics of only some apatite grains in a rock and not in other apatite grains located a few millimeters away, unless permeability varies dramatically on such a small scale. Also, the group of high-H₂O apatite in the brecciated lithology of NWA 773 displays large variations in H₂O contents from ~5400 ppm up to 16700 ppm with relatively restricted δD values of ~200–300‰ (Fig. 6). If these very high H₂O contents resulted from apatite alteration by terrestrial waters, one would expect a decrease of δD to values of approximately 50‰ for ~16000 ppm H₂O analysis, which is not observed. The large range in δD values between ~50‰ and 900‰, observed in Matrix 1 apatite in NWA 4472, is also inconsistent with modification by terrestrial waters. Adding around 1200 ppm of Saharan water to the low-H₂O and high-δD analysis in this grain (5200 ppm H₂O and δD of ~900‰) would only lower the δD by about 175‰. Finally, the δ³⁷Cl measured in apatite range between ~7‰ and 20‰ for NWA 4472 and ~5‰ and 12‰ for SaU 169. These values are distinctly higher than the δ³⁷Cl of terrestrial materials, including most of the waters and hydrothermal fluids (the range of δ³⁷ClEarth could be averaged to 0 ± 2‰, e.g., Stewart and Spivack 2004; Sharp et al. 2013b). It is worth noting that two large SIMS pits were created on Matrix 1 apatite in NWA 4472 during the course of U-Pb dating by Joy et al. (2011). Therefore, if our NanoSIMS spots for H and Cl isotope analyses overlapped with these previously sputtered areas, it may not be possible to completely rule out the disturbance of the volatile H and Cl in the apatite lattice by previous SIMS analyses, which could account for some of the variability observed for δD and δ³⁷Cl values in this grain. On the other hand, Matrix 2 apatite in NWA 4472 (Fig. 3b) has also been dated by SIMS by Joy et al. (2011), who sputtered three large SIMS pits on this grain. In this grain, our NanoSIMS analyses yielded a range of H₂O contents (~3400 to 5300 ppm H₂O), associated with δD values consistent with each other considering uncertainties (~243 ± 150‰ to ~12 ± 84‰). From our data set, it is not possible to argue for the presence of an evident and systematic effect induced by previous SIMS analyses, an issue that would merit further investigation in a future study.

To summarize, considering all the above lines of evidence, we are confident that most if not all of the apatite grains we have analyzed in brecciated meteorites NWA 4472, NWA 773, SaU 169, and Kal 009 have retained their original lunar isotopic signatures.

**Inferring Source Lithology From H and Cl Isotope Systematics of Apatite**

In brecciated meteorites, the petrogenetic context within which an isolated mineral, or a small assemblage of minerals of interest, occurs can unfortunately be lacking. This may hamper interpretation of chemical or geochronological data, as deciphering the source lithology may not be possible. As the U-Pb geochronometer in phosphates is easily disturbed by thermal events above ~500 °C (Cherniak et al. 1991), disentangling crystallization and impact-resetting ages in phosphate U-Pb data can be challenging. Even when lithic clasts are preserved, the question of their representativeness is also an issue (e.g., Warren 2012). Abundances of certain elements such as Fe, Mg, or REEs in apatite do not seem to enable straightforward discrimination among the different lunar lithologies (Fig. 9). Apatite in rocks from the Mg-suite have low Fe contents, high Mg#, and moderate Ce contents, while apatite in low-Ti mare basalts is generally characterized by high Fe contents, low Mg#, and relatively high Ce contents (Fig. 9). In other lithologies such as the alkali-suite rocks, impact-melt rocks, KREEP basalts, and high-Ti mare basalts, apatite Fe, Mg, and Ce contents largely overlap (Fig. 9). This is precisely in this overlapping area where the majority of the apatite analyses carried out in NWA 4472, NWA 773, and SaU 169 plot. The Fe, Mg, and Ce contents of the apatites analyzed would indicate possible genetic relationships with the Mg- and alkali-suite or with KREEP basalts (Fig. 9).

**NWA 4472**

In NWA 4472, Matrix 2 and 3 apatite grains and apatite in the KREEP clast have H₂O-D/H systematics consistent with the H₂O-D/H characteristics of H₂O-rich apatite in KREEP basalts (Tartèse et al. 2014a) and in the Mg- and alkali-suite rocks (Barnes et al. 2014) (Fig. 6), which is consistent with the KREEP-rich...
nature of NWA 4472 (Korotev et al. 2009; Joy et al. 2011). On the other hand, apatite in the KREEP clast and Matrix 3 apatite are characterized by \( \delta^{37} \text{Cl} \) values below \( \sim 20 \)\%o, which is more consistent with data reported for apatite from “typical” mare basalts rather than from KREEP-rich lithologies such as KREEP basalt and highland samples from the Mg- and alkali-suites (Sharp et al. 2010a; Boyce et al. 2013; Treiman et al. 2014) (Fig. 7). Overall, these apatite grains are, therefore, characterized by unfractionated \( \delta \text{D} \) values compared to most carbonaceous chondrites, but have highly fractionated \( \delta^{37} \text{Cl} \) values.

The isolated Matrix 1 apatite grain (Fig. 3c), is characterized by \( \text{H}_2\text{O} \)-\( \delta \text{D} \) and \( \text{Cl}-\delta^{37} \text{Cl} \) signatures akin to “typical” mare basalts rather than to KREEP-rich lithologies (Figs. 6 and 7a). It displays relatively large ranges in \( \delta \text{D} \) and \( \delta^{37} \text{Cl} \) values (\( \sim 500 \)\%o to \( \sim 900 \)\%o, and \( \sim 7 \)\%o to \( \sim 15 \)\%o, respectively) with narrow ranges in \( \text{H}_2\text{O} \) and \( \text{Cl} \) contents (\( \sim 5300-6400 \) ppm and \( \sim 2300-3000 \) ppm, respectively). In this grain, it is difficult to define any obvious relationship between the \( \text{H}_2\text{O} \) and \( \text{Cl} \) contents and their corresponding \( \delta \text{D} \) and \( \delta^{37} \text{Cl} \) signatures, or with the locations where analyses were carried out in the grain (Fig. 3c). Moreover, the grain might only be a fragment of an originally larger grain, hampering identification of core and rim regions. Generally, one might have invoked rapid crystallization of the grain during degassing of H-bearing species as \( \text{H}_2 \) in the vapor phase, as proposed to explain the large variations of \( \delta \text{D} \) and the narrow range of \( \text{H}_2\text{O} \) contents observed in apatites in high-Ti mare basalts (Tartèse et al. 2013). However, such a mechanism seems to be incompatible with the \( \delta^{37} \text{Cl} \) characteristics of this apatite grain. To explain the elevated \( \delta^{37} \text{Cl} \) of most lunar samples compared to other planetary materials Sharp et al. (2010a) argued for kinetic fractionation of the Cl isotopes during degassing of metal-chloride species, such as \( \text{FeCl}_2 \) or \( \text{ZnCl}_2 \). The strongest constraint associated with the mechanism proposed by Sharp et al. (2010a) is that it requires anhydrous melts to prevent formation of \( \text{HCl} \), as they argue that \( \text{HCl} \) degassing does not fractionate Cl isotopes, despite fractionation of up to \( \sim 10 \)\%o in \( \delta^{37} \text{Cl} \) have been observed in experiments involving \( \text{H}_2\text{O} \)-rich systems (Sharp et al. 2010b). Sharp et al. (2013a) reconciled this requirement of anhydrous melts for Cl isotope fractionation and the growing evidence indicating that lunar basaltic melts can contain non-negligible amounts of water by proposing that H-bearing species degases earlier than Cl-bearing species in lunar magmas (Ustunisik et al. 2011; Sharp et al. 2013a). Yet in Matrix 1 apatite in NWA 4472, the variations of \( \delta \text{D} \) and \( \delta^{37} \text{Cl} \) would require crystallization during degassing of both H-bearing and Cl-bearing species, pointing toward \( \text{HCl} \) degassing. Hence, there is a critical need for degassing experiments of both \( \text{HCl} \) and metal chlorides under lunar conditions (in vacuum and at low \( f \text{O}_2 \)) in order to further assess the likely mechanisms responsible for elevated \( \delta^{37} \text{Cl} \) signatures in mare basalts.

Diffusive gain or loss of OH and Cl can also kinetically fractionate H and Cl isotopes, provided that apatite resided at high temperatures for a prolonged period of time in order to enable diffusive mobility of...
the volatiles (e.g., Boyce and Hervig 2008; Anand et al. 2014). As Matrix 1 apatite lacks petrogenetic context, this possibility is difficult to assess; on the other hand, the Pb/Pb and U-Pb chronometers have not been disturbed in this grain (Joy et al. 2011), which likely rules out extensive isotopic mobility by high-temperature diffusion, since diffusion of OH and Cl is faster than diffusion of Pb in the apatite lattice (Cherniak et al. 1991; Brenan 1993). Whichever mechanism caused large variations of δD and δ37Cl in Matrix 1 apatite, its H and Cl isotope characteristics are consistent with those observed in “typical” mare basalts (Figs. 6 and 7a). With a U-Pb crystallization age of approximately 4.35 Ga (Joy et al. 2011), this grain could, therefore, be a remnant of some of the oldest known basaltic volcanism on the Moon (e.g., Terada et al. 2007a).

**SaU 169**

In the IMB lithology of SaU 169, the H2O-D/H systematics of the analyzed apatite grains are also consistent with the H2O-D/H characteristics of apatite rich in H2O in KREEP basalts (Tartèse et al. 2014a) and in the Mg- and alkali-suite rocks (Barnes et al. 2014) (Fig. 6), in good agreement with the KREEP-rich nature of SaU 169 (Gnos et al. 2004; Korotev et al. 2009; Lin et al. 2012). Combined together, the Cl contents and Cl isotope characteristics of apatites in the IMB lithology of SaU 169 differ from those reported so far for apatite in KREEP-poor mare basalts and KREEP-rich rocks of the lunar highlands (breccias and Mg-suite rocks). Apatite in SaU 169 have δ37Cl values similar to those measured in apatite in mare basalts (weighted average δ37Cl is 7.6 ± 2.1‰, 2σ; Fig. 7), but contain much higher Cl contents. The IMB lithology of SaU 169 is geochemically unique, containing ~300–1000 times Cl chondrite abundances of ITE (Gnos et al. 2004). Most of the apatite grains we analyzed are associated with even more evolved lithic clasts (i.e., VHK KREEP clasts; Lin et al. 2012), which are characterized by abundances of KREEP at ~1500 × Cl chondrites. Apatite in this unique lithology appear to be characterized by a distinct Cl-δ37Cl systematics with the limited amount of apatite data currently available for other lunar lithologies. More importantly, the Cl-δ37Cl systematics of apatite in the KREEP-rich IMB lithology of SaU 169 seems to break down the dichotomy of “low-δ37Cl/low KREEP content vs. high-δ37Cl/high KREEP content” observed from previously available data (Fig. 7). Considering that almost the entire spread of δ37Cl values observed in solar system materials has thus far been observed only in lunar samples, it is likely that Cl isotopes have been fractionated by some processes specific to the Moon (e.g., low-fO2 degassing of HCl or of metal chlorides; Sharp et al. 2010a, 2010b), but such process(es) have yet to be identified and proven experimentally. In addition, several Cl reservoirs with different isotopic characteristics might occur in and on the Moon, opening the possibility that measured δ37Cl values correspond to mixing signatures. These observations lead us to conclude that our current understanding of Cl isotopes in lunar materials is far from being complete. Further Cl and δ37Cl analyses of apatite in a broad range of lunar lithologies, coupled with specific experimental investigation of Cl isotope fractionation processes at lunar conditions, are required in order to improve our understanding of the Cl geochemical cycle in and on the Moon.

**NWA 773 (breccia)**

In the brecciated lithology of NWA 773, the H2O-D/H systematics of apatite defines two groups. In the first group, apatite grains contain moderate H2O contents between ~700 and ~2500 ppm associated with chondrite-like D/H ratios (weighted average δD = −54 ± 82‰) (Fig. 6). The H2O-D/H systematics of this first group of apatite analyses is consistent with results obtained on apatite grains analyzed in the OC lithology (Tartèse et al. 2014a), indicating that they likely originated from a similar lithological source. In the second group, apatite grains are characterized by high to very high H2O contents (~5400–16,700 ppm H2O) and δD values of approximately 250 ± 50‰ (Fig. 6). Such characteristics are unique among apatite in all the lunar samples analyzed so far. This suggests that these apatite grains are either related to a unique, unknown, source lithology or that their parent rock(s) were affected by specific petrogenetic processes. We favor the second possibility as discussed in the Behavior of Volatiles During Silicate Liquid Immiscibility section.

**Kalahari 009**

Compared with NWA 4472, NWA 773, and SaU 169, which all contain a significant KREEP component, Kal 009 has very low bulk-ITE abundances (Sokol et al. 2008). However, it is interesting to note that apatite grains analyzed in Kal 009 display a KREEP-like H2O-D/H signature. Kal 009 has bulk FeO and Al2O3 abundances similar to those of the Apollo 14 high-Al mare basalts. Very few data exist for the H2O-D/H systematics of apatite in high-Al mare basalts; Greenwood et al. (2011) reported approximately 600–900 ppm H2O and δD values (weighted average of −188 ± 13 ‰) for apatite in sample 14053 (group C of Neal and Kramer 2006). However, the low δD values measured in apatites in 14053, which has a unique...
petrologic history (e.g., Taylor et al. 2004), could have resulted from interaction with solar wind-implanted hydrogen in the lunar regolith during an impact-heating event (Greenwood et al. 2011), and may not be indicative of original indigenous D/H signatures. Tartèse et al. (2014b) have presented preliminary data for two additional Apollo 14 high-Al mare basalts, 14072 (group D), and 14321,1238 (group B). In 14321,1238,apatite grains analyzed contain very low H₂O contents (<80 ppm) with δD values ranging between 144 ± 336‰ and 462 ± 328‰. In 14072, apatite H₂O contents range from ~70 to 320 ppm, with δD values ranging between 10 ± 410 ‰, and 434 ± 308 ‰. In Kal 009, apatite have higher H₂O contents (~530–2390 ppm; Fig. 6), but display a similar range of δD values (~95 ± 118‰ to 451 ± 213‰; Fig. 6). The crystallization age of Kal 009 of ~4.35 Ga (Terada et al. 2007a; Sokol et al. 2008) and bulk-rock composition of ~13 wt% Al₂O₃ is also consistent with the range of crystallization ages (~3.9 to ~4.3 Ga) and bulk chemistry of Apollo 14 high-Al (>11 wt% Al₂O₃) mare basalts (Neal and Kramer [2006] and references therein). Therefore, the H₂O-D/H systematics and other geochemical similarities between Kal 009 and high-Al mare basalts (sampled at the Apollo 14 landing site) indicate a possible genetic link between them.

Behavior of Volatiles During Silicate Liquid Immiscibility

Soon after initial studies of Apollo samples it was argued that some rock types, such as the felsites, could have formed due to silicate liquid immiscibility (SLI). This process is likely a common process and a result of extensive low-P fractional crystallization of many lunar volcanic products, producing a Fe-rich basaltic melt enriched in REE and P and a Si-rich rhyolitic melt enriched in K (e.g., Roedder and Weiblin 1970, 1971; Rutherford et al. 1974; Hess et al. 1975; Philpotts 1982; Roedder 1984; Longhi 1990). Evidence for SLI has been recognized, for example, in melt inclusions from mare basalts (e.g., Roedder 1984), within late-stage melt pockets (mesostasis) in mare basalts, and in some plutonic rocks that crystallized at shallow depths in the lunar upper crust (e.g., Jolliff 1991, 1998). To comprehensively characterize the volatile inventory of lunar magmatic products, the effects of SLI on the partitioning behavior of volatiles between immiscible melts, and on the extent of isotopic fractionation of volatiles such as H and Cl, if any, needs to be investigated (e.g., Pernet-Fisher et al. 2014). It should be pointed out, however, that due to the lack of relevant data, notably experimental, this section of the discussion remains speculative.

Fagan et al. (2014) have argued that the highly ferroan lithic clasts (Fig. 4c) in the brecciated lithology of NWA 773 were likely formed after SLI occurred, the symplectite (SP) assemblages representing the Fe-rich fraction while the alkali-ferroan (AF) clasts correspond to the Si-rich liquids. It is, therefore, a possibility that the unusual H₂O-δD characteristics of some apatites analyzed in the brecciated lithology of NWA 773 might be related to the effect of SLI. Ap#22 for example is clearly associated with an AF clast comprising fayalite + K-rich glass (compare Fig. 3i with the Fig. 7d of Fagan et al. 2014). Ap#17 is associated with an unusual plagioclase + silica assemblage (Fig. 3h) surrounded by some ferroan pyroxene (Fig. 4c). These apatite grains contain very high amounts of H₂O (~5400–16,700 ppm) reaching almost pure hydroxylapatite composition (17900 ppm H₂O). As discussed by Boyce et al. (2014), apatite H₂O content is not solely related to the H₂O content of its parental melt. This is because water is as an essential structural constituent (as OH⁻) of the apatite X-site, and as such its incorporation depends on stoichiometric constraints; F, Cl, and OH all reside in this X-site, and are competing for it, implying that the abundance of any of these elements is inevitably related to the abundance of the other ones. These H₂O-rich apatite contain approximately 2–7 times more H₂O compared to those of the OC lithology (Fig. 6), and seem to have crystallized from the highly ferroan alkaline and Si-rich melt fraction formed after SLI. Again, this does not necessarily imply that this Si-rich melt fraction was enriched in H₂O compared to residual melt from which apatite crystallized in the OC lithology. This could indicate instead that F and/or Cl were depleted in the Si-rich melt fraction during SLI, resulting in higher H₂O/F and H₂O/Cl ratios. Unfortunately data on partitioning of F and Cl during SLI are extremely scarce. There is no measurement of F and Cl in coexisting Fe-rich and Si-rich melt inclusions found to have formed from SLI in lunar basalts. Lester et al. (2013) have investigated experimentally element partitioning during SLI for volatile-rich systems relevant to terrestrial conditions ([O₂ at or above QFM). Lester et al. (2013) found that F behavior is quite unpredictable as it can be concentrated either in the Fe-rich melt fraction or in the Si-rich one (average \( D_F^{Fe-rich/Si-rich} \sim 1 \pm 0.6 \)), in contrast to sulphur, for example, which is strongly partitioned into the Fe-rich fraction. We propose that the very high H₂O contents measured in some apatites in the brecciated lithology of NWA 773 might be a direct result of SLI, which would have depleted the Si-rich melt fraction in F and Cl, and in some extreme cases left H₂O as the only competitor for the apatite X-site. Further constraints, analytical or experimental, on the behavior of F and Cl during SLI
in lunar magmas would be required to investigate this issue further.

Besides being H₂O-rich, these apatite grains are characterized by homogeneous δD values with a weighted average of ~255 ± 46‰. These δD values are ~200–300‰ higher than those measured in apatite in the OC lithology in NWA 773. Following the discussion above on the possible role of SLI in producing Si-rich melt with elevated H₂O/F and/or H₂O/Cl ratios, which would have resulted in the crystallization of H₂O-rich apatite, SLI could have also resulted in an increase of δD by ~200–300‰. It has been shown that SLI induces fractionation of O isotopes, the δ¹⁸O in the Si-rich melt fraction increasing by approximately 0.6‰ compared to the Fe-rich melt fraction (Kyser et al. 1998). Kyser et al. (1998) also showed that thermal gradients induce isotopic fractionation in silicate melts, the lighter isotope getting enriched toward hotter regions; they measured fractionation of δ¹⁸O of 1.2–1.4‰ per 100 °C. More recent studies added Mg, Si, Ca, and Fe to the list of isotopic systems fractionated due to thermal gradients in silicate melts (Richter et al. 2008, 2009; Huang et al. 2010). Bindeman et al. (2013) recently demonstrated that the presence of H₂O in the melt greatly enhances thermal isotopic fractionation, and that H isotopes of the water itself are fractionated, δD increasing by approximately 45‰ per 100 °C gradient in their experiments. The absence of data on the possible effect of SLI sensu stricto on fractionation of H isotopes prevents us from being certain about SLI to be the cause of the increase in δD by ~200–300‰. Nevertheless, on balance, the existing data and observations point toward a potential role of SLI in modifying δD signatures of lunar melts and further work is necessary to confirm this hypothesis both through actual measurements of appropriate samples and experimental work.

**SUMMARY**

In this study, we have investigated the H isotope systematics of apatite from four brecciated lunar meteorites (NWA 4472, NWA 773, SaU 169, and Kal 009), and measured the Cl isotopic composition of apatite in two of these meteorites (NWA 4472 and SaU 169) using secondary ion mass spectrometry. Most of the apatite analyses carried out in the regolith breccia NWA 4472 yielded ~2000–6000 ppm H₂O, with associated δD values between −200 and 0‰. One isolated apatite grain located in the matrix of the breccia is completely different as it contains ~6000 ppm H₂O with associated δD values of ~500–900‰. In NWA 4472, the low-δD apatite grains also contain ~2500–7500 ppm Cl associated with δ³⁷Cl values of ~15–20‰, while the high-δD grain isolated in the matrix yielded ~2500 ppm Cl and heterogeneous δ³⁷Cl values of ~7–15‰. In the regolith breccia part of NWA 773, apatite grains we analyzed define 2 groups. In the first one, apatite grains contain 700 to 2500 ppm H₂O, associated with homogeneous δD values around ~0 ± 100‰. In the second group, apatite analyses yielded elevated H₂O abundances (~5500–16,500 ppm), associated with δD values ~250 ± 50‰. Apatite in the impact-melt breccia SaU 169 and the fragmental basaltic breccia Kal 009 yielded similar H₂O contents (~600–3000 ppm) and δD values (~100 to 200‰). In SaU 169, these apatite grains contain ~6000–10,000 ppm Cl, characterized by δ³⁷Cl values of ~5–12‰.

As the δ³⁷Cl of terrestrial materials cluster around 0‰, the elevated δ³⁷Cl values above 5‰ obtained on apatite in NWA 4472 and SaU 169 suggest that apatite in these hot-desert meteorites have retained their original lunar isotopic signatures. Regarding H isotopes, most of the analyzed apatite grains have δD values within the range reported for carbonaceous chondrites, and are consistent with compositions measured in H₂O-rich apatite analyzed in ancient (>3.9 Ga) magmatic rocks from the Mg- and alkali-suites, as well as that of KREEP basalts. On the other hand, one apatite grain in NWA 4472 is characterized by H and Cl isotope compositions similar to those reported for apatite from typical mare basalts. This grain could represent a remnant of some of the oldest known lunar volcanic activity as it has previously been dated at 4.35 Ga. Lastly, we found a group of apatite in the brecciated lithology of NWA 773 characterized by high to extremely-high H₂O contents, reaching pure hydroxylapatite composition. As it has been argued that numerous evolved clasts in NWA 773 formed through silicate liquid immiscibility of their parent melts, these H₂O-rich apatites could provide important information regarding the potential effects of such a process on the evolution of volatiles in lunar magmas.

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REFERENCES

Alexander C. M. O’D., 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.

Al-Katri et al., Gnos E., and Hofmann B. A. 2007. The regolith portion of the lunar meteorite Sayh al Uhaymir 169. Meteoritics & Planetary Science 42:2137–2152.

Anand M., Taylor L. A., Neal C. R., Snyder G. A., Patchen A., Sano Y., and Terada K. 2003. Petrogenesis of lunar meteorite EET 96008. Geochimica et Cosmochimica Acta 67:3499–3518.

Anand M., Taylor L. A., Floss C., Neal C. R., Terada K., and Tanikawa S. 2006. Petrology and geochemistry of LaPaz Icefield 02205: A new unique low-Ti mare-basalt meteorite. Geochimica et Cosmochimica Acta 70:246–264.

Anand M., Tartèse R., and Barnes J. J. 2014. Understanding the origin and evolution of water in the Moon through lunar sample studies. Philosophical Transactions of the Royal Society A 372:20130254. doi:10.1098/rsta.2013.0254.

Arai T., Misawa K., Tomiyama T., Yoshitake M., and Irving A. J. 2009. Constraints on lunar KREEP magmatism: A variety of KREEP basalt derivatives in lunar meteorite NWA 4485 (abstract #2292). 40th Lunar and Planetary Science Conference. CD-ROM.

Arai T., Yoshitake M., Tomiyama T., Niihara T., Yokoyama T., Kaiden H., Misawa K., and Irving A. J. 2010. Support for a prolonged KREEP magmatism: U-Pb age dating of zircon and baddeleyite in lunar meteorite NWA 4485 (abstract #2379). 41st Lunar and Planetary Science Conference. CD-ROM.

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. Chemical Geology 337–338:48–55.

Barnes J. J., Tartèse R., Anand M., McCubbin F. M., Franchi I. A., Starkey N. A., and Russell S. S. 2014. The origin of water in the primitive Moon as revealed by the lunar highlands samples. Earth and Planetary Science Letters 390:244–252.

Beatty J. W., Hill S. M. R., and Albee A. L. 1979. The petrology and chemistry of basaltic fragments from the Apollo 11 soil, part I. Proceedings, 10th Lunar and Planetary Science Conference. pp. 41–75.

Bindeman I. N., Lundstrom C. C., Bopp C., and Huang F. 2013. Stable isotope fractionation by thermal diffusion through partially molten wet and dry silicate rocks. Earth and Planetary Science Letters 365:51–62.

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. Geochimica et Cosmochimica Acta 73:3963–3980.

Boyce J. W. and Hervig R. L. 2008. Magmatic degassing histories from apatite volatile stratigraphy. Geology 36:63–66.

Boyce 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.

Boyce 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 (abstract #2851). 44th Lunar and Planetary Science Conference. CD-ROM.

Boyce J. W., Tomlinson S. M., McCubbin F. M., Greenwood J. P., and Treiman A. H. 2014. The lunar apatite paradox. Science 344:400–402.

Brenan J. 1993. Kinetics of fluorine, chlorine, and hydroxyl exchange in fluorapatite. Chemical Geology 110:195–210.

Chaussidon M. and Robert F. 1999. Lithium nucleosynthesis in the Sun inferred from the solar-wind 7Li/6Li ratio. Nature 402:270–273.

Chernik D. J., Lanford W. A., and Ryerson F. J. 1991. Lead diffusion in apatite and zircon using ion implantation and Rutherford backscattering techniques. Geochimica et Cosmochimica Acta 55:1663–1673.

Connolly H. C. Jr., Zipfel J., Folco L., Smith C., Jones R. H., Benedix G., Righter K., Yamaguchi A., Chennoua Aoudjehane H., and Grossman J. N. 2007. The Meteoritical Bulletin, No. 91. Meteoritics & Planetary Science 42:413–466.

Epstein S. and Taylor H. P. 1973. The isotopic composition and concentration of water, hydrogen and carbon in some Apollo 15 and 16 soils and in the Apollo 17 orange soil. Proceedings, 4th Lunar Science Conference. pp. 1559–1575.

Eugster O. 2003. Cosmic-ray exposure ages of meteorites and lunar rocks and their significance. Chemie der Erde—Geochimie 63:3–30.

Fagan T. J., Taylor G. J., Kel K., Hicks T. L., Killgore M., Bunch T. E., Wittke J. H., Mittlefehldt D. W., Clayton R. N., Mayeda T. K., Eugster O., Lorenzetti S., and Norman M. D. 2003. Northwest Africa 773: Lunar origin and iron-enrichment trend. Meteoritics & Planetary Science 38:529–554.

Fagan T. J., Kashima D., Wakabayashi Y., and Sugino H. 2014. Case study of magmatic differentiation trends on the Moon based on lunar meteorite Northwest Africa 773 and comparison with Apollo 15 quartz monzodiorite. Geochimica et Cosmochimica Acta 133:97–127.

Fernandes V. A., Burgess R., and Turner G. 2003. 40Ar–39Ar chronology of lunar meteorites Northwest Africa 032 and 773. Meteoritics & Planetary Science 38:555–564.

Gancarz A. J., Albee A. L., and Chodos A. A. 1971. Petrologic and mineralogic investigation of the Apollo 11 crystalline rocks returned by the Apollo 11 mission. Earth and Planetary Science Letters 12:1–18.

Gnos E., Hofmann B. A., Al-Kathiri A., Lorenzetti S., Eugster O., Whitehouse M. J., Villa I. M., Jull A. J. T., Eikenberg J., Spettel B., Krähenbühl U., Franchi I. A., and Greenwood R. C. 2004. Pinpointing the source of a lunar meteorite: Implications for the evolution of the moon. Science 305:657–659.

Greenwood J. P., Itoh S., Sakamoto N., Warren P., Taylor L. A., and Yurimoto H. 2011. Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. Nature Geoscience 4:79–82.
Hashizume K., Chaussidon M., Marty B., and Robert F. Hauri E. H., Weinreich T., Saal A. E., Rutherford M. C., and 2000. Solar wind record on the moon: Deciphering presolar from planetary nitrogen. Science 290:1142–1145.
Hashizume K., Chaussidon M., Marty B., and Terada K. 2004. Protosolar carbon isotopic composition: Implications for the origin of meteoritic organics. The Astrophysical Journal 600:480–484.
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., Rutherford M. J., Guillemette R. N., Ryerson F. J., and Tuchfeld H. A. 1975. Residual products of fractional crystallization in lunar magmas: An experimental study. Proceedings, 6th Lunar Science Conference, pp. 895–910.
Huang F., Chakraborthy P., Lundstrom C. C., Holmden C., Glessner J. J. G., Kieffer S. W., and Lesher C. E. 2010. Isotope fractionation in silicate melts by thermal diffusion. Nature 464:396–399.
Hui H., Peslier A. H., Zhang X., and Neal C. R. 2013. Water in lunar anorthosites and evidence for a wet early Moon. Nature Geoscience 6:177–180.
Jolliff B. L. 1991. Fragments of quartz monzodiorite and felsite in Apollo 14 soil particles. Proceedings, 21st Lunar and Planetary Science Conference, pp. 101–118.
Jolliff B. L. 1998. Large-scale separation of K-fac and REEP-fac in the source regions of Apollo impact-melt breccias, and a revised estimate of the KREEP composition. International Geology Review 10:916–935.
Jolliff B. L., Korotev R. L., and Haskin L. A. 1991. Geochemistry of 2–4 mm particles from Apollo 14 soil (14161) and implications regarding igneous components and soil-forming processes. Proceedings, 21st Lunar and Planetary Science Conference, pp. 193–219.
Jolliff B. L., Korotev R. L., Zeigler R. A., and Floss C. 2003. Northwest Africa 773: Lunar mare breccia with a shallow-formed olivine-cumulate component, inferred very-low-Ti (VLT) heritage, and a KREEP connection. Geochimica et Cosmochimica Acta 67:4587–4879.
Joy K. H., Burgess R., Hinton R., Fernandes V. A., Crawford I. A., Kearsley A. T., and Irving A. J. 2011. Petrogenesis and chronology of lunar meteorite Northwest Africa 4472: A KREEPy regolith breccia from the Moon. Geochimica et Cosmochimica Acta 75:2420–2452.
Joy K. H., Nemchin A., Grange M., Lapen T. J., Peslier A. H., Ross D. K., Zolensky M. E., and Kring D. A. 2014. Petrography, geochronology and source terrain characteristics of lunar meteorites Dhofar 925, 961 and Sayh al Uhaymir 449. Geochimica et Cosmochimica Acta 144:299–325.
Korotev R. L., Zeigler R. A., Jolliff B. L., Irving A. J., and Bunch T. E. 2009. Brecciated lunar meteorites of intermediate iron concentration. Meteoritics & Planetary Science 44:1287–1322.
Korotev R. L., Jolliff B. L., Zeigler R. A., Seddio S. M., and Haskin L. A. 2011. Apollo 12 revisited. Geochimica et Cosmochimica Acta 75:1540–1573.
Kyser T. K., Lesher C. E., and Walker D. 1998. The effects of liquid immiscibility and thermal diffusion on oxygen isotopes in silicate liquids. Contributions to Mineralogy and Petrology 133:373–381.
Lécuyer C., Gillet P., and Robert F. 1998. The hydrogen isotope composition of seawater and the global water cycle. Chemical Geology 145:249–261.
Lester G. W., Clark A. H., Kyser T. K., and Naslund H. R. 2013. Experiments on liquid immiscibility in silicate melts with H2O, P, S, F and Cl: Implications for natural magmas. Contributions to Mineralogy and Petrology 166:329–349.
Lin Y., Shen W., Liu Y., Xu L., Hofmann B. A., Mao Q., Tang G. Q., Wu F., and Li X. H. 2012. Very high-K KREEP-rich clasts in the impact melt breccia of the lunar meteorite SaU 169: New constraints on the last residue of the lunar magma ocean. Geochimica et Cosmochimica Acta 85:19–40.
Liu D., Jolliff B. L., Zeigler R. A., Korotev R. L., Wan Y., Xie H., Zhang Y., Dong C., and Wang W. 2012. Comparative zircon U-Pb geochronology of impact melt breccias from Apollo 12 and lunar meteorite SaU 169, and implications for the age of the Imbrium impact. Earth and Planetary Science Letters 319–320:277–286.
Longhi J. 1990. Silicate liquid immiscibility in isothermal crystallization experiments. Proceedings, 20th Lunar and Planetary Science Conference, pp. 12–24.
Lorenzetti S., Busemann H. and Eugster O. 2005. Regolith history of lunar meteorites. Meteoritics & Planetary Science 40:315–327.
McCubbin F. M., Steele A., Nekvasil H., Schnieders A., Rose T., Fries M., Carpenter P. K., and Jolliff B. L. 2010a. Detection of structurally bound hydroxyl in fluorapatite from Apollo mare basalt 15058,128 using TOF-SIMS. American Mineralogist 95:1141–1150.
McCubbin F. M., Steele A., Hauri E. H., Nekvasil H., Yamashita S., and Hemley R. 2010b. Nominally hydrous mantatism on the Moon. Proceedings of the National Academy of Sciences 107:11,223–11,228.
McCubbin F. M., Jolliff B. L., Nekvasil H., Carpenter P. K., Zeigler R. A., Steele A., Elardo S. M., and Lindsley D. H. 2011. Fluorine and chlorine abundances in lunar apatite: Implications for heterogeneous distributions of magmatic volatiles in the lunar interior. Geochimica et Cosmochimica Acta 75:5073–5093.
McCubbin F. M., Hauri E. H., Elardo S. M., Vander Kaaden K. E., Wang J., and Shearer C. K. 2012. Hydrous melting of the Martian mantle produced both depleted and enriched shergottites. Geology 40:683–686.
Merlivat L., Leli M., Neif G., and Roth E. 1976. Spallation deuterium in rock 70215. Proceedings, 7th Lunar Science Conference, pp. 649–658.
Neal C. R. and Kramer G. Y. 2006. The petrogenesis of the Apollo 14 high-Al mare basalts. American Mineralogist 91:1521–1535.
Nishiizumi K., Hillegronds D. J., McHargue L. R., and Jull A. J. T. 2004. Exposure and terrestrial histories of new lunar and Martian meteorites (abstract #1130). 35th Lunar and Planetary Science Conference, CD-ROM.
Pernet-Fisher J. F., Howarth G. H., Liu Y., Chen Y., and Taylor L. A. 2014. Estimating the lunar mantle water budget from phosphates: Complications associated with silicate-liquid-immiscibility. Geochimica et Cosmochimica Acta 144:326–341.
Philpotts A. R. 1982. Composition of immiscible liquids in volcanic rocks. Contributions of Mineralogy and Petrology 80:201–218.
Richter F. M., Watson E. B., Mendybaev R., and Janney P. E. 2008. Magnesium isotope fractionation in silicate melts by chemical and thermal diffusion. Geochimica et Cosmochimica Acta 72:206–220.
Richter F. M., Watson E. B., Mendybaev R., Dauphas N., Georg B., Watkins J., and Valley J. W. 2009. Isotopic fractionation of the major elements of molten basalt by chemical and thermal diffusion. Geochimica et Cosmochimica Acta 73:4250–4263.

Roedder E. 1984. Fluid inclusions. Reviews in Mineralogy, vol. 12. Washington, D.C.: Mineralogical Society of America. 646 p.

Roedder E. and Weiblin P. W. 1970. Lunar petrology of silicate melt inclusions, Apollo 11. Proceedings, Apollo 11 Lunar Science Conference, pp. 801–837.

Roedder E. and Weiblin P. W. 1971. Petrology of silicate melt inclusions, Apollo 11 and Apollo 12 and terrestrial equivalents. Proceedings, 2nd Lunar Science Conference, pp. 507–528.

Rutherford M. J., Hess P. C., and Daniel G. H. 1974. Lunar petrology of silicate melt inclusions, Apollo 11. Proceedings, Apollo 11 Lunar Science Conference, pp. 569–583.

Saa 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 454:192–195.

Saa 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.

Saighi O., Michelot J. L., and Filly A. 2001. Isotopic characteristic of meteoric water and groundwater in Ahaggar massif (central Sahara). International Atomic Energy Agency TECDOC 1207:7–25.

Sharp Z. D., Shearer C. K., McKeegan K. D., Barnes J. D., and Wang Y. Q. 2010a. The chlorine isotope composition of the Moon. Science 329:1050–1053.

Sharp Z. D., Barnes J. D., Fischer T. P., and Halick M. 2010b. An experimental determination of chlorine isotope fractionation in acid systems and applications to volcanic fumaroles. Geochimica et Cosmochimica Acta 74:264–273.

Sharp Z. D., McCubbin F. M., and Shearer C. K. 2013a. A hydrogen-based oxidation mechanism relevant to planetary formation. Earth and Planetary Science Letters 380:88–97.

Sharp Z. D., Mercer J. A., Jones R. H., Brearley A. J., Selverstone J., Bekker A., and Stachel T. 2013b. The chlorine isotope composition of chondrites and Earth. Geochimica et Cosmochimica Acta 107:189–204.

Shaulis B. J., Righter M., Lapen T. J., and Irving A. J. 2013. 3.1 Ga crystallization age of magnesian and ferroan gabbro lithologies in lunar meteorites Northwest Africa 773, 3170, 6950 and 7007, and evidence for 3.95 Ga gabbro lithologies in lunar meteorites Northwest Africa 773, 3170, 6950 and 7007, and evidence for 3.95 Ga crystallization age of magnesian and ferroan gabbro lithologies in lunar meteorites Northwest Africa Kalahari 008 and 009: New constraints on early lunar evolution. Geochimica et Cosmochimica Acta 72:4845–4873.

Stéphan A. and Robert F. 2014. The negligible chondritic contribution in the lunar soils water. Proceedings of the National Academy of Sciences 111:12,007–12,012.

Stewart M. A. and Spivack J. A. 2004. The stable-chlorine isotope compositions of natural and anthropogenic materials. Reviews in Mineralogy & Geochemistry 55:231–254.

Tartèse R., Anand M., Barnes J. J., Starkey N. A., Franchi I. A., and Sano Y. 2013. 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. Geochimica et Cosmochimica Acta 122:58–74.

Tartèse R., Anand M., McCubbin F. M., Elardo S. M., Shearer C. K., and Franchi I. A. 2014a. Apatites in lunar KREEP basalts: The missing link to understanding the KREEP isotope systematics of the Moon. Geology 42:363–366.

Taylor L. A., Patchen A., Mayne R. G., and Taylor D.-H. 2004. The most reduced rock from the moon, Apollo 14 14053: Its unique features and their origin. American Mineralogist 89:1617–1624.

Terada K., Saiki T., Oka Y., Hayasaka Y., and Sano Y. 2005. Ion microprobe U-Pb dating of phosphates in lunar basaltic breccia, Elephant Moraine 87521. Geophysical Research Letters 32:L20202.

Terada K., Anand M., Sokol A. K., Bischoff A., and Sano Y. 2007a. Cryptomare magmatism 4.35 Gyr ago recorded in lunar meteorite Kalahari 009. Nature 450:849–853.

Terada K., Sasaki Y., Anand M., Joy K. H., and Sano Y. 2007b. Uranium-lead systematics of phosphates in lunar basaltic regolith breccia, Meteorite Hills 01210. Earth and Planetary Science Letters 259:77–84.

Terada K., Sasaki Y., Anand M., Sano Y., Taylor L. A., and Horie K. 2008. Uranium-lead systematics of low-Ti basaltic meteorite Dhofar 287A: Affinity to Apollo 15 green glasses. Earth and Planetary Science Letters 270:119–124.

Treiman A. H., Boyce J. W., Gross J., Guan Y., Eiler J. M., and Stolper E. M. 2014. Phosphorus-halogen metasomatism of lunar granulate 79215: Impact-induced fractionation of volatiles and incompatible elements. American Mineralogist 99:1860–1870.

Ustunisik G., Nekvasil H., and Lindsley D. H. 2011. Differential degassing of H2O, Cl, F, and S: Potential effects on lunar apatite. American Mineralogist 96:1650–1653.

Warren P. H. 1989. KREEP: Major-element diversity, trace-element uniformity (almost). In Workshop on Moon in Transition: Apollo 14, KREEP, and Evolved Lunar Rocks, edited by Taylor G. J. and Warren P. H. LPI Technical Report 89-03. Houston: Lunar and Planetary Institute. pp. 149–153.

Warren P. H. 2012. Let’s get real: Not every lunar rock sample is big enough to be representative for every purpose (abstract #9034). 2nd Conference on the Lunar Highlands Crust.
SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

Data S1. The supporting information file contains twelve figures (Figs. S1–S12) displaying backscattered electron images and composite X-ray element maps of the studied polished sections of lunar meteorites. It also contains further details regarding secondary ion mass spectrometry protocols for H and Cl isotope analyses, as well as a figure displaying an example of calibration obtained for Cl content measurements on terrestrial apatite standards (Fig. S13).

Table S1: Semi-quantitative EDS analyses of selected silicates.

Table S2: Beam conditions and calibration parameters for the D/H analytical sessions.

Table S3: Electron microprobe analyses of apatite in NWA 4472 and NWA 773.