Nominally hydrous magmatism on the Moon
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For the past 40 years, the Moon has been described as nearly devoid of indigenous water; however, evidence for water both on the lunar surface and within the lunar interior have recently emerged, calling into question this long-standing lunar dogma. In the present study, hydroxyl (as well as fluoride and chloride) was analyzed by secondary ion mass spectrometry in apatite [Ca5(PO4)3(F,Cl,OH)] from three different lunar samples in order to obtain quantitative constraints on the abundance of water in the lunar interior. This work confirms that hundreds to thousands of ppm water (of the structural form hydroxyl) is present in apatite from the Moon. Moreover, two of the studied samples likely had water preserved from magmatic processes, which would qualify the water as being indigenous to the Moon. The presence of hydroxyl in apatite from a number of different types of lunar rocks indicates that water may be ubiquitous within the lunar interior, potentially as early as the time of lunar formation. The water contents analyzed for the lunar apatite indicate minimum water contents of their lunar source region to range from 64 ppm to 5 ppm H2O. This lower limit range of water contents is at least two orders of magnitude greater than the previously reported value for the bulk Moon, and the actual source region water contents could be significantly higher.

fluorapatite | lunar water | magma ocean | mare basalt | NWA 773

One of the scientific discoveries resulting from the Apollo missions was the pervasive waterless nature of the Moon and its rocks. The initial studies of the returned samples were pristine and showed no evidence of aqueous alteration, and water analyses were below detection limits. Moreover, hydrous phases were absent from the lunar rocks aside from a few unconfirmed reports of possible amphibole grains (1), which are now considered by many to represent either misidentifications or terrestrial contamination (as summarized by ref. 2). The subsequent forty years of lunar sample analysis have only supported and strengthened the idea that indigenous water was nearly absent from the Moon’s interior. In fact, this conclusion has been incorporated into many petrologic and geophysical models constructed to aid in our understanding of lunar formation and lunar geology (3–11). The bulk water content of the Moon was recently estimated to be less than 1 ppm (11), which would make the Moon at least six orders of magnitude drier than the interiors of Earth (12, 13) and Mars (14). This extremely low water content is in keeping with the pervasive volatile-element depletion signature recorded in all lunar materials, because hydrogen is the most volatile of the elements. The exact cause for this volatile-element depletion is still under question; however, many have argued that it stems from the high temperatures associated with the Moon-forming giant-impact event at ~4.5 Ga (i.e., refs. 3, 8, 15, and 16).

Facilitated by advancements in analytical detection sensitivities for water, several recent discoveries have indicated that the story of water on the Moon is far from complete. Evidence for hydroxyl/water on the lunar surface has been detected by using remote sensing data from the Moon Mineralogy Mapper (M3) instrument on board the Chandrayaan-1 spacecraft (17–19). Moreover, evidence for water within the lunar interior has been reported through ongoing lunar sample analysis efforts. Specifically, up to 46 ppm water has been directly measured in some pyroclastic lunar glasses (16), and hydroxyl has been qualitatively identified in fluorapatite grains (fluorapatite is a calcium phosphate mineral depicted as [Ca5(PO4)3(F,Cl,OH)]) from Apollo 15 mare basalt 15058 (20). Whereas the remote sensing studies are likely providing a glimpse into water formation during space weathering processes, the sample analysis studies provide evidence that the water content of the lunar interior may have been underestimated. Depending on the magnitude of the underestimation, profound changes in our understanding of the Moon’s geologic history, from models of lunar formation to our understanding of its thermal and magmatic evolution, may be required.

The current view of lunar formation and its subsequent magmatic evolution begins with the Moon-forming giant-impact event at ~4.5 Ga (i.e., refs. 3, 8, 15, and 16). Following the initial stages of lunar accretion, the lunar-wide magma ocean began to cool and crystallize, marking the start of lunar magmatism and differentiation (21–25). During lunar magma ocean crystallization, it is believed that early-forming ferromagnesian minerals (olivine and pyroxene) sank to the magma ocean floor, resulting in a lunar mantle composed of stratified cumulate mineral layers (21–25). During the middle-to-late stages of magma ocean crystallization, anorthositic feldspar began to crystallize and float to the surface because of its lower density with respect to the residual magma ocean liquid from which it crystallized (21–25). This process resulted in the formation of the lunar ferroan anorthosite lithology that comprises well over 50% of the present-day lunar surface. During the last stages of magma ocean crystallization, the residual liquid became increasingly enriched in incompatible trace elements. These last dregs of unsolidified, incompatible trace element-rich residual liquid are referred to as “urKREEP,” which was named after the high abundances of potassium (K), rare earth elements (REE), and phosphorus (P) that were present in the late-stage liquid (as summarized by refs. 10 and 26). In addition to potassium, this residual urKREEP liquid was also enriched in other heat-producing elements such as uranium and thorium, making it an important potential heat source for generating magmatism subsequent to magma ocean crystallization (21–25). Virtually nothing is known about the role of water in the lunar magma ocean. However, given that water is highly insoluble in the major silicates that crystallize from lunar magmas, any water dissolved in the magma ocean liquid should have been concentrated in urKREEP; however, there is currently no quantitative data supporting the presence of water in the urKREEP liquid.

Lunar magmatism continued for at least a billion years (i.e., refs. 10, 27, and 28) after magma ocean crystallization had ceased, resulting in a diverse array of lunar lithologic types (ref. 29 and references therein). It is important to note, however, that all of the lithologies discussed here are within the Procellarum KREEP Terrain (30), a terrain that is not typical of the bulk lunar surface.


The authors declare no conflict of interest.

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A number of post magma ocean lithologies even have KREEP-like incompatible trace element signatures, which is typically explained (or partially explained) as resulting from assimilation or mixing of urKREEP with the source magma (21, 22, 31–36). The rock types that are reported to have resulted from this process include KREEP basalts, some Apollo 14 high-aluminum basalts, and the plutonic lithologies of the highlands magnesia suite and alkali suite (21, 22, 31–36). There is also a group of rock types in the Procellarum KREEP Terrain that do not typically exhibit KREEP-like incompatible trace element signatures. These are generally grouped as mare volcanic materials, and they include mare basalts (exclusive of the high-Al basalts) and the pyroclastic fire-fountain glasses (21, 25, 37–39). The two studies that have reported evidence for water in the Moon’s interior both investigated igneous materials associated with mare volcanism that do not exhibit KREEP-like incompatible trace element signatures (16, 20). Evidence for elevated water contents in the source regions of the mare materials is profound and supports the possibility of the presence of water in the lunar magma ocean. However, linking mare basalts to the magma ocean is complex, and insight into the water budget of the lunar interior as a whole could be better accomplished by obtaining constraints on the water contents of a variety of lunar rock types, including those with KREEP-like incompatible trace element signatures.

In the present study,apatites from three different lunar samples were analyzed for hydroxyl by using secondary ion mass spectrometry (SIMS). The hydroxyl analyses were subsequently used to infer information about magmatic water contents and the water contents of the magmatic source regions (where possible). The samples investigated here span three distinct rock types, and they all have KREEP-like incompatible trace element signatures. The samples investigated include an Apollo 14 high-Al basalt (14053,16), a clast-bearing impact melt rock (15404,15), and an olivine-gabbro cumulate lunar meteorite (Northwest Africa 2977). The magmatic water contents inferred from this study are compared to previous investigations of water in mare volcanic materials to summarize the current state of knowledge regarding water in the lunar interior.

Results

High-Aluminum Basalt 14053,16. High-Al basalt 14053 is among the most well-studied samples in the lunar collection. Previous petrographic observations have indicated that sample 14053 is a coarse-grained high-Al basalt (40, 41). Previous isotopic studies of the rock have indicated a Rb-Sr crystallization age of 3.92 Ga (e.g., refs. 27 and 42); however, the Sm-Nd isotope systematics were found to be disturbed (43). This observation is anomalous, because normally it is the Rb-Sr system that is prone to disturbance by post-crystallization processes. This dichotomy was considered to reflect the postcrystallization open-system behavior of apatite, which crystallization processes. This dichotomy was considered to reflect the postcrystallization open-system behavior of apatite, which crystallization processes. This dichotomy was considered to reflect the postcrystallization open-system behavior of apatite, which crystallization processes. This dichotomy was considered to reflect the postcrystallization open-system behavior of apatite, which crystallization processes. This dichotomy was considered to reflect the postcrystallization open-system behavior of apatite, which crystallization processes.

Consistent with previous petrographic observations, our analysis confirms this sample to consist primarily of pyroxene and plagioclase with volumetrically minor fayalitic olivine, fluorapatite, baddeléite, K-feldspar, Fe-Ti oxides, Fe-metal, silica, trolite, and Cr-Ba-rich glass. Much of the olivine is surrounded by intergrowths of Fe-metal and silica that are likely breakdown products of olivine (Fig. 1A). This texture has been described previously and has been suggested to arise from the rock interacting with solar-wind-implanted hydrogen at the lunar surface during impact-induced shock metamorphism (41).

The apatites in 14053 are typically subhedral to anhedral, and they range in size from ~2 μm to larger than 200 μm in the longest dimension. The fluorapatite is typically associated with late-stage melt pockets that are in the proximity of the olivine, Fe-metal, and silica (Fig. 1). Fluorine, chlorine, and hydroxyl concentrations of the apatites in 14053 were determined by SIMS, and the results are presented in Table 1. The apatites from this sample have fluorine concentrations ranging from 2.48 ± 0.03 to 2.9 ± 0.1 wt%, confirming that these are fluorapatites. The chlorine concentrations of these fluorapatites range from 1.730 ± 50 to 4.660 ± 50 ppm, and the hydroxyl concentrations range from 1.300 ± 200 to 2.700 ± 400 ppm. The SIMS analysis spots of apatite from this sample are indicated in Fig. 1.

Alkali-Suite Clast in 15404,51. Apollo sample 15404,51 is a soil grain from the 4–10 mm sieve fraction collected during the Apollo 15 mission; no crystallization or exposure age information is available for this individual grain. This particular grain consists of two lithologies, an impact melt breccia and a lithic clast (Fig. 2A). The lithic clast primarily consists of two pyroxenes and plagioclase that are typically >100 μm in their longest dimension (up to approximately 500 μm). The relative coarse-grained nature of this lithic clast is consistent with it being a plutonic rock. Electron probe microanalysis of the pyroxene and plagioclase were conducted for the purpose of lithologic classification. The pyroxenes in this sample range in Mg number [Mgmol/(Mgmol + Feomol)] from 43 to 58, with an average Mg number of approximately 49 (averaged from 15 analyses). The plagioclase compositions ranged from An45 to An56, with an average composition of An48 (averaged from 12 analyses). On the basis of the plagioclase and pyroxene compositions as well as the coarse-grained nature of the clast (Fig. 2A), this clast is likely a member of the alkali suite from the lunar highlands (Fig. S1, adapted from ref. 45). In addition to the two pyroxenes and the plagioclase, abundant K-rich feldspar and minor silica, fluorapatite, merrillite, Cr-rich spinel, and Fe-Ti oxides are also present in the clast. The texture and mineralogy of this clast are consistent with other alkali-suite samples (i.e., refs. 29, 46, and 47).

Table 1. SIMS analyses of lunar apatite

<table>
<thead>
<tr>
<th>Sample*</th>
<th>F (wt%)</th>
<th>Cl (ppm)†</th>
<th>OH (ppm)†</th>
</tr>
</thead>
<tbody>
<tr>
<td>14053_1</td>
<td>2.48 ± 0.03</td>
<td>4,660 ± 50</td>
<td>2,700 ± 400</td>
</tr>
<tr>
<td>14053_2</td>
<td>2.70 ± 0.06</td>
<td>4,300 ± 200</td>
<td>1,700 ± 300</td>
</tr>
<tr>
<td>14053_3</td>
<td>2.83 ± 0.08</td>
<td>4,570 ± 80</td>
<td>1,400 ± 200</td>
</tr>
<tr>
<td>14053_4</td>
<td>2.9 ± 0.1</td>
<td>1,730 ± 50</td>
<td>1,300 ± 200</td>
</tr>
<tr>
<td>14040_1</td>
<td>2.47 ± 0.04</td>
<td>11,600 ± 200</td>
<td>1,000 ± 300</td>
</tr>
<tr>
<td>14040_2</td>
<td>2.62 ± 0.03</td>
<td>3,940 ± 20</td>
<td>320 ± 200</td>
</tr>
<tr>
<td>15404_3</td>
<td>2.54 ± 0.06</td>
<td>10,770 ± 40</td>
<td>220 ± 40</td>
</tr>
<tr>
<td>NWA 2977_1</td>
<td>2.7 ± 0.2</td>
<td>2,100 ± 100</td>
<td>7,000 ± 1,000</td>
</tr>
<tr>
<td>NWA 2977_2</td>
<td>2.7 ± 0.4</td>
<td>330 ± 50</td>
<td>4,000 ± 700</td>
</tr>
</tbody>
</table>

*Numbers next to the sample refer to the analysis number indicated on the respective BSE image.

†All reported uncertainties are 2σ.
Apatite in the alkali-suite clast from 15404.51 exists as anhedral grains, ranging in size from approximately 10 to >100 μm in the longest dimension, and they are typically associated with merrillite (Fig. 2 B and C). Fluorine, chlorine, and hydroxyl concentrations for theapatites were determined by SIMS, and they are presented in Table 1. The apatites from this sample have fluorine concentrations ranging from 2.54 ± 0.06 to 2.62 ± 0.03 wt%, verifying that these are fluorapatite. The chlorine concentrations of these fluorapatites range from 9.344 ± 20 to 10,770 ± 40 ppm, and the hydroxyl concentrations range from 220 ± 40 to 1,000 ± 200 ppm. The SIMS analysis spots of apatite from this sample are indicated in Fig. 2 B and C.

Very Low-Titanium Basalt Northwest Africa 2977. Lunar meteorite Northwest Africa (NWA) 2977 is an olivine-gabbro cumulate that is paired with lunar meteorite NWA 773 (48), which contains clasts of the same olivine-gabbro cumulate lithology (49, 50). The crystallization age of the olivine-gabbro cumulate in NWA 773 is 2.86 Ga (51), and no trapped solar wind was detected in this lithology, indicating a very limited residence time at the lunar surface (52). Preliminary reports indicate the same is true for NWA 2977. This rock has bulk chemical characteristics similar to the very low-titanium basalts; however, its incompatible trace element signature is similar to that of KREEP (50, 51), making this a unique sample among other lunar mare basalts (50, 51). The mineralogy of NWA 2977 is broadly consistent with the olivine-gabbro cumulate clasts described in NWA 773, consisting primarily of olivine, pyroxene, and plagioclase. In addition to these phases, merrillite, fluorapatite, baddeleyite, K-feldspar, Fe-Ti oxides, Fe-Ni metal, troilite, and pentlandite are present in minor abundances.

Theapatites in NWA 2977 are typically subhedral to anhedral, and they range in size from approximately 5 μm to grains larger than 100 μm in the longest dimension. The apatites typically fill the late-stage mesostasis between the larger olivine, pyroxene, and plagioclase grains, and the apatites commonly coexist with the other minor phases that occur in the meteorite (Fig. 3). Fluorine, chlorine, and hydroxyl concentrations for the apatites in NWA 2977 were determined by SIMS, and the results are presented in Table 1. The apatite from this sample have approximately 2.7 ± 0.4 wt% fluorine, verifying that these are fluorapatites. The chlorine concentrations of these fluorapatites range from 330 ± 50 to 2,100 ± 100 ppm, and the hydroxyl concentrations range from 4,000 ± 700 to 7,000 ± 1,000 ppm. The SIMS analysis spots of apatite from this sample are indicated in Fig. 3.

Discussion

Secondary Processes That Could Have Affected Igneous Apatite Compositions. The volatile contents reported in Table 1 demonstrate that none of these lunar samples containapatite of homogeneous composition, as might be expected from a simple magmatic crystallization history and subsequent behavior as a closed system. Before the analyzed volatile contents of the lunar apatite can be used to infer anything regarding lunar magmas, one must first consider the processes that could have altered the igneous apatite compositions. These processes include both terrestrial contamination that has taken place subsequent to the samples arriving to Earth as well as alteration and/or contamination that could have taken place within the Moon or on the lunar surface. Apatite has been shown to rapidly equilibrate with its geologic surroundings in high-temperature and high-pressure environments (53); however, this equilibration is not likely to occur at ambient terrestrial conditions unless the apatite is nanocrystalline, analogous to that involved in biomineralization processes (54, 55).

Of the three samples studied here, two are Apollo samples and one is a lunar meteorite recovered from a hot desert environment. The Apollo samples were very carefully collected and stored in curatorial facilities with controlled environments for almost the entire duration of their terrestrial history. Therefore, it is extremely unlikely that terrestrial contamination could have altered theapatite compositions within these materials. However, lunar meteorite NWA 2977 has been exposed to a terrestrial weathering environment, and terrestrial contamination and weathering is common for meteorite “finds” (i.e., those not observed to have fallen and immediately collected; see refs. 56 and 57). Although NWA 2977 has not been previously investigated for terrestrial contamination, carbonate deposits have been reported to occur on the exterior portions of lunar meteorite NWA 773 [paired with NWA 2977 (48)], and calcite-rich fracture fillings have also been observed within thin sections of this meteorite (50). Importantly, the silicates in NWA 773 lack observable alteration in thin section, even along fracture boundaries (50), and the same holds true for NWA 2977. Moreover, the Fe-rich Fe-Ni metal grains in both meteorites are intact and unaltered (ref. 50; Fig. 3B), which would not be the case if the rocks underwent sufficient contamination to “reset” the volatile contents of the apatite. Therefore, terrestrial
Volatile Contents of Lunar Magmas at the Time of Apatite Crystallization. The mineral apatite is structurally depicted as $A[1]_2A[2]_4(BO_4)_3X$ (64), where the $X$ site represents the monovalent anion site typically occupied by fluorine, chlorine, and hydroxyl. Analyses of apatite group minerals can be used to estimate the relative amounts of fluorine, chlorine, and water in coexisting melt, provided apatite-silicate melt partitioning data exist for these volatiles. Several studies have determined the apatite-melt and apatite-fluid partitioning behavior of F, Cl, and OH in terrestrial systems (65–68). Importantly, these studies show that Cl, F, and OH do not partition equally into the apatite X site; thus, the relative volatile abundances of the apatite are not directly proportional to those of the melt. Complicating the issue further, apatite/melt partition coefficients are dependent upon melt composition (i.e., refs. 65 and 67); therefore, understanding the composition of the liquids from which apatite has crystallized is an additional important step in understanding the magmatic volatile load of a given liquid. For basaltic liquids, which represent the closest analogs to the lunar compositions investigated here, $D_{\text{H}_2\text{O}}^{\text{apat}}/\text{basalt} = 3.4$ and $D_{\text{Cl}}^{\text{apat}}/\text{basalt} = 0.67$, although the partition coefficient for chlorine is only applicable to basaltic liquids that are fluid-undersaturated. Whereas the $D_{\text{H}_2\text{O}}^{\text{apat}}/\text{basalt}$ was not determined in the study in ref. 67, it can be estimated by using the calculated hydroxyl components of the apatite and the minimum melt volatile contents from each of the experiments; this estimate results in a range of possible apatite-basalt melt partition coefficients of approximately 0.10–0.25 for $\text{H}_2\text{O}$. The larger value is used here because it provides a minimum estimate for the magmatic water contents at the time of apatite crystallization (i.e., we assume $D_{\text{H}_2\text{O}}^{\text{apat}}/\text{basalt} = 0.25$).

The two samples from the present study deemed appropriate for assessing lunar magmatic water contents had different volatile loads at the time of apatite crystallization. The residual liquid in NWA 2977 contained 7,000–17,000 ppm water, 7,000–9,000 ppm fluorine, and 350–2,800 ppm chlorine at the time of apatite crystallization. In contrast, the residual magma from which the apatite crystallized in the alkali-suite clast in sample 15404,51 contained 200–2,800 ppm water, 7,300–7,800 ppm fluorine, and 11,700–14,800 ppm chlorine. The range in values reported indicates the variability in apatite composition within each sample. Although some of these magmatic volatile contents are quite high, apatite is typically one of the last minerals to enter the phase assemblage of a crystallizing lunar magma. Therefore, the parental magmatic volatile contents of these magmas were significantly lower than the values at the time of apatite crystallization for all three volatiles.

Minimum Water Contents of the Parental Magmas and Lunar Magmatic Source Regions. Water behaves incompatibly during closed-system crystallization of a magma; therefore, parental magmatic water contents can be calculated from apatite if the amount of crystallization that occurred before apatite entered the phase assemblage can be determined (see SI Text for the open-system crystallization scenario). The amount of crystallization before the appearance of apatite is very difficult to determine for the samples analyzed here because one of them is a coarse-grained plutonic rock (alkali-suite clast in 15404,51) and the other is a partial cumulate (NWA 2977), so lower limit estimates on the basis of the modal abundance of apatite will be meaningless. Although we cannot definitively determine when apatite entered the phase assemblage, the parental magmatic water contents can be modeled for each sample as a function of crystallinity (Fig. S2). If, for example, apatite did not enter the phase assemblage until 95% crystallization, the parental magmatic water content for NWA 2977 would range from 360 to 850 ppm $\text{H}_2\text{O}$, and the parental magmatic water content for the alkali-suite clast in 15404,51 would range from 10 to 140 ppm $\text{H}_2\text{O}$ (Fig. S2). These values are similar to the preeruptive magmatic water contents calculated for the
pyroclastic lunar glasses (i.e., 70–745 ppm H$_2$O depending on the duration of post-eruptive degassing 16).

For comparison to the previous estimate of the bulk water content of the Moon (i.e., <1 ppb, from ref. 11), we will take a conservative approach to estimate a minimum parental magmatic water content that assumes 99% crystallization occurred before apatite began to crystallize from the parental magmas of these samples. From this assumption, we can use the range of parental magmatic water contents from Fig. S2 (i.e., 70–170 ppm H$_2$O for NWA 2977 and 2–28 ppm H$_2$O for the alkali-suite clast in 15404.51) to calculate the minimum water contents of the magmatic source regions. The water content of the magmatic source region can be calculated as a function of the amount of partial melting that occurred to produce each parental magma composition (Fig. 4). At least a few percent of melting is typically required for partial melts to coalesce and separate from their source (69); therefore, by using 3% as a lower limit of partial melting, we arrive at a minimum range of 60–830 ppb H$_2$O for the alkali-suite clast source region and a minimum range of 2–5 ppm H$_2$O for the NWA 2977 source region; assuming closed-system crystallization, apatite is the only H$_2$O-bearing mineral phase in the assemblage, and apatite began to crystallize from the parent melt after 99% crystallization. For comparison, the pyroclastic glasses analyzed in ref. 16 require a minimum source region water content ranging from 2 to 21 ppm H$_2$O at 3% partial melting, assuming that the glasses represent partial melt compositions that did not experience any fractionation (Fig. 4). The amount of partial melting could have been much higher than 3% (i.e., ref. 70), which would result in a higher range in water contents for the magmatic source regions (i.e., 10% partial melting would yield a range of 200 ppb to 3 ppm H$_2$O for the alkali-suite clast source region and a range of 7–17 ppm H$_2$O for the NWA 2977 source region).

The minimum range in water contents for these lunar magmatic source regions (64 ppb to 21 ppm H$_2$O) are between two and five orders of magnitude higher than the previous estimate for the bulk water content of the Moon (i.e., <1 ppb, from ref. 11). Moreover, these values are lower limits, and the actual source region water contents could be much higher. The identification of water from multiple types of lunar rocks that display a range of incompatible trace element signatures indicates that water may be ubiquitous within the lunar interior, potentially as early as the time of lunar formation and magma ocean crystallization.

Materials and Methods

SIMS. The measurements of F, OH, Cl, and C in lunar fluorapatite were performed on a Cameca 6f ion microprobe at the Department of Terrestrial Magnetism, Washington, DC, by using the procedure of ref. 71. The focused (5–10 nA) 10 kV Cs$^+$ primary ion beam was rastered on the sample to a 25 by 25 μm area. The secondary ion beam was extracted at ~5 kV from an 8-μm diameter portion of the rastered area with a field aperture. An electron flood gun (~5 kV) was used to compensate for charge buildup in the analysis area. A mass resolution of 6,000 was used to resolve 17$^{30}$O/16$^{18}$O. Standardization on three terrestrial apatites was performed at the beginning of the session. Information concerning the compositions of the standards used is presented in Table S1, and the calibration curve for hydroxyl (reported as H$_2$O equivalent) is shown in Fig. S3. The H$_2$O calibration curve resulted in 2σ uncertainties of about 17%. Each analysis lasted about 10 min. The detection limit for water (~3 ppm H$_2$O) was determined by analyzing a dry synthetic forsterite crystal (blank) that was mounted with our terrestrial apatite standards; on the lunar thin sections containing apatite, our blank was determined from analyses of coexisting feldspar, pyroxene, or olivine. These analyses gave similar water contents as the synthetic forsterite (~3 ppm). As a result, we estimate our H$_2$O detection limit at 3 ppm or better for all of the samples analyzed in this study.

Care was taken in the apatite analyses to observe the direct ion beam for 12$^{30}$C and 14$^{30}$C for every location because grain boundaries and cracks within the sample are clearly illuminated by carbon and chlorine contamination. These analyses gave similar water contents as the synthetic forsterite (~3 ppm). Therefore, it was possible to obtain analyses on reasonably large areas of crack-free apatite within individual grains, and all of the data reported in Table 1 were obtained from such crack-free areas.

Caution should be taken when SIMS analysis is carried out on epoxy mounted thin sections because the possibility exists for OH contamination from the epoxy, which can invade cracks in the sample that may not be visible in the ion probe optics. Therefore, to avoid false positive SIMS results, the lunar thin sections was analyzed in the same way as our standards and unknowns in order to determine C/OH ratios for the epoxy and estimate possible maximum H$_2$O contributions from epoxy contamination on the surfaces of the thin section. On the basis of these epoxy analyses and the measured C/OH ratios of our apatites, if we assume that all of the C in our apatite analyses comes from epoxy, the maximum contribution is 5% of the total OH, with two exceptions (36% for analysis 14503.4 and 39% for analysis 14503.3). However, the lack of correlation between measured C and OH counts leads us to conclude that epoxy is not the major contributor to our measured C counts; this conclusion is supported by the fact that epoxy used on lunar thin sections is also exceedingly rich in Cl, and there is no relationship between measured carbon and chlorine counts in our apatite analyses. The most likely sources of carbon in our analyses are not epoxy but rather some combination of residual carbon from prior generations of carbon coat and carbon contained in the apatite mineral structure.

A detailed description of the analytical methods employed for classifying the terrestrial apatite standards used for SIMS calibration can be found in SI Text.

Field-Emission Scanning Electron Microscopy. Back-scattered electron (BSE) imaging and energy-dispersive spectroscopy (EDS) were performed at the Geophysical Laboratory, Washington, DC, on a JEOL JSM 6500F scanning electron microscope with a field-emission gun equipped with a liquid N$_2$-cooled sapphire Si(Li) EDS detector (EDAX). An operating voltage of 15 kV and a beam current of approximately 1 nA was used for all imaging and EDS acquisitions. EDS was used to chemically identify the fluorapatite grains analyzed in this study prior to SIMS analysis.

ACKNOWLEDGMENTS. We thank the Lunar Curatorial staff at the Lyndon B. Johnson Space Center in Houston, TX for allocation of the thin sections of Apollo samples 15404.51 and 14053.16. We thank Jianhua Wang for his technical assistance with the Carnegie SIMS. We also thank Tazue Nogi for expert assistance with the terrestrial apatite standards used is presented in Table S1, and the calibration curve for hydroxyl (reported as H$_2$O equivalent) is shown in Fig. S3. The H$_2$O calibration curve resulted in 2σ uncertainties of about 17%. Each analysis lasted about 10 min. The detection limit for water (~3 ppm H$_2$O) was determined by analyzing a dry synthetic forsterite crystal (blank) that was mounted with our terrestrial apatite standards; on the lunar thin sections containing apatite, our blank was determined from analyses of coexisting feldspar, pyroxene, or olivine. These analyses gave similar water contents as the synthetic forsterite (~3 ppm). As a result, we estimate our H$_2$O detection limit at 3 ppm or better for all of the samples analyzed in this study.

Field-Emission Scanning Electron Microscopy. Back-scattered electron (BSE) imaging and energy-dispersive spectroscopy (EDS) were performed at the Geophysical Laboratory, Washington, DC, on a JEOL JSM 6500F scanning electron microscope with a field-emission gun equipped with a liquid N$_2$-cooled sapphire Si(Li) EDS detector (EDAX). An operating voltage of 15 kV and a beam current of approximately 1 nA was used for all imaging and EDS acquisitions. EDS was used to chemically identify the fluorapatite grains analyzed in this study prior to SIMS analysis.

ACKNOWLEDGMENTS. We thank the Lunar Curatorial staff at the Lyndon B. Johnson Space Center in Houston, TX for allocation of the thin sections of Apollo samples 15404.51 and 14053.16. We thank Jianhua Wang for his technical assistance with the Carnegie SIMS. We also thank Tazue Nogi for technical assistance with H$_2$-manometry. Mihaela Glamoclija is acknowledged for assistance with digital image stitching. Insightful and constructive reviews were provided by E. Bruce Watson, James Day, Steven Symes, and G. Jeffery Taylor. Bradley Jolliff, Stephen Elardo, Charles Shearer, and Donald Lindsey are acknowledged for productive and fruitful discussions on this topic. Financial support for this work was provided by the US National Aeronautics and Space Administration (NASA) Grant NNX08BAZ04G from the Lunar Advanced Science and Exploration Research program (to H.N.)
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Supporting Information

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SI Text

Characterization of SIMS Standards and 15404,51 Lithology. Electron probe microanalysis (EPMA). EPMA was employed for two different purposes in this study. The first was to analyze the three fluorapatite standards used for secondary ion mass spectrometry (SIMS) analysis to corroborate the SIMS calibration for fluorine and chlorine. The second purpose was to classify the lithologic clast in sample 15404,51. All the samples were analyzed with a JEOL JXA-8800L electron microprobe, housed at the Geophysical Laboratory in Washington, DC. An accelerating voltage of 15 kV and a nominal beam current of 15 nA were used for all analyses. The beam diameter for each analysis was 10 μm. The terrestrial apatite standards were analyzed for the elements Ca, P, F, Cl, Fe, Na, Mn, Mg, Si, Ce, and Y, Ca, P, and F were standardized using Durango apatite; Na and Cl were standardized using scapolite; Fe, Mn, Mg, and Si were standardized using a basaltic glass; and Ce and Y were standardized using the phosphates CePO$_4$ and YPO$_4$, respectively. The compositions of the terrestrial fluorapatite standards are presented in Table S1.

The fluorine analyses determined by electron probe microanalysis and reported in Table S1 may be higher than the actual amount of fluorine in the apatites because fluorine X-ray count rates can increase during electron beam exposure (i.e., refs. 1 and 2). The chlorine and fluorine concentrations determined by electron probe microanalysis for the apatite standards were used only as a comparison to the values obtained by SIMS (i.e., the electron microprobe values obtained for F and Cl were not used as the concentration of F and Cl in the SIMS standards).

For petrologic classification of the clast in 15404,51, the elements Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, and K were analyzed. Si and K were standardized using orthoclase, Ti and Fe were standardized using ilmenite, Al and Ca were standardized on anorthite, Cr and Mg were standardized on MgCr$_2$O$_4$, and Na was standardized using scapolite.

Hydrogen manometry. H$_2$ manometry was carried out at the Institute for Study of the Earth’s Interior, Okayama University, on three natural terrestrial fluorapatites. The concentrations of OH in the fluorapatites were determined so that the apatites could be used for standardization of the ion microprobe. The three fluorapatites were from different localities, including Durango, Mexico, Eagle, Colorado, and Morocco. The OH concentrations (reported as the H$_2$O equivalent) determined by H$_2$ manometry are presented in Table S1.

H$_2$ manometry was carried out following the following procedure. First, the fluorapatite samples were ground and sieved into a 0.038–0.075 mm size fraction for the analysis. Next, the ground sample powders (ranging in mass from 0.14985 to 0.20751 grams) were placed in an oven overnight at 110 °C and then stored in a Pt crucible (P$_2$O$_5$ was used as the desiccant). Before the analysis, empty Pt crucibles were placed in silica glass vessels and heated to 1,050 °C for 20 min under high vacuum to drive off surface-adsorbed contaminants. The Pt crucibles were then transferred to the dry glove box, and the sample powders were placed in the Pt crucibles and sealed in the silica glass vessels. The silica glass vessels were then connected to a high vacuum line and preheated at 200 °C under continuous evacuation for 2 hours with electrical resistance heaters to drive off any remaining adsorbed water. Subsequent to this step, each vessel was connected to the H-manometry line (one at a time), and the Pt crucible containing the sample was heated (~100°C/min) from room temperature to 1,000°C using an induction furnace. The sample was then held at 1,000°C for 20 min. Degassing was monitored throughout the sample heating process with a Pirani gauge. Degassing typically started at around 300°C and ended by approximately 900°C. The released gas passed through a copper oxide furnace at 400°C to oxidize any possible reduced species, and the gas was condensed using liquid nitrogen. The H$_2$O was then cryogenically purified within a mixture of acetone and solid CO$_2$ (dry ice), and it was converted to H$_2$ in a uranium furnace at 700°C. The H$_2$ gas was then transferred into two separate calibrated volumes by a Toeppler pump, and the pressure of the H$_2$ gas was determined.

The two calibrated volumes resulted in two water concentrations for each analysis, which were averaged in order to determine the bulk water content. The two water concentrations for each measurement were within 54–60 ppm of each other for each analysis. The remaining analytical error of this technique lies within the uncertainty of the pressure measurement, which was typically between 100 and 260 ppm H$_2$O. The uncertainty of each analysis is reported in Table S1. Each of the analyses was corrected against a blank measurement, which typically resulted in corrections of 26–35 ppm H$_2$O.

Secondary processes that can perturb parental magmatic volatile signatures. Before the volatile abundance of the parental liquid (and hence the magmatic source region) can be determined from the analyzed apatite compositions, one must consider the effects of secondary processes that commonly perturb magmatic volatile abundances during crystallization. Secondary processes can include (but are not limited to) degassing, metasomatism, lithologic assimilation, and magma mixing.

Magmatic degassing is a secondary process that is likely experienced by all lunar magmas, as fluid saturation is eventually reached during crystallization of any volatile-bearing magma. Degassing of a magma will generally drive magmatic volatile contents towards fluorine-enriched (relative to water and chlorine) compositions because water and, to a lesser extent, chlorine would partition into the exsolved fluid/vapor phase, while fluorine is more compatible in the silicate liquid (as summarized by refs. 5–7). Consequently, apatites will yield compositions reflecting a drier and more chlorine-deficient parental magma if degassing has taken place. If metasomatism, lithologic assimilation, and/or magma mixing have occurred, magmatic volatile compositions can be driven in any direction depending on what is being mixed. Therefore, information about parental magmatic volatile contents cannot be extracted from apatite if this process has occurred.

Unfortunately, we cannot definitively determine whether any of these secondary processes have occurred for the samples studied here. For simplicity in modeling the parental magmatic water contents for comparison to the previous estimate of the bulk lunar water content (<1 ppb water; i.e., ref. 8), we assume here that secondary processes have not affected the magmas during crystallization of NWA 2977 or the lithic clast in 15404,51. However, because magmatic degassing likely occurred at some stage during the petrogenesis of our samples, the estimates of the parental magmatic water contents will represent lower limits.
Fig. S1. Plot of anorthite content in plagioclase vs. Mg number of coexisting ferromagnesian silicates for ferroan anorthosites (FAN), the magnesian suite, and the alkali suite adapted from ref. 4. The average composition of pyroxene and plagioclase grains from the lithic clast 15404,51 determined by EPMA is plotted as a blue circle with the black letter A. The range in pyroxene and plagioclase values is indicated by the red box. This plot supports assigning the lithic clast in 15404,51 to the alkali suite.

Fig. S2. Computed range of parental magmatic water contents for NWA 2977 and the alkali-suite clast in 15404,51. The water contents were calculated as a function of the percentage of crystallization before apatite entered the phase assemblage. The upper and lower lines for each range represent the calculated range in magmatic water contents at the time of apatite crystallization for each of the samples.
Calibration curve determined for quantifying water contents of apatite by SIMS. The data points used to construct the curve were from our three terrestrial apatite standards (Table S1). The water contents for these apatite grains were determined by H manometry. The regression line is forced to the origin because the detection limit of our analysis routine is approximately 3 ppm H$_2$O. The discrepancy between the data point with the lowest water content (Durango apatite) and our regression line could be explained by the presence of minor fluid inclusions in the apatite that were not driven off during the initial drying steps before analysis by H manometry. The $2\sigma$ error for the slope of the calibration curve is about 17% (i.e., $m = 0.20 \pm 0.03$).

Table S1. Chemical analyses of terrestrial apatite standards

<table>
<thead>
<tr>
<th>Oxide (wt%)</th>
<th>Durango</th>
<th>Colorado</th>
<th>Morocco</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_2$O$_5$</td>
<td>40.1 (4)</td>
<td>40.8 (4)</td>
<td>40.5 (2)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.35 (2)</td>
<td>0.26 (2)</td>
<td>0.44 (2)</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>0.64 (4)</td>
<td>0.58 (6)</td>
<td>0.29 (4)</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>0.08 (3)</td>
<td>0.05 (3)</td>
<td>0.06 (2)</td>
</tr>
<tr>
<td>FeO</td>
<td>0.03 (2)</td>
<td>0.07 (2)</td>
<td>0.03 (2)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01 (1)</td>
<td>0.08 (2)</td>
<td>0.02 (1)</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01 (1)</td>
<td>0.01 (1)</td>
<td>0.00 (0)</td>
</tr>
<tr>
<td>CaO</td>
<td>54.4 (2)</td>
<td>54.6 (2)</td>
<td>55.2 (2)</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.26 (5)</td>
<td>0.09 (1)</td>
<td>0.06 (1)</td>
</tr>
<tr>
<td>H$_2$O*</td>
<td>0.09 (2)</td>
<td>0.36 (2)</td>
<td>0.38 (3)</td>
</tr>
<tr>
<td>F</td>
<td>4.03†</td>
<td>2.6 (1)</td>
<td>2.5 (1)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.45 (6)</td>
<td>0.95 (3)</td>
<td>0.41 (2)</td>
</tr>
<tr>
<td>−O = F + Cl</td>
<td>1.80</td>
<td>1.32</td>
<td>1.15</td>
</tr>
<tr>
<td>Total</td>
<td>98.65</td>
<td>99.13</td>
<td>98.74</td>
</tr>
</tbody>
</table>

Structural formulas based on 13 anions

| P           | 2.94 | 2.96 | 2.93 |
| Si          | 0.03 | 0.02 | 0.04 |
| Ce          | 0.02 | 0.02 | 0.01 |
| Y           | 0.00 | 0.00 | 0.00 |
| Fe          | 0.00 | 0.01 | 0.00 |
| Mn          | 0.00 | 0.01 | 0.00 |
| Mg          | 0.00 | 0.00 | 0.00 |
| Ca          | 5.04 | 5.01 | 5.07 |
| Na          | 0.04 | 0.01 | 0.01 |
| F           | 1.10†| 0.71 | 0.68 |
| Cl          | 0.07 | 0.14 | 0.06 |
| OH          | 0.05 | 0.21 | 0.22 |
| Cation sum  | 8.07 | 8.04 | 8.06 |
| X-site sum  | 1.22 | 1.06 | 0.96 |

Data collected by EPMA unless otherwise noted.
*Reported H$_2$O value determined by H manometry.
†Analysis experienced fluorine count rate increase during the analysis (i.e., refs. 1 and 2); therefore, the reported value is too high. Published Durango apatite has 3.53 wt% fluorine (3). The parenthetical numbers represent the uncertainty in the last digit of each reported value.