Early degassing of lunar urKREEP by crust-breaching impact(s)

Jessica J. Barnes\textsuperscript{a},\textsuperscript{*,a}, Romain Tartèse\textsuperscript{a,b}, Mahesh Anand\textsuperscript{a,c}, Francis M. McCubbin\textsuperscript{d}, Clive R. Neal\textsuperscript{e}, Ian A. Franchia\textsuperscript{a}

\textsuperscript{a} Planetary \& Space Sciences, The Open University, Walton Hall, MK7 6AA, UK
\textsuperscript{b} Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Muséum National d’Histoire Naturelle, Sorbonne Universités, CNRS, UPMC \& IRD, 75005 Paris, France
\textsuperscript{c} Earth Sciences department, Natural History Museum, London, SW7 5BD, UK
\textsuperscript{d} NASA Johnson Space Center, Mailcode X22, 2101 NASA Parkway, Houston, TX 77058, USA
\textsuperscript{e} Department of Civil \& Environmental Engineering \& Earth Science, University of Notre Dame, IN 46556, USA

**Abstract**

Current models for the Moon’s formation have yet to fully account for the thermal evolution of the Moon in the presence of H\textsubscript{2}O and other volatiles. Of particular importance is chlorine, since most lunar samples are characterised by unique heavy $\delta^{37}$Cl values, significantly deviating from those of other planetary materials, including Earth, for which $\delta^{37}$Cl values cluster around $-3\%$. In order to unravel the cause(s) of the Moon’s unique chlorine isotope signature, we performed a comprehensive study of high-precision in situ Cl isotope measurements ofapatite from a suite of Apollo samples with a range of geochemical characteristics and petrologic types. The Cl-isotopic compositions measured in lunar apatite in the studied samples display a wide range of $\delta^{37}$Cl values (reaching a maximum value of $+36\%$), which are positively correlated with the amount of potassium (K), Rare Earth Element (REE) and phosphorous (P) (KREEP) component in each sample. Using these new data, integrated with existing H-isotope data obtained for the same samples, we are able to place these findings in the context of the canonical lunar magma ocean (LMO) model. The results are consistent with the urKREEP reservoir being characterised by a $\delta^{37}$Cl $\sim+30\%$. Such a heavy Cl isotope signature requires metal-chloride degassing from a Cl-enriched urKREEP LMO residue, a process likely to have been triggered by at least one large crust-breaching impact event that facilitated the transport and exposure of urKREEP liquid to the lunar surface.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).  

1. Introduction

Existing models for the formation of the Moon (Čuk and Stewart, 2012; Canup, 2012) predict widespread melting and partial vaporisation of silicate material. Hydrodynamic escape (Pahlevan and Stevenson, 2007) may have facilitated the extensive loss of volatiles to the vacuum of space during the proto-lunar disk phase. Pahlevan and Stevenson (2007) also presented an elegant model to explain the isotopic similarity of oxygen isotopes (e.g., Wiechert et al., 2001) between the Earth and the Moon. In addition, Canup et al. (2015) have recently provided possible mechanisms to explain some isotopic differences between these two bodies (e.g., Zn). However, collectively these models have yet to fully reconcile the thermal evolution of the early Moon with the presence of H\textsubscript{2}O and other associated volatile signatures in the lunar interior, that have been recognised through studies of lunar samples.

In lunar rocks, apatite [Ca$_5$(PO$_4$)$_3$(F,CLOH)] is the most common volatile-bearing mineral (McCubbin et al., 2015a). A multitude of studies have investigated the abundances of volatiles (H\textsubscript{2}O, F, and Cl, e.g., McCubbin et al., 2010a, 2010b, 2011; Boyce et al., 2010) and the hydrogen isotopic compositions of lunar apatite (e.g., Greenwood et al., 2011; Barnes et al., 2013, 2014; Tartèse et al., 2013, 2014a, 2014b; Boyce et al., 2015). These studies have shown that (i) parental melts to the mare basalts contained H\textsubscript{2}O $>$ F $>$ Cl, whilst the parent melts to the lunar highlands rocks were characterised by Cl $>$ H\textsubscript{2}O $\approx$ F (McCubbin et al., 2015a), and (ii) that apatite in mare basalts were generally characterised by elevated H-isotope signatures ($>600\%$, Greenwood et al., 2011; Tartèse et al., 2013). These H-isotope compositions are similar to those measured in the lunar picritic glasses (Saal et al., 2013; Füri et al., 2014), which have been interpreted, at least in part, as resulting from degassing of molecular H\textsubscript{2} during ascent and emplacement of basaltic magmas on the lunar surface under reducing conditions. Currently, it has been argued that only a few samples (olivine-hosted melt inclusions trapped within picritic
glass beads, some KREEP basalts and a few plutonic highlands rocks) may have preserved primitive lunar H-isotopic compositions (Saal et al., 2013; Barnes et al., 2014; Tartèse et al., 2014a). In the context of the lunar magma ocean (LMO) model, late-stage LMO residual melts are thought to have been enriched in incompatible elements such as K, REEs, and P, which are collectively called uKREEP or a KREEP-component, when referred to as a geochemical reservoir or geochemical component, respectively (Warren and Wasson, 1979). It is anticipated that chlorine (and other volatiles) should have been concentrated in the residual LMO melts given its incompatibility in olivine and pyroxene, which were the dominant early phases to crystallise in the cumulate pile of the LMO (e.g., Snyder et al., 1992; Elkins-Tanton et al., 2002, 2011; Elkins-Tanton and Grove, 2011; Elardo et al., 2011). When compared to chondritic meteorites and terrestrial rocks (e.g., Sharp et al., 2013a), most lunar samples have exotic Cl isotopic compositions (Sharp et al., 2010; Treiman et al., 2014; Tartèse et al., 2014b; Boyce et al., 2015), which are difficult to explain in light of the abundance and isotopic composition of other volatile species, especially H, and the current estimates for Cl and H2O in the Bulk Silicate Moon (BSM) (Hauri et al., 2015; McCubbin et al., 2015a).

In order to fully understand the meaning and significance of the unique Cl-isotope compositions displayed by the majority of lunar rocks and to place these in the context of the differentiation of the Moon, we investigated the Cl-isotopic composition of apatite from a diverse set of lunar samples from Apollo missions: 11 (10044 & 10058), 14 (14304), 15 (15386 & 15555), and 17 (70035, 76535, 78235 & 79215). Our sample set covers a range of lunar lithological types, including KREEP and very high potassium (VHK) basalts, and selected plutonic highlands rocks (full details can be found in the Supplementary Information).

2. Analytical protocols

High-precision in situ measurements of Cl-isotopes and volatiles in apatite from the following nine Apollo thin-sections were carried out in this work: 10044,645; 10058,254; 14304,177; 15386,46; 15555,206; 70035,195; 76535,51; 78235,43 and 79215,50. Twenty eight apatite grains were identified as being suitable for analysis by ion probe (see below). During the analytical campaign, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out in order to characterise mineral chemistry in the thin-sections studied, following the methods detailed in Barnes et al. (2014).

The abundance and isotopic composition of Cl in lunar apatite grains were measured using the Cameca NanoSIMS 50L at the Open University and a protocol modified after Tartèse et al. (2014b) over three analytical campaigns from November 2014 to August 2015. Analyses were carried out using a Cs+ primary beam of ~1 μm diameter, with an accelerating voltage of ~16 kV. Before each analysis, the area of interest was pre-sputtered using a ~120 pA probe current for 3 minutes at 8 x 8 μm to ensure the area was thoroughly cleaned of surface contamination. Analyses were performed using a primary probe current of between 40 and 60 pA, for ~5 minutes, over rastered areas of between 3 x 3 μm and 5 x 5 μm. Electronic gating was used to collect secondary ions emitted from only the inner 25% of the rastered areas. Secondary negative ions of 16O1H+, 18O, 35Cl−, 37Cl−, and 40Ca19F− were collected simultaneously on electron multipliers (EMs). 40Ca19F− was used to easily identify apatite on real-time secondary ion images during pre-sputtering and to monitor F contents, but it was not used to precisely quantify apatite F contents due to the poor ionisation efficiency of 40Ca19F−. A mass resolving power of ~8000 ( Cameca definition) was used in order to readily resolve isobaric interferences, particularly between peaks of 17O and 16O1H+. Each 1-inch round thin-section was coated with ~30 nm of gold and an electron flood gun was used for charge compensation. Secondary ion images of 16O1H+ were monitored in real time during pre-sputtering and after analysis to ensure that the analysed areas were free of any surficial contamination, cracks, or hotspots.

Apatite Cl contents were calibrated using the measured 35Cl/18O ratios and the known Cl contents of terrestrial apatite standards (described in McCubbin et al., 2010a, 2012), which were pressed into an indium mount along with a San Carlos olivine crystal that was used to estimate background abundances of H2O (between ~10 and 90 ppim) and Cl (<5 ppm). The slopes of the calibration lines (Fig. 1) defined byapatite standards with varying Cl contents were used to calculate the Cl contents of apatite in the Apollo samples. The uncertainties reported on the Cl contents of the ‘unknown’ apatite combine the 2σ uncertainty associated with the calibrations and the analytical uncertainties associated with each individual measurement.

Finally, two of the reference apatite grains, Ap005 or Ap004 (McCubbin et al., 2012), were used to correct the measured 35Cl/37Cl ratios for instrumental mass fractionation. The isotopic composition of chlorine is reported using the standard delta (δ) notation with respect to the 37Cl/35Cl ratio of the standard mean ocean chloride (SMOC, 37Cl/35Cl ratio = 0.31977), and is reported with the associated 2σ uncertainties, which combine the reproducibility of 37Cl/35Cl measurements on the reference apatite (either Ap005 or Ap004) and the internal uncertainty of each analysis. Fig. 2 shows an example of the reproducibility of δ37Cl values measured on a secondary apatite standard (Ap003) run during the February session and referenced to Ap004 (Ap004 has a δ37Cl value of ~+0.11‰, Zach Sharp, University of New Mexico, pers. comm.). All Ap003 analyses are within error of the terrestrial value of ~0 ± 1‰ (Sharp et al., 2013a), with an average δ37Cl value for the analytical week of +0.17 ± 1.26‰.

3. Results

3.1. Petrographic context of lunar apatite

In thin-section 10044,645, apatite occurs in contact with nonmesostasis pyroxene, plagioclase and sometimes with troilite (apatite 5, for example, which is one of the largest apatite grains in this sample at ~200 μm in the longest dimension; Fig. 3A). Apatite also occurs enclosed, almost exclusively, within clinopyroxene crystals. For example apatite 6C, which is <50 μm in the longest dimension and is euhedral (showing basal section habit) on one side but displays a partially resorbed texture on the other side of
Fig. 2. Plot of δ³⁷Cl values for secondary apatite standard (Ap003) for analyses from 13th February to 18th February 2015. The error bars represent the 2σ uncertainties and are a combination of the reproducibility on the primary reference apatite and analytical error associated with individual measurements. The red diamond at the extreme right hand side of the plot, is the average δ³⁷Cl value for that session and the error bars represent the standard deviation of the measured values (n = 32). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Back-scattered electron (BSE) images of selected apatite crystals in the mare basalts studied: 10044,645; 10058,254; 15555,206 and 70035,195. A = 10044 apatite 5, B = 10044 apatite 6C, C = 10044 apatite 6D, D = 10058 apatite 5, E = 10058 apatite 6, F = 15555 apatite 1, G = 15555 apatite 5, H = 70035 apatite 15, and I = 70035 apatite 17. Where: Ap = apatite, Bdy = baddeleyite, Cpx = clinopyroxene, Kfs = potassium-rich (often Ba-rich) alkali feldspar, Fa = fayalite, Ilm = ilmenite, Pl = plagioclase, Sym = symplectite assemblage (Ca-rich pyroxene, fayalite, silica), Tro = troilite, and Trq = tranquillityite.

The crystal (Fig. 3B). Apatite analysed in this study is also present in direct contact with mesostasis minerals, mostly K-feldspar, silica, fayalite, and a symplectite assemblage consisting of fayalite, silica, and Ca-rich pyroxene that is enclosed by plagioclase laths (e.g., the ∼60 μm acicular apatite 6D in Fig. 3C). The majority of apatite in sample 10044 contain small <5 μm-sized inclusions of plagioclase, K-feldspar and occasionally, iron sulphide (troilite).

In thin-section 10058,254, apatite is commonly found in late-stage mesostasis areas comprised of K-rich phases (K-feldspar and occasionally K-rich glass), troilite, baddeleyite, pyroxene, silica, Fe-pyroxene, tranquillityite, ilmenite, fayalite, and a symplectite assemblage. We observed apatite in contact with either late-stage K-feldspar, silica and other phases (e.g., Fig. 3D) or in contact with plagioclase, pyroxene, and a symplectite assemblage (e.g., Fig. 3E). We did not observe a relationship between apatite crystal size and petrographic setting, and apatite occurs as subhedral hexagonal to tabular crystals of up to ∼90 μm in length.

In thin-section 15555,206, apatite occurs enclosed in pyroxene (type 1) or, more commonly, in contact with plagioclase, pyroxene, silica, and K-feldspar (type 2). Apatite 1 analysed in this work is in the type 2 setting (Fig. 3F) where it forms acicular rods of up to 100 μm in length. Apatite 5 also analysed here is found between type 1 and type 2 settings (Fig. 3G) where it
is most commonly enclosed in clinopyroxene as euhedral to subhedral crystals of up to ~30 μm in the longest dimension and typically containing plagioclase inclusions.

In thin-section 70035,195, apatite crystals 15 and 17 both occur as basal sections (hexagonal) of ~20 μm in diameter (Fig. 3H and 3I). Apatite in this section is very rare and occurs mostly in mesostasis areas in contact with K-feldspar and silica. Apatite 17 is enclosed within a troilite grain (Fig. 3I).

VHK basalt 14304,177 contains interstitial K-rich areas and vein-like structures that are situated between pyroxene and plagioclase crystals. In places the K-rich veins contain K-feldspar, K-rich glass (appearing brown in plane polarised light), merrillite, baddeleyite, and apatite (an example is shown in Fig. 4A). In this sample, the apatite crystals are restricted to the K-rich regions and typically range from ~50 to >300 μm in the longest dimension. Most of the apatite observed are subhedral and are usually heavily fractured (Fig. 4B).

Apatite in sample 15386 is almost exclusively found within mesostasis pockets surrounded by plagioclase and/or pyroxene crystals. Apatite 2 is found in contact with K-feldspar, ilmenite, and pyroxene, and it surrounds a pocket of K-feldspar. Apatite 2 is subhedral and occurs as blades up to ~100 μm in length (Fig. 4C). Apatite 5 is an anhedral grain ~250 μm in length that is in direct contact with merrillite, plagioclase and K-feldspar (Fig. 4D). Apatite 10 is a subhedral crystal that is ~25 μm in the longest dimension occurring inter-grown with merrillite. The crystal is enclosed in mesostasis glass and troilite.

Sample 76535,51 contains three crystals of apatite as reported in Barnes et al. (2014). Each crystal co-exists with merrillite and is located between plagioclase crystals. The largest apatite crystal is also found in contact with a symplectite assemblage (consisting of Mg-Al chromite and two pyroxenes, Elardo et al., 2012) and clinopyroxene (Fig. 5A, Barnes et al., 2014). Apatite crystals range from anhedral to subhedral and range in size from ~50 μm to ~250 μm. Apatite in thin-section 78235,43 are either found in small pockets of mesostasis containing Fe-metal, silica, merrillite, and clinopyroxene or associated with the main rock-forming orthopyroxene and plagioclase grains. Apatite occurs as subhedral grains up to ~95 μm in length and are generally heavily cracked (Fig. 5B).

Granulitic breccia 79215 is composed of both a matrix portion dominated by an anorthositic troctolite composition and a troc-
tolicitic portion. Apatite is abundant in this thin-section of sample 79215, occurring exclusively in the troctolite portion and in direct contact with olivine, plagioclase, and troilite. Texturally, the apatite contains rounded blebs of pre-existing plagioclase and olivine, with lobate crystal edges. All of the apatite crystals are anhedral to subhedral and range from ~30 to >300 µm in the longest dimension (Fig. 5C).

3.2. Intra-sample variations of the isotopic and chemical composition of apatite

A total of twenty nine apatite grains from the eight samples were analysed for their Cl abundances and Cl-isotopic signatures and the results are provided in Table 1 and shown in Fig. 6. The Cl-isotopic composition of apatite in 10044 is variable and seems to be related to the textural context of the grains. Apatite crystal Ap5, which is characterised by $\delta^{37}$Cl value of +16.1 ± 4.0‰, can be assumed to have formed early because it is in contact with plagioclase and pyroxene but not with the late-stage mesostasis assemblage. In contrast, apatite grains 6C and 6D are located in separate mesostasis areas (Fig. 3) and yet record similar Cl-isotopic compositions of +0.5 to +2.0‰. Cl content is variable between, and within, the grains ranging from 0.02 to 111 wt% Cl. Among the troctolite basalt, sample 10058 yielded apatite Cl contents from 0.04 to 0.25 wt% and $\delta^{37}$Cl values from +2.2 ± 2.6 to +9.9 ± 3.0‰. Given the analytical uncertainties, it is not possible to distinguish between the average $\delta^{37}$Cl values (+3.8 ± 4.5‰) for apatite crystals 4 and 5, both located in contact with K-feldspar, and apatite 3 and 6, which are in contact with other late-crystallised minerals (average $\delta^{37}$Cl values,
+7.7 ± 4.2‰). Apatite crystals in mare basalt 70035 have comparatively restricted CI-isotopic compositions with $\delta^{37}$Cl values ranging from +10.8 ± 2.5‰ to +14.4 ± 2.1‰. There is inter- and intra-grain variability in CI content, with apatite 15 containing ~0.07 wt% CI whereas CI content varies between ~0.10 and 0.14 wt% CI for apatite 17. Low-Ti basalt 15555 contains apatite characterised by CI abundances between 0.08 and 0.33 wt% CI and almost invariant $\delta^{37}$Cl values of approximately +13 ± 2‰ in all of the exhibited petrographic contexts.

In contrast, VHK basalt 14304.177 contains more CI-rich apatite, with CI contents between 0.29 and 0.59 wt% associated with heavy $\delta^{37}$Cl compositions falling in the range between +24.5 ± 2.8 and +31.7 ± 2.5‰. In the case of KREEP basalt 15386, all three apatite crystals analysed are located in mesostasis, so it is challenging to determine the relative timing of crystallisation, which was previously done for D/H ratios and H2O content in another thin-section of 15386 (Tartèse et al., 2014a). Apatite in the thin section of 15386 studied here are characterised by a large range of $\delta^{37}$Cl values from +14.1 ± 2.2‰ to +30.8 ± 1.3‰ and display a similarly large spread in CI contents from ~0.1 to 0.4 wt%. There is a positive correlation between apatite CI contents and associated isotopic composition in KREEP basalt 15386.

With regards to the apatite crystals in lunar highlands samples, lunar troctolite 76535 contains CI-rich apatite containing ~1.32 ± 0.02 wt% CI and uniform $\delta^{37}$Cl values of between +31.1 ± 1.2 and +32.1 ± 1.2‰ (Table 1). Similarly, apatite grains in cumulate norite 78235 contain between 1.01 and 1.37 wt% CI associated with $\delta^{37}$Cl values ranging between +28.9 ± 1.7 and +33.8 ± 1.2‰. Finally, apatite in the impact-related granulite 79215 are characterised by homogeneous CI contents (weighted average 0.74 ± 0.02 wt% CI, n = 11) but display a large range of CI isotopic compositions, with $\delta^{37}$Cl values ranging from +25.1 ± 1.8 up to +36.3 ± 2.0‰.

4. Discussion

4.1. Comparing the CI-isotopic compositions of lunar apatite

Generally, apatite in the mare basalts studied here and previously (Sharp et al., 2010; Tartèse et al., 2014b; Boyce et al., 2015) shows a broad range of $\delta^{37}$Cl values that extend from ~4 to +18‰, lower than those measured in apatite in lunar highlands samples and the VHK basalt (~+25 to +36‰, Fig. 6). To date, the only lunar basalts to exhibit very heavy apatite chlorine isotopic compositions (> +18‰) are KREEP-related basalts (Sharp et al., 2010; Tartèse et al., 2014b; McCubbin et al., 2015). The KREEP basalts are those whose parental melts assimilated a significant KREEP component, hence they have geochemical characteristics of both their mantle source and urKREEP. Collectively, apatite in the KREEP (15386 (this study) and 72275 (Sharp et al., 2010)) and VHK (14304) basalts are characterised by $\delta^{37}$Cl values between +14.1 ± 2.2 and +31.7 ± 2.5‰ and display a large spread of chlorine contents from approximately 0.1 to 1.2 wt% (Fig. 6). Apatite from lunar highlands samples (76535 and 78235) are characterised by more homogeneous CI-isotopic compositions ($\delta^{37}$Cl in the range of ~+29 to +34‰) and have the highest CI abundances when compared to apatite from mare basalts. Apatite in lunar granulite 79215 display some of the highest chlorine isotopic compositions recorded for Solar System materials (Fig. 7), up to +36.3 ± 2.0‰ (Table 1).

4.2. Reconciling H- and CI-isotope measurements of lunar apatite

The hydrogen isotopic compositions of OH in apatite from the high-Ti and low-Ti mare basalts are highly variable, but some of the observed values can be reconciled if the parent magmas had undergone H2-degassing upon ascent and eruption. This process would have caused non-degassed H2O left behind in the magmas to have elevated $\delta^{18}$O values, which is recorded by apatite that crystallised during or after degassing (Tartèse et al., 2013). The modelled un-degassed (or pre-degassing) $\delta^{18}$O value for the parental magmas of the mare basalts is approximately ~0 ± 200‰ (e.g., Tartèse et al., 2014a), which is consistent with that modelled for the un-degassed parent magmas of lunar ultramafic glass beads (Saal et al., 2013; Füri et al., 2014). However, a direct link between degassing of H2 and elevated H-isotopic composition remains elusive because of the paucity of spatially resolved H-isotopic analyses in support of the degassing model. A study of lunar KREEP basalts by Tartèse et al. (2014a) was able to bridge the gap between measured data and modelling of H2-degassing based on spatially correlated H-isotopic analyses of apatite in KREEP basalt 15386. Specifically, they observed that earlier-formed apatite included within pyroxene exhibited lower $\delta^{18}$O values (+98 ± 99‰)
and elevated H$_2$O abundances in comparison to later-formed apatite within late-stage mesostasis areas (highest $\delta D$ values of $\sim$+615 to $\sim$+778$\%_o$). This observation marked the first direct link between degassing of H$_2$ and elevated $\delta D$ values in lunar basalts. Furi et al. (2014) also observed an inverse correlation between $\delta D$ values and H$_2$O abundances in high-Ti picritic glass beads, which they interpreted as the consequence of extensive Rayleigh-type degassing of H$_2$ from melts initially containing H$_2$O characterised by a $\delta D$ value $\sim$+100$\%_o$. Interestingly, the lowest $\delta D$ value recorded in apatite from 15386 is $+98 \pm 99\%_o$, which is consistent with the estimates of the parental melt $\delta D$ values modelled previously from apatite in low- and high-Ti mare basalts (Tartèse et al., 2013), as well as the pyroclastic glass beads (e.g., Saal et al., 2013; Furi et al., 2014).

Magmatic degassing has also been invoked to explain the departure of lunar Cl-isotopic compositions from the terrestrial mantle value ($\sim$−0.2±1.0$\%_o$, Fig. 7; Sharp et al., 2013a). Sharp et al. (2010) suggested that the volatilisation of metal chlorides during magma ascent and eruption could fractionate the lighter $^{35}$Cl isotope from heavier $^{37}$Cl, a process requiring very low H/Cl ratios at the time of chloride degassing in order to promote the loss of metal chlorides relative to HCl, because degassing of HCl from a magma would not fractionate Cl isotopes. In such a model, degassing would favour the loss of light metal chloride isotopologues (i.e., those containing $^{35}$Cl instead of $^{37}$Cl), for example FeCl$_2$ or ZnCl$_2$, leaving residual chlorine dissolved in the magma enriched in $^{37}$Cl (Sharp et al., 2010; Ustunisik et al., 2011, 2015). This $^{37}$Cl-enriched signature would then be recorded in the rocks through the incorporation of Cl into Cl-bearing mineral phases like apatite that crystallise from the residual melt.

In fact, it has recently been demonstrated experimentally that during ascent of volatile-rich magmas, hydrogen is likely to be the earliest volatile to degas, and after H is depleted in the melt, Cl becomes the preferred volatile that is lost (Sharp et al., 2013b; Ustunisik et al., 2015), supporting the requirement for very low H/Cl ratios in magmas at the time of Cl degassing. However, it remains unclear whether successive episodes of volatile-degassing from a single magma could explain both elevated $\delta D$ and elevated $\delta^{37}$Cl values measured in apatite in mare basalts. Indeed, the requirements of very low H/Cl ratios in the melt to account for the elevated $\delta^{37}$Cl values measured, which was proposed by Sharp et al. (2010), seems incompatible with the occurrence of OH-rich apatite relative to Cl in the mare basalts (Tartèse et al., 2013; McCubbin et al., 2015a) given the relative preference of Cl over H into crystallising apatite (Boyce et al., 2014; McCubbin et al., 2015b), which should result in very OH-poor apatite (Ustunisik et al., 2015). In addition, the effects of HCl degassing from basaltic melts on the fractionation of Cl isotopes has never been investigated under conditions relevant to mare basalt petrogenesis (e.g., low oxygen fugacity under vacuum), adding to the complexity of interpreting combined apatite $\delta D$ and $\delta^{37}$Cl values. In any case, it is likely that variations of apatite $\delta D$ and $\delta^{37}$Cl values have resulted from the interplay between different magmatic processes such as degassing or mixing, potentially overprinting of any geochemical signatures inherited from previously-formed isotopic reservoirs. As stated above, there is a positive correlation between apatite Cl contents and associated isotopic composition in KREEP basalt 15386. If degassing of a Cl-bearing vapour was influencing the Cl-isotopic composition, then the opposite correlation would be expected (Ustunisik et al., 2011, 2015). However, a positive correlation between Cl abundance and $\delta^{37}$Cl values of apatite is consistent with the assimilation of a $^{37}$Cl-enriched component, which has also been reported recently in martian rocks (Williams et al., in press).

To identify the primordial chlorine and hydrogen isotopic compositions of the lunar interior and identify any specific isotopic reservoirs, pristine samples that are unlikely to have undergone magmatic degassing of volatiles during ascent and crystallisation should be targeted. From the literature, there are at least two KREEP-rich samples, KREEP basalt 72275 (Tartèse et al., 2014a) and Mg-suite norite 78235 (Barnes et al., 2014), which are considered to directly record the H-isotopic composition of their un-degassed parent melts, so we will first address the isotopic composition of H in the Moon. Apatite in 72275 contain appreciable amounts of OH that appears not to have undergone magmatic degassing, since apatite in this sample seems to have retained the original undegassed $\delta D$ value of the parent melt (i.e., average $−113\%_o \pm 62\%_o$; Tartèse et al., 2014a). Sample 78235 is a plutonic norite sample containing apatite that exhibits relatively homogeneous H-isotopic compositions (i.e., average $−27\%_o \pm 98\%_o$; Barnes et al., 2014). These samples have had different petrological histories (see Supplementary Information), but the parental magmas of both samples are considered to have assimilated urKREEP, or interacted with a derivative of urKREEP (Barnes et al., 2014; Tartèse et al., 2014a; Shearer et al., 2015). Therefore, the H-isotopic signatures of OH in apatite from these samples, $−27\%_o \pm 98\%_o$ for 78235 (Barnes et al. 2014) and $−113\%_o \pm 62\%_o$ for 72275 (Tartèse et al., 2014a), identical within error, can be interpreted as reflecting the H-isotopic composition of H$_2$O in urKREEP. Notably, the H-isotopic composition of urKREEP determined from these un-degassed samples matches the measured and modelled values for the mare source in the lunar mantle (Saal et al., 2013; Furi et al., 2014; Tartèse et al., 2014a). Consequently, it appears that the H-isotopic composition of the bulk Moon could be relatively homogeneous (within a few hundred $\%_o$) and similar to the terrestrial mantle (e.g., Lécuyer et al., 1998; Hallis et al., 2015), consistent with assertions that the Earth–Moon system acquired water from a similar source (Alexander et al., 2012; Saal et al., 2013; Barnes et al., 2014; Sarafian et al., 2014).

We now consider the Cl-isotopic compositions of apatite from these same un-degassed samples, 72275 and 78235. Apatite in both samples are characterised by heavy chlorine isotopic compositions (this study and Sharp et al., 2010), which is perplexing, given the existing evidence that these samples did not undergo substantial magmatic degassing (i.e., measurable OH abundances inconsistent with very high melt Cl/H ratios and homogeneous intra-sample $\delta D$ values). Alternatively, the parental melts of these samples were derived from, or mixed with, a heavy Cl component, and the elevated $\delta^{37}$Cl values are unrelated to degassing at or before the time of apatite crystallisation. As noted previously, both samples have a substantial KREEP-component, which has been identified previously as a potential reservoir characterised by elevated $\delta^{37}$Cl (McCubbin et al., 2015a; Boyce et al., 2015). Additionally, Mg-suite troctolite 76535, another KREEP-rich sample, and one of the few un-shocked pristine lunar cumulate samples available for study, is also characterised by elevated $\delta^{37}$Cl values of $\sim+30\%_o$ (Table 1). Based on existing petrogenetic models for the highlands samples, their inventory of volatiles, including Cl, comes predominantly from urKREEP (Barnes et al., 2014; McCubbin et al., 2015a; Shearer et al., 2015), and so these samples are likely representative of the Cl-isotopic composition of urKREEP (McCubbin et al., 2015a). Together these observations provide strong evidence that the Cl-isotopic composition of urKREEP is elevated and is likely to be $\sim+30\%_o$. In contrast, samples from the mare basalt source region(s) within the lunar mantle exhibit a wide range of Cl isotopic compositions that extend down to $−4\%_o$ (Sharp et al., 2010; Boyce et al., 2015), indicating that different reservoirs in the Moon’s interior may have different Cl-isotopic composition.

### 4.3. Relating heavy Cl-isotopic compositions to a KREEP component

We further investigated whether the heavy Cl-isotope signature could be related to the proportion of KREEP component
lunar samples by correlating Cl isotope compositions with bulk-rock incompatible trace element (La, Sm and \(8^{143}\)Nd initial) data (Supplementary Table 2). Fig. 8A shows a strong positive correlation between apatite \(8^{37}\)Cl values and La/Sm ratios (La/Sm\(_a\)), which strongly indicates mixing between a mantle source with low \(8^{37}\)Cl isotopic composition (~0‰, Y-intercept in Fig. 8A) and a KREEP-rich component characterised by a \(8^{37}\)Cl value ~+30‰. Similarly, basaltic rocks originating from KREEP-poor LMO source regions characterised by lighter \(8^{37}\)Cl values are associated with positive bulk-rock \(8^{143}\)Nd initial values >2–3 (Fig. 8B and Supplementary Table 2).

In summary, there is a clear grouping between KREEP-rich rocks, such as those from the Mg-suite, KREEP basalts, and VH KREEP basalts, characterised by elevated \(8^{37}\)Cl values, and less KREEP-rich rocks, such as the high- and low-Ti mare basalts, characterised by lower \(8^{37}\)Cl values. These observations confirm that the KREEP component, and by extension urKREEP, was characterised by extremely heavy \(8^{37}\)Cl values while the mantle source regions of mare basalts had a terrestrial-like Cl-isotopic composition.

4.4. LMO degassing and vapour speciation: Implications for H-isotopes

Hydrogen and chlorine are both incompatible elements that are soluble in silicate melts (Cl more so than H), so it is reasonable to assume that both would be concentrated in urKREEP (e.g., review by McCubbin et al., 2015a). Furthermore, the H/Cl ratio of urKREEP is reported to be <1 (McCubbin et al., 2015a). Based on the work of Fegley (1991), in which thermodynamic activities of volatiles under lunar conditions were considered, he concluded that the dominant species likely to be degassed when H/Cl <1 were HCl and HF in the case of H species and metal chlorides (and fluoride species) as the dominant species carrying the halogens. For lunar magmas, H\(_2\) is also likely to be an important degassing species (Richet et al., 1977; Ustunisik et al., 2015). Any degassing of H in the form of HCl or H\(_2\) would result in similar H and D fractionations (Richet et al., 1977), as calculated by Tartèse et al. (2013) (Supplementary Fig. 2).

It is important to consider the possibility that H degassing could have occurred simultaneously with Cl loss. The current estimates for the H-isotopic composition of H\(_2\)O in urKREEP range from as low as −400 to +200‰ (Barnes et al., 2014; Tartèse et al., 2014a). In the framework of Cl degassing (metal chlorides as the major Cl carrier) from urKREEP, it is likely that H was also degassed in the form of HCl and/or H\(_2\). If the lowest measured \(\delta\)D value of highlands apatite is considered as the pre-degassing urKREEP signature (77215, ~−400‰, Barnes et al., 2014), then the observations from KREEPy lithologies can be reconciled with differential (0 to 99‰) degassing of H\(_2\) and/or HCl (Supplementary Fig. 2). Such low initial \(\delta\)D values are consistent with recently proposed values for the Earth’s upper mantle (Sharp et al., 2013b; Hallis et al., 2015) or for some evolved lithologies from the Moon (Robinson et al., 2014). If the pre-degassing H-isotopic composition of H in urKREEP was heavier than ~−400‰, for example −200 or 0‰, then 99‰ degassing of H\(_2\) would increase the \(\delta\)D value to >+400–500‰. However, such signatures have yet to be observed in apatite from KREEP-rich lithologies considered to be unaffected by degassing (e.g., KREEP basalt 72275 and Mg-suite nortite 78235), which implies that either in this scenario only partial (~95‰) degassing of H occurred, or that the heavy degassed signature was overprinted by volatiles added by carbonaceous chondrites during late accretion (e.g., Alexander et al., 2012; Bottke et al., 2010). The LMO period in the Moon’s evolution is highly unlikely to have been quiescent and it has been proposed by many (e.g., Day et al., 2007; Bottke et al., 2010; Kamata et al., 2015) that impactors were accreting to the Moon during the LMO phase (Fig. 9). Therefore, it is not unreasonable to assume that some of these impactors contributed H\(_2\)O to the lunar interior during differentiation or after urKREEP degassing (e.g., Bottke et al., 2010) (Fig. 9 and calculations in the Supplementary Material). Importantly, if exogenous addition of volatiles to the Moon from objects with H/Cl ratios >1 (i.e., comets and carbonaceous asteroids) occurred, then it did not cause the resultant H/Cl ratio of the LMO residual liquid to exceed 1. If it had then this would have inhibited the fractionation of Cl in the LMO (discussed further in the next section).

In summary, our model does not preclude (a) the presence of H prior to metal chloride degassing from urKREEP nor (b) the possibility of at least some degassing of H in the form of HCl and/or H\(_2\) during metal chloride loss from urKREEP.

4.5. LMO degassing and timing of \(37^{Cl}\) enrichment of urKREEP

The internal differentiation of the Moon via a LMO predicts a volatile-rich urKREEP layer dominated by Cl, containing at least 1350 ppm Cl (McCubbin et al., 2015a). Boyce et al. (2015) have proposed that degassing of Cl from the LMO would account for fractionation of Cl isotopes and \(8^{37}\)Cl values ~+30‰ in the residual urKREEP layer. In this model, the residual LMO becomes progressively enriched in \(37^{Cl}\) relative to \(35^{Cl}\) as metal chlorides are degassed (Boyce et al., 2015). Although this model fits the geochemical trends observed by Boyce et al. (2015) and in the present
study (Fig. 8), there are a number of shortcomings to this early LMO degassing model. (1) The solubility of chloride in silicate melts is relatively high, even at low pressure (Webster and De Vivo, 2002). In fact, chloride solubility in basaltic liquids could have been on the order of >2.9 wt% (Cl\textsuperscript{−} solubility from Webster et al., 1999; Webster and De Vivo, 2002) at depths just below the lunar surface; consequently, Cl\textsuperscript{−} solubility was not likely to have been a driving factor for Cl loss. (2) Chloride is degassed from magmas even at low concentrations in an open system where the equilibrium partial pressure of chloride vapour cannot be attained (i.e., Ustunisik et al., 2011, 2015). This scenario is consistent with the one envisioned by Boyce et al. (2015); however, prior to the formation of a conductive lid in the LMO, there would have been an atmosphere in contact with the LMO surface (e.g., Saxena et al., 2016). It is difficult to determine the precise composition or pressure of that atmosphere, but it would have certainly hindered the early loss of metal chlorides, which is maximised when the magma is in contact with a vacuum. (3) Before the formation of a conductive lid (i.e., early LMO degassing), metal chloride vapours that degassed would condense into chloride salts upon cooling and rain back into the atmosphere or the LMO (i.e., they would be unlikely to escape lunar gravity), and it is not clear that a heavy Cl isotopic reservoir would result from this process. Consequently, we agree with Boyce et al. (2015) that loss of Cl from the LMO could have occurred throughout the lifetime of the LMO, but we are not convinced that it would have necessarily resulted in a δ\textsuperscript{37}Cl-enriched urKREEP layer at the base of the anorthosite crust.

A model in which urKREEP was exposed to high vacuum subsequent to the formation of the anorthosite crust, after the dissipation of the LMO atmosphere, circumvents all three of the potential issues raised above with the Boyce et al. (2015) model of early LMO degassing of metal chlorides. Consequently, we envisage a scenario in which during the latter stages of LMO crystallisation (>95%), a large bolide, or series of bolides, punctured the lunar crust (Kamata et al., 2015) to a depth sufficient to expose the CI-rich urKREEP layer, or bring KREEP-rich melts up to the strong vacuum at the lunar surface, which initiated degassing of metal chlorides (Sharp et al., 2010). The degassed metal chlorides would be drawn into cold traps (i.e., regions of the surface surrounding the melt pool that would be substantially cooler than the melt) in the surrounding crust and regolith where the metal chloride vapour would condense back into chloride salts, leading to the formation of 37Cl-rich urKREEP residual melts (Fig. 9).

Degassing of >80% of the initial Cl content by such a process would have resulted in an urKREEP layer with a heavy δ37Cl value of around +30‰ (Supplementary Fig. 1). Interestingly, the Bulk Silicate Moon (BSM) estimate of ∼10 ppm Cl (McCubbin et al., 2015a) corresponds to a pre-degassing BSM Cl content of ∼100–500 ppm (for 90 to 98% Cl degassed), which is well within the range of Cl abundances in carbonaceous chondrites (e.g., Sharp et al., 2013a). It is possible that the isotopic composition of other moderately volatile elements, such as Zn (e.g., Kato et al., 2015), S (Wing and Farquhar, in press) and even refractory elements such as Fe (Wang et al., 2015), in the urKREEP liquid could have been fractionated by the same event(s) that degassed CI (Fig. 9).

The scenario we propose to account for the elevated Cl isotope composition of urKREEP involves a large (or multiple) impact event(s) during the first 150 to 200 million years (Kamata et al., 2015) of the Moon’s history, which is consistent with the requirement for post-core formation addition of highly siderophile elements (HSEs) (Day et al., 2007) and other volatiles such as H (Albarède et al., 2013; Tartèse et al., 2013; Füri et al., 2014; Hauri et al., 2015) and N (Füri et al., 2015) to the lunar mantle. Given the spatial association of the Apollo sampling sites and the Procellarum KREEP Terrane (PKT), the surface expression of KREEP is presumably represented by the PKT region (Jolliff et al., 2000). Although the PKT does not show evidence from gravity data as being an impact basin (Andrews-Hanna et al., 2014), impacts as early as those required to expose the residual LMO liquid may not be preserved due to viscous effects of the early hot lunar crust (e.g., Kamata et al., 2015). Consequently, one would expect that samples from outside of the PKT and nearside Apollo-sampled region of the Moon to have chondritic and terrestrial-like Cl-isotopic compositions. This hypothesis could be tested through future sample return missions that target regions on the lunar surface far outside the PKT region.

5. Summary

The aims of this study were to (i) thoroughly investigate the apparently unique Cl isotope compositions of lunar samples, (ii) to reconcile new and existing H and Cl data for lunar samples in order to identify potential volatile reservoirs within the Moon, and (iii) to assess the requirement for early CI degassing from the lunar magma ocean as predicted by previous work. To achieve this, we have measured the Cl-isotopic compositions of apatite in a diverse range of lunar samples, ranging in lithologies from mare basalts, to KREEP and VHK basalts and pristine highlands samples. The samples studied show Cl-isotopic compositions ranging from ~+2 to ~+36‰, and reveal a stark difference between KREEP-poor and KREEP-rich samples. We have provided strong evidence...
that lunar samples obtained their exotic heavy Cl-isotopic compositions by variable incorporation of urKREEP ($^{43}$Cl of ~30%). We hypothesise that the differentiation of the Moon via a LMO provides the most elegant mechanism for concentrating volatiles, especially Cl, into a residual melt (urKREEP). In order to account for the Cl-isotopic composition of urKREEP, this residual melt had to degas following enrichment at relatively low pressures, and for this we invoke puncturing of the lunar crust by one or several large impact events, prior to the solidification of the urKREEP liquid in the LMO.

Acknowledgements

We thank NASA CAPTEM for allocation of lunar samples (to MA and CRN). This research was supported by a grant from the UK Science and Technology Facilities Council (grant # ST/L000776/1 to M.A. and I.A.F.), FMM acknowledges support from NASA’s LASER program during this study through grant NNX13AK2G. We thank Erik Hauri and Evelyn Füri for their insightful reviews which helped to improve this manuscript, and we thank the editor Bernard Marty for his handling of this manuscript.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.04.036.

References


Supplementary Material accompanying

Early degassing of lunar urKREEP by crust-breaching impact(s)

by

Jessica J. Barnes, Romain Tartèse, Mahesh Anand, Francis, M. McCubbin, Clive R. Neal, and Ian A. Franchi

1. Extended Methods

During the first two analytical sessions, secondary ions of $^{19}$F$^-$ were not collected due to the very high count rates (being $>$1 million counts per second), which would have caused significant aging of the EM detector over the duration of a single analysis. During the final analytical session (August 2015), measurement of $^{19}$F on EM#4 was achieved by counting for $\sim$30 s during each analysis using the baseline function of the NanoSIMS, which was enough to obtain a precision comparable to that obtained using electron probe microanalysis (EPMA) (Tartèse et al., 2013; Barnes et al., 2014; Tartèse et al., 2014a).

2. Sample Descriptions

10044, 645

Sample 10044 was collected in the area between the Apollo 11 Lunar Module (LM) and a double elongated crater to the southwest of the LM. Thin-section 10044,645 represents a medium to coarse-grained (grain size up to 2 mm) ophitic ilmenite mare basalt, with high-Ti and low-K contents (Beaty and Albee, 1978). This sample is relatively fresh and is not significantly affected by shock. 10044 is composed of pyroxene, plagioclase, ilmenite, silica, and interstitial areas filled with mesostasis (Beaty and Albee, 1978). This rock has a
crystallisation age of ca. 3.72 Ga based on Rb-Sr and Ar-Ar systematics (Albee et al., 1970; Papanastassiou et al., 1970; Guggisberg et al., 1979).

**10058, 254**

Sample 10058 is a high-Ti, low-K type basalt, and belongs to the B1 group of Apollo 11 basalts (Beaty and Albee, 1970). It is a coarse-grained sub-ophitic ilmenite basalt mainly composed of pyroxene, plagioclase, ilmenite and interstitial silica. This rock has an Rb-Sr age of ca. 3.63 ± 0.20 Ga (Albee et al., 1970) and an Ar-Ar age of 3.71 ± 0.04 (Guggisberg et al., 1979).

**70035, 195**

Apollo 17 sample 70035 is a medium-grained, vesicular, high-Ti basalt. It is a large, partially crystalline basalt with large (>1 mm) clinopyroxene crystals, plagioclase, ilmenite, spinel, armalcolite, olivine and mesostasis areas (Weigand, 1973). The Rb-Sr dates of 3.82 ± 0.06 Ga and 3.73 ± 0.11 Ga determined for 70035 are consistent with each other (Nyquist et al., 1977; Evensen et al., 1973) and with an Ar-Ar date of 3.75 ± 0.07 Ga (Stettler et al., 1973).

**15555, 206**

15555 is a coarse-grained low-Ti olivine-normative basalt composed of olivine, pyroxene (clinopyroxene with pigeonite zonations and Fe-rich rims) and plagioclase with trace amounts of ilmenite and silica (Rhodes et al., 1973). Crystallisation of this rock has been dated by Rb-Sr to be between 3.3-3.54 Ga (Chappell et al., 1972; Murthy et al., 1972; Birck et al., 1975) and 3.32 Ga by Ar-Ar (Podeosek et al., 1972).
14304, 177

14304, 177 is a thin-section of a very high-potassium (VHK) basalt. It is a coarse-grained sample with areas that have been granulated. Mineralogically it is composed of plagioclase, pyroxene (mostly clinopyroxene), olivine, K-feldspar, and K-rich glass (Neal et al., 1989a,b). This sample contains interstitial K-rich areas and vein like structures running through pyroxene, plagioclase, and apatite grains (e.g., Figure 4A). This VHK basalt yielded a Rb-Sr age of 3.95 ± 0.04 Ga and a Sm-Nd age of 4.04 ± 0.11 Ga (Shih et al., 1987). Both ages are within error and the crystallisation age is taken as ~4 Ga.

15386, 46

15386 is the largest sample of pristine KREEP basalt in the Apollo sample collection with a total mass of 7.5 grams. Mineralogically, sample 15386 is composed of plagioclase laths surrounded by interstitial pyroxene. The mesostasis has significant cristobalite (10%), ilmenite, and minor phosphate, iron and sulphide (Meyer et al., 2010). This sample has a crystallisation age of 3912 ± 25 Ma ago (weighted average age calculated by Tartèse et al., 2014a by combining Rb-Sr and Sm-Nd isochron dates from the literature). Note that the studied thin-section is different to the one analysed for apatite D/H-H₂O by Tartèse et al. (2014a).

76535, 51

76535 was collected at the Apollo 17 Station 6 site in the Taurus-Littrow Valley, and is part of a rake sample. It is a remarkably pristine, coarse-grained plutonic rock which has not been altered by shock (Warren and Wasson, 1979). This sample is composed of plagioclase, olivine, orthopyroxene, plus accessory minerals and mesostasis (Gooley et al., 1974; Dymek et al, 1975; Warren, 1993; McCallum and Schwartz, 2001; Elardo et al., 2012). The
mesostasis mineral assemblage consists of spinel, clinopyroxene, orthopyroxene, apatite, merrillite, baddeleyite, native Fe-metal, and K-feldspar. 76535 has a crystallisation age of ~4.373 ± 0.011 Ga (weighted average age from Papanastassiou and Wasserburg, 1976; Hinthorne et al., 1979; Premo and Tatsumoto, 1992; Nyquist et al., 2012; Carlson et al., 2014).

78235,43

78235 was chipped from a glass covered boulder at Station 8 on the Apollo 17 mission (Jackson et al., 1975). It is classified as a coarse-grained norite (grain size ~ 0.5 mm). This norite is heavily shocked and thin-section 78235,43 contains a sliver of the impact glass that covered the boulder at Station 8. Sample 78235 is mainly composed of orthopyroxene, plagioclase, and trace amounts of clinopyroxene, silica, apatite, merrillite, and glass (e.g., McCallum and Mathez, 1975). Recent age determinations seem to indicate a weighted average crystallisation age of 4.39 ± 0.04 Ga: Nyquist et al., 1982; Edmunson et al., 2009; Andreasen et al., 2013) making 78235 one of the oldest lunar samples in the Apollo collection.

79215, 50

79215 was collected at Station 9 on the Apollo 17 mission. It has been classified as a holocrystalline feldspathic granulitic impactite. 79215 is composed of ~ 72 % matrix and ~28 % relict lithic clasts of anorthosite and troctolite rocks (McGee et al., 1978). The matrix portion is composed of plagioclase, olivine, high-Ca pyroxene, low-Ca pyroxene, and minor to trace amounts of oxides, metals and troilite (Bickel et al., 1976; Treiman et al., 2014). The troctolite portion is composed of plagioclase, olivine, orthopyroxene, clinopyroxene, and minor apatite, oxides, spinel and troilite (McGee et al., 1978). Both matrix and a troctolitic clast are present in the studied thin-section, but apatite was only found in the troctolitic
portion. This sample has a peak metamorphism age of ca. 3.9 Ga (Oberli et al., 1979; Hudgins et al., 2009).

3. Petrological histories of the lithologies studied

A) Magnesian suite (MGS) samples

The MGS group includes the troctolite (76535) and norite (78235) studied in this work. The parent melts to these rocks are considered to have been formed by partial melting of early LMO Mg-rich olivine-dominated cumulates (Shearer et al., 2015) with melting likely initiated by mantle cumulate overturn. The Mg-rich melts are expected to have either assimilated urKREEP en route to the crust or have interacted with urKREEP at the base of the crust, before being intruded into the lunar crust where they experienced slow cooling likely in layered intrusions (reviewed in Shearer et al., 2015). In the case of these samples, the volatile signatures of the primitive melts have been overprinted by the KREEP contamination.

B) Metasomatised samples

Whilst troctolite 76535 is a pristine un-shocked sample (Warren, 1993) it is considered to have been affected by post-crystallisation metasomatism (e.g., Elardo et al., 2012). This alteration was likely facilitated by the infiltration of a KREEPy melt that was rich in Cl, Fe and Cr (Elardo et al., 2012). Likewise, granulite 79215 was annealed by impact and is thought to have been subsequently affected by metasomatism, probably of an agent (melt, vapour or fluid) derived from a KREEP component infiltrating the lunar crust that had been mobilised by impact (e.g., Treiman et al., 2014). Thus the volatiles in these samples can be directly related to the varying KREEP component added.
C) KREEP-rich basalts

KREEP basalts, inclusive of 15386 which is one of the most KREEP-rich basalts from the Moon, are considered to have formed from the partial melting of primitive olivine and pyroxene cumulates that either already contained an urKREEP component (incorporated during cumulate overturn) or assimilated urKREEP en route to the crust before being erupted onto the lunar surface (Warren and Wasson, 1979).

The very high potassium (VHK) basalts including 14304, are thought to be formed through the assimilation of lunar granite lithologies by a high-aluminium (HA) mare basaltic magma (Shervais et al., 1985; Neal and Taylor, 1989). The variations in texture observed between VHK samples was attributed to different cooling rates within a single lava flow. Recently, Roberts et al. (2014), used textural and petrographic relationships of K-rich glass with host minerals and breccia matrix to invoke an impact origin. They suggested that following breccia formation the breccia was covered in a hot impact melt sheet that melted the low melting point components, such as granite, also present in Apollo 14 breccias, and infiltrated the breccia.

D) Mare basalts

The source regions for the mare basalts (e.g., 10044, 10058, 70035, 15555) formed after cumulate overturn. This event is expected to have created the heterogeneous mixture of olivine, pyroxene, and ilmenite cumulates and small degrees of partial melting of these sources created the mare basalts (e.g., reviewed by Grove and Krawczynski, 2009 and Hallis et al., 2014). Limited incorporation of KREEP component is expected in the source regions of the mare basalts, together with varying degrees of ilmenite contamination, and possibly small amounts of trapped instantaneous residual liquid in the mantle cumulates, all would have contributed to the volatile inventory of the source regions for the mare basalts.
4. Electron Probe Microanalysis (EPMA) data

EPMA data collected following the protocol of Barnes et al. (2014) is shown in Supplementary Table 1. Electron microprobe analyses were conducted on apatite in some of the studied samples (10058, 14304, 78235 and 79215) for which data were not available in the literature using the method outlined in Barnes et al. (2014) (Supplementary Table 1).

Supplementary Table 1. Chemical compositions of apatite in samples 10058, 14304, 78235, and 79215. Numbers in parentheses represent the number of analyses. S.d. is the standard deviation of each oxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>10058 (4)</th>
<th>s.d.</th>
<th>14304 (6)</th>
<th>s.d.</th>
<th>78235 (3)</th>
<th>s.d.</th>
<th>79215 (4)</th>
<th>s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2O5</td>
<td>39.85</td>
<td>1.62</td>
<td>42.15</td>
<td>0.38</td>
<td>42.46</td>
<td>1.72</td>
<td>42.06</td>
<td>0.20</td>
</tr>
<tr>
<td>SiO2</td>
<td>2.25</td>
<td>0.30</td>
<td>0.04</td>
<td>0.45</td>
<td>0.46</td>
<td>0.18</td>
<td>0.18</td>
<td>0.02</td>
</tr>
<tr>
<td>Ce2O3</td>
<td>0.41</td>
<td>0.08</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Y2O3</td>
<td>1.20</td>
<td>0.12</td>
<td>0.06</td>
<td>0.01</td>
<td>0.02</td>
<td>0.07</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>MgO</td>
<td>0.03</td>
<td>0.35</td>
<td>0.07</td>
<td>0.11</td>
<td>0.02</td>
<td>0.18</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>52.38</td>
<td>1.32</td>
<td>55.49</td>
<td>0.25</td>
<td>54.50</td>
<td>0.97</td>
<td>56.05</td>
<td>0.41</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>0.68</td>
<td>0.36</td>
<td>0.07</td>
<td>0.26</td>
<td>0.19</td>
<td>0.22</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SO2</td>
<td>0.09</td>
<td>0.01</td>
<td>0.01</td>
<td>0.07</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>F</td>
<td>3.46</td>
<td>0.29</td>
<td>0.24</td>
<td>3.14</td>
<td>0.53</td>
<td>3.94</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Cl</td>
<td>0.06</td>
<td>0.03</td>
<td>0.11</td>
<td>0.78</td>
<td>0.06</td>
<td>0.66</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>F=O</td>
<td>1.46</td>
<td>1.54</td>
<td>1.32</td>
<td>1.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl=O</td>
<td>0.01</td>
<td>0.10</td>
<td>0.18</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>98.96</td>
<td>101.34</td>
<td>100.29</td>
<td>101.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Stoichiometry based on 13 anions

<table>
<thead>
<tr>
<th>P</th>
<th>2.87</th>
<th>2.97</th>
<th>3.00</th>
<th>2.96</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.19</td>
<td>0.03</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Ce</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Y</td>
<td>0.05</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00</td>
<td>0.04</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca</td>
<td>4.78</td>
<td>4.95</td>
<td>4.88</td>
<td>5.01</td>
</tr>
<tr>
<td>Mn</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Na</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>S</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>F</td>
<td>0.93</td>
<td>0.96</td>
<td>0.83</td>
<td>1.04</td>
</tr>
<tr>
<td>Cl</td>
<td>0.01</td>
<td>0.06</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>OH</td>
<td>0.06</td>
<td>0.00</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>Sum</td>
<td>7.96</td>
<td>8.02</td>
<td>7.95</td>
<td>8.03</td>
</tr>
<tr>
<td>P site</td>
<td>3.06</td>
<td>2.99</td>
<td>3.04</td>
<td>2.98</td>
</tr>
<tr>
<td>Ca site</td>
<td>4.90</td>
<td>5.03</td>
<td>4.91</td>
<td>5.05</td>
</tr>
</tbody>
</table>
For the other samples, apatite compositions are given by Tartèse et al. (2013) for 10044 and 15555, Tartèse et al. (2014a) for 15386, McCubbin et al. (2011), Elardo et al. (2012) and Barnes et al. (2014) for 76535, and Treiman et al. (2014) for 79215. EMPA data has not yet been collected for apatite in 70035. Stoichiometry was calculated on the basis of thirteen anions (see McCubbin et al., 2011 for a discussion of the various stoichiometric normalisation methods specific to apatite). The analytical reproducibility of fluorine values on apatite standards was better than 0.3 wt.%, except for analysis of apatite in 79215, which all exhibited anomalously high F contents. All other analyses resulted in satisfactory stoichiometric totals. As already recognised in previous studies, one of the main characteristics of lunar apatite is their F-rich nature (McCubbin et al., 2011; Tartèse et al., 2013; McCubbin et al., 2015). In all the studied samples excluding mare basalt 15555, all of the apatite crystals have >3 wt.% fluorine, corresponding to > ~80 mol.% F in the apatite volatile site.

5. Relating the heavy Cl-isotopic composition of lunar apatite to a KREEP component

Supplementary Table 2 provides the data and literature references used to assess whether variable KREEP contamination might be responsible for the unique Cl-isotopic compositions of lunar samples (Figure 8).