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

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## ABSTRACT

Current models for the Moon's formation have yet to fully account for the thermal evolution of the Moon in the presence of $H_2O$ 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 $\sim$0‰. 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 of apatite 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.

## 1. Introduction

Existing models for the formation of the Moon (Ćuk 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 $H_2O$ and other associated volatile signatures in the lunar interior, that have been recognised through studies of lunar samples.

In lunar rocks, apatite $[Ca_5(PO_4)_3(F,Cl,OH)]$ is the most common volatile-bearing mineral (McCubbin et al., 2015a). A multitude of studies have investigated the abundances of volatiles ($H_2O$, 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 $H_2O >$ F $>$ Cl, whilst the parent melts to the lunar highlands rocks were characterised by Cl $>$ $H_2O \approx$ 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 $H_2$ 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

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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 urKREEP 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 $H_2O$ 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 $8 \times 8$ 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 $3 \times 3$ μm and $5 \times 5$ μm. Electronic gating was used to collect secondary ions emitted from only the inner 25% of the rastered areas. Secondary negative ions of $^{16}O^1H$, $^{18}O$, $^{35}Cl$, $^{37}Cl$, and $^{40}Ca^{19}F$ were collected simultaneously on electron multipliers (EMs). $^{40}Ca^{19}F$ 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 $^{40}Ca^{19}F$. A mass resolving power of ~8000 (Cameca definition) was used in order to readily resolve isobaric interferences, particularly between peaks of $^{17}O$ and $^{16}O^1H$. Each 1-inch round
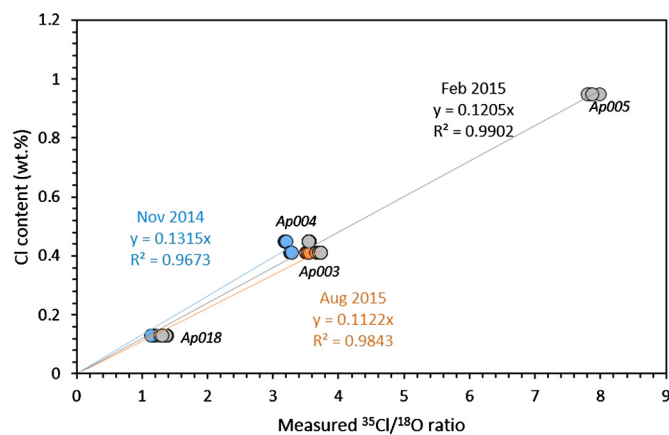


**Fig. 1.** Calibrations for the apatite standards used in this study of known Cl content (wt%) versus the measured $^{35}Cl/^{18}O$ ratio, for a representative analytical day during each of the three analytical sessions.

thin-section was coated with ~30 nm of gold and an electron flood gun was used for charge compensation. Secondary ion images of $^{16}O^1H$ 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 $^{35}Cl/^{18}O$ 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 $H_2O$ (between ~10 and 90 ppm) and Cl (<5 ppm). The slopes of the calibration lines (Fig. 1) defined by apatite 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 $2\sigma$ 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 $^{37}Cl/^{35}Cl$ ratios for instrumental mass fractionation. The isotopic composition of chlorine is reported using the standard delta ($\delta$) notation with respect to the $^{37}Cl/^{35}Cl$ ratio of the standard mean ocean chloride (SMOC, $^{37}Cl/^{35}Cl$ ratio = 0.31977), and is reported with the associated $2\sigma$ uncertainties, which combine the reproducibility of $^{37}Cl/^{35}Cl$ 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 $\delta^{37}Cl$ values measured on a secondary apatite standard (Ap003) run during the February session and referenced to Ap004 (Ap004 has a $\delta^{37}Cl$ value of ~+0.11‰, Zach Sharp, University of New Mexico, *pers. comm.*). All Ap003 analyses are within error of the terrestrial value of ~$0 \pm 1$‰ (Sharp et al., 2013a), with an average $\delta^{37}Cl$ value for the analytical week of $+0.17 \pm 1.26$‰.

## 3. Results

### 3.1. Petrographic context of lunar apatite

In thin-section 10044,645, apatite occurs in contact with non-mesostasis 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