Chlorine isotopic compositions of apatite in Apollo 14 rocks: Evidence for widespread vapor-phase metasomatism on the lunar nearside ~4 billion years ago

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ABSTRACT

Compared to most other planetary materials in the Solar System, some lunar rocks display high δ37Cl signatures. Loss of Cl in a H<Cl environment has been invoked to explain the heavy signatures observed in lunar samples, either during volcanic eruptions onto the lunar surface or during large scale degassing of the lunar magma ocean. To explore the conditions under which Cl isotope fractionation occurred in lunar basaltic melts, five Apollo 14 crystalline samples were selected (14053,19, 14072,13, 14073,9, 14310,171 along with basaltic clast 14321,1482) for in situ analysis of Cl isotopes using secondary ion mass spectrometry. Cl isotopes were measured within the mineral apatite, with δ37Cl values ranging from +14.6 ± 1.6 ‰ to +40.0 ± 2.9 ‰. These values expand the range previously reported for apatite in lunar rocks, and include some of the heaviest Cl isotope compositions measured in lunar samples to date. The data here do not display a trend between increasing rare earth elements contents and δ37Cl values, reported in previous studies. Other processes that can explain the wide inter- and intra-sample variability of δ37Cl values are explored. Magmatic degassing is suggested to have potentially played a role in fractionating Cl isotope in these samples. Degassing alone, however, could not create the wide variability in isotopic signatures. Our favored hypothesis, to explain small scale heterogeneity, is late-stage interaction with a volatile-rich gas phase, originating from devolatilization of lunar surface regolith rocks ~4 billion years ago. This period coincides with vapor-induced metasomatism recorded in other lunar samples collected at the Apollo 16 and 17 landing sites, pointing to the possibility of widespread volatile-induced metasomatism on the lunar nearside at that time, potentially attributed to the Imbrium formation event.
1. **Introduction**

Compared to most other planetary materials in the Solar System, lunar rocks are unique in their wide-ranging chlorine isotopic signatures (Barnes et al., 2016; Boyce et al., 2015; Sharp et al., 2010a; Tartèse et al., 2014a; Treiman et al., 2014). Lunar rocks display $\delta^{37}\text{Cl}$ signatures [$^{37}\text{Cl}/^{35}\text{Cl}$ relative to standard mean ocean chloride (SMOC; $0.31977$); Kaufmann et al., (1984)] that range from $\sim-4$ ‰ up to $\sim+40$ ‰, which is in stark contrast to the Earth, where the reported values cluster around $0$ ‰ $\pm$ 1 ‰ (Barnes et al., 2008; Sharp et al., 2007; Sharp et al., 2013). This deviation in Cl isotope signatures, between the Earth and Moon, is contrary to the isotopic similarity observed for most other elements, including oxygen (Herwartz et al., 2014; Wiechert et al., 2001; Young et al., 2016), calcium (Dauphas et al., 2015; Valdes et al., 2014), chromium (Lugmair and Shukolyukov, 1998), stable chromium (Bonnand et al., 2016), stable strontium (Charlier et al., 2012), silicon (Armytage et al., 2011; Armytage et al., 2012; Zambardi et al., 2013), titanium (Zhang et al., 2012), and zirconium (Schönbächler et al., 2003). Isotopic similarities between the Earth and the Moon have been interpreted that the Moon, most likely, formed from reconsolidation of proto-Earth material after a Moon forming event (Canup, 2012; Canup et al., 2015; Ćuk and Stewart, 2012; Rubie et al., 2015). Thus, Cl isotope fractionation must have occurred during and/or after Moon formation and, therefore, provides unique insight into volatile processing in/on the Moon.

Two competing mechanisms are believed to fractionate Cl isotopes in terrestrial systems: (i) the lighter isotope $^{35}\text{Cl}$ is preferentially vaporized (Graham’s Law), in volcanic gases for example, while (ii) the heavier $^{37}\text{Cl}$ becomes incorporated into HCl(g) as a result of its relatively high bond strength (Schauble et al., 2003) in systems where H>>Cl (Sharp et al., 2010a). Most bulk primitive terrestrial basalts measured to date have $\delta^{37}\text{Cl}$ values clustering...
around \(\sim 0 \pm 2\%\), suggesting that these two fractionation mechanisms cancel each other out in terrestrial systems (Sharp et al., 2013). To explain the elevated \(\delta^{37}\text{Cl}\) values (i.e. > 0 \(\%\)) of lunar samples, Sharp et al. (2010a) favored the hypothesis in which lunar basaltic melts were characterized by \(\text{H}<<\text{Cl}\), which promoted the degassing of Cl as metal chlorides (e.g., NaCl, etc.) instead of HCl(g). This process would have preferentially incorporated the lighter isotope \(^{35}\text{Cl}\) into the degassed metal chloride phase, resulting in residual melts that were enriched in \(^{37}\text{Cl}\) (Sharp et al., 2010a).

Subsequent studies, of chlorine isotopes in lunar apatite, argued that preferential outgassing of \(^{35}\text{Cl}\) from erupting lavas was unlikely to be the main driver for the large Cl isotope fractionation in lunar melts, notably because (i) apatite in plutonic samples tend to have higher \(\delta^{37}\text{Cl}\) values than apatite in erupted volcanic samples, and (ii) there seems to be a broad positive correlations between chlorine isotopes and abundances (Boyce et al., 2015; Barnes et al., 2016). Indicating that whatever mechanism(s) caused the extreme fractionation of chlorine isotopes must have been capable of producing a reservoir that is rich in Cl, and is characterized by an elevated Cl isotopic composition (Boyce et al., 2015). This assumption, and dismissal of degassing as the mechanism for Cl isotope fractionation, is only valid if all samples had the same initial Cl concentration and \(\delta^{37}\text{Cl}\) value; a highly unlikely scenario.

In addition, positive correlations between apatite \(\delta^{37}\text{Cl}\) values and some bulk-rock trace element characteristics, such as La/Lu ratios and Th contents (Barnes et al., 2016; Boyce et al., 2015), have been used to suggest heavy \(\delta^{37}\text{Cl}\) are somehow linked to the involvement of a KREEP (potassium (K), rare earth elements (REE), phosphorous (P); (Warren and Wasson, 1979) component. Boyce et al. (2015) attributed large-scale Cl isotope fractionation to the
degassing of metal chlorides from the molten lunar magma ocean (LMO). In their model, the elevated $\delta^{37}$Cl values recorded by apatite, within the mare basalts, would have been acquired during assimilation of a KREEP-component either (i) into the mare basalt source regions or (ii) as the basalts ascended towards the lunar surface. While Barnes et al. (2016) suggested that the ~34 to ~43 km of lunar crustal material (Wieczorek et al., 2013) was sufficiently thick to prevent loss of Cl-bearing species from the LMO via continuous degassing, especially given the high solubility of Cl in basaltic melts (Webster et al., 2009). Instead, they proposed that crust-breaching impact events exposed KREEP-rich melt to low pressure environments, promoting degassing of metal chlorides, and subsequent Cl isotope fractionation (Barnes et al., 2016).

One of the heaviest lunar $\delta^{37}$Cl values measured to-date, ~ +32 ‰, is from the granulite sample 79215, whose signature is not thought to be from any process described above (Treiman et al., 2014). This sample is characterized by an elevated P content (~200 × CI chondrite P contents) but low K or REE contents (~10 × CI; e.g., P/Sm = ~20) suggested that in 79215, P, and the halogens, were largely added during vapor-phase metasomatism, likely originating from impact-induced devolatilization of a KREEP-rich target. Vapor-phase metasomatism is favored given that lunar conditions are too reduced for abundant H$_2$O or CO$_3^{2-}$ to be present and the lack of supporting evidence for fluid metasomatism in lunar samples. This suggest that surface processes can also be responsible for modifying Cl isotope composition in lunar samples.

Detailed understanding of the individual petrological histories of the rocks investigated in Cl isotope studies is, therefore, critical to deciphering the mechanism(s) by which Cl isotopes may have fractionated in lunar samples. In order to investigate the potential processes that
contributed to the elevated $\delta^{37}$Cl values observed in lunar apatite, five Apollo 14 samples were studied: high-Al basalts 14053 and 14072, a basaltic clast from breccia 14321,1482 and impact melt rocks 14073 and 14310. These Apollo 14 samples have distinct petrogenetic histories, and all pre-date the main period of mare volcanism, providing unique insight into the timing of, and process(es) responsible for, Cl isotope fractionation in/on the Moon. Furthermore, the high modal abundance and large size (typically > 50 $\mu$m in the longest dimension) of apatite grains in these samples permitted a thorough investigation of intra-grain and inter-sample variations in volatile abundances and Cl isotope systematics.

2. Apollo 14 High-Al rocks

The Apollo 14 mission landed on the Fra Mauro Formation, which is part of the ejecta blanket that formed from the excavation of the Imbrium Basin (Nemchin et al., 2009; Snape et al., 2016). Mare Imbrium is the largest basin-affiliated mare deposit on the Moon (assuming that the Procellarum KREEP Terrane is not an impact feature), and is thought to have excavated lower lunar crust material during the basin-forming event (Nemchin et al., 2009). It remains unclear, however, which Apollo 14 samples represent true Imbrium ejecta and which are locally derived (Hiesinger and Head, 2006). The consistent dates obtained by $^{40}$Ar/$^{39}$Ar dating on whole rocks and fines (Alexander and Davis, 1974; Turner et al., 1972; Turner et al., 1971) and Rb-Sr dating (Papanastassiou and Wasserburg, 1971; Compston et al., 1972; Compston et al., 1972) of ~3.87 Ga were interpreted as representing the timing of formation of the Imbrium Basin (Stöffler and Ryder, 2001; Wilhelms et al., 1987). Recent high-precision U-Pb dating of phosphates and zircons in Apollo 14 impact melt breccias has provided an improved estimate for the formation of the Imbrium Basin at ~3.93 Ga (Snape et al., 2016, and references therein). Other studies of zircon grains from Apollo 14 lunar breccias have yielded U-Pb dates ranging from ~4.0 to ~4.4 Ga, with distinct date peaks at ~4.35 and ~4.20 Ga (Meyer et al., 1996;
Nemchin et al., 2008), suggesting that a significantly older pre-Imbrium history is recorded by
the breccias. The temperature and shock effects associated with the development of the Fra
Mauro Formation were, therefore, sufficient to reset $^{40}\text{Ar}/^{39}\text{Ar}$ and Rb-Sr dates but not to reset
the zircon U-Pb systems in all samples (Nemchin et al., 2010).

Some basalts from the Fra Mauro region record volcanism older than 4 billion years on the
Moon (Neal and Kramer, 2006). Basaltic clasts from this region indicate a period of ~400
million years of volcanism, from ~4.3 to ~3.9 Ga (Compston et al., 1972; McKay et al., 1979;
Papanastassiou and Wasserburg, 1971; Snape et al., 2016), pre-dating the main period of mare
volcanism (Snyder et al., 2000). Volcanics from the Fra Mauro region may provide insights
into the evolution of the Moon from solidification of the crust, at around ~4.5 Ga to ~4.3 Ga
(Elkins-Tanton et al., 2011), to the beginning of the main period of mare volcanism that
commenced around ~3.85 Ga (Shearer et al., 2006). Crystallization and/or impact-resetting
ages for all the Apollo 14 samples studied here are given in Table 1, and range between ~4.1
Ga and ~3.8 Ga (Compston et al., 1972; Dasch et al., 1987; Hui et al., 2013; Husain et al.,
1971; Mark et al., 1974; Papanastassiou and Wasserburg, 1971; Tatsumoto et al., 1972; Turner
et al., 1972; York et al., 1972).

In addition to their old age, the Apollo 14 basalts are also geochemically distinct in that
they are relatively enriched in Al$_2$O$_3$ (11 – 16 wt.%), leading to their classification as ‘high-Al’
basalts (Neal and Kramer, 2006; Ridley, 1975). Two petrological models have been proposed
for the formation of these high-Al samples: (1) “pristine” volcanic rocks that formed solely
through endogenous lunar processes and (2) impact generated melts referred to as “impact
melts” (Hui et al., 2011).
Based on incompatible trace element (ITE) abundances and crystallization ages, the Apollo 14 high-Al basalts have been separated into three distinct groups: Group A (~4.3 Ga), Group B (~4.1 Ga), and Group C (~3.9 Ga) (Neal and Kramer, 2006). Samples within these groups are thought to be related via a closed-system crystal fractionation model for Group A, and an open-system evolution model, involving assimilation of a KREEP component and/or granitic melts, for Groups B, and C (Hui et al., 2011; Neal et al., 1988; Neal et al., 1989; Neal and Kramer, 2006; Neal and Taylor, 1989). The main geochemical features of the samples studied here are summarized in Table 1. The impact-melt samples, 14073 and 14310, are crystallization products of impact-melted lunar regolith and/or feldspathic crust (Schonfeld and Meyer, Charles, 1972), and could have inherited their high-Al contents from melting of anorthosite-rich targets (Hui et al., 2011). In contrast, for the endogenous pristine basalts (14053, 14072, and 14321,1482), the high-Al content is not related to any contribution from the melting of anorthosite-rich rocks and it is more likely that elevated Al contents were directly inherited from the mantle source regions of these basalts (Hui et al., 2011; Neal and Kramer, 2006). These different formational mechanisms have been used to explain the compositional differences between the Apollo 14 pristine basalts and impact melt samples. Detailed descriptions of all the samples studied here is given in the Supplementary Material.

3. Analytical techniques

Before secondary ion mass spectrometry (SIMS) measurements, each polished thin-section was carbon-coated and studied using a dual beam FEI Quanta 3D Scanning Electron Microscope (SEM) at The Open University, following the protocol described in Tartèse et al. (2013). The SEM was used to locate apatite crystals suitable for SIMS analyses, and to characterize the petrographic context of each grain. The carbon coat was removed after SEM work and the samples were cleaned with isopropanol and stored in a vacuum oven at ~55 °C
for a minimum of 48 hours. Subsequently, samples were coated with ~30 nm of gold using an EMITECH K575X peltier cooled gold sputter coater. After coating, the samples were immediately loaded into the Cameca NanoSIMS 50L at The Open University. Apatite was located following initial pre-sputtering for several minutes of large (>10 × 10 µm) areas. Smaller ~8 × 8 µm areas, containing the target apatite grains, were then pre-sputtered by rastering a Cs⁺ beam of ~40 pA with an accelerating voltage of 16 kV for ~2 minutes, in order to clean the target surface. For analysis, the 40 pA probe was then rastered over ~4 × 4 µm areas in the apatite grains for ~4 minutes. An electron flood gun was used for charge compensation. During analysis the vacuum in the analysis chamber remained around ~5 × 10⁻⁹ Torr. The NanoSIMS was tuned to achieve a mass resolving power of ~8000 and the negative secondary ions of ¹⁶O⁺₁H, ¹⁸O, ¹⁹F, ³⁵Cl, ³⁷Cl, and ⁴⁰Ca¹⁹F were collected simultaneously on electron multipliers. ¹⁹F ions were monitored, but only for ~66s per analysis to avoid saturating the detectors.

The abundances of Cl, F, and H₂O were calibrated using the published Cl, F, and H₂O contents and the measured ³⁵Cl/¹⁸O, ¹⁹F/¹⁸O, and ¹⁶OH/¹⁸O ratios of Ap004 and Ap018 reference apatite crystals mounted in epoxy resin (McCubbin et al., 2012). Background measurements of Cl and OH were collected on San Carlos olivine and nominally anhydrous minerals within sample sections (~100 ppm H₂O and ~4 ppm Cl) and were subtracted from the measured values. Reported uncertainties for abundances incorporate the 2σ uncertainty of the calibration slopes and analytical uncertainties associated with individual measurements. Ap004 was used to correct the measured ³⁷Cl/³⁵Cl ratios of unknown samples for instrumental mass fractionation (IMF; (³⁷Cl/³⁵Cl_{unknown}/³⁷Cl/³⁵Cl_{standard})-1)*1000). The Cl isotope composition is reported using standard delta notation with respect to ³⁷Cl/³⁵Cl of standard mean ocean chloride. Isotope measurements are reported with their associated 2σ uncertainties, which
combine the reproducibility of the $^{37}\text{Cl}/^{35}\text{Cl}$ measurements on an appropriate standard and the internal uncertainty of each analysis.

4. Results

In the following section, textural descriptions and $\delta^{37}\text{Cl}$ values of apatite, with corresponding Cl and H$_2$O abundances, are given for each sample. High-resolution back-scattered electron (BSE) images including the petrographic setting of individual apatite grains analyzed in this study are shown in Supplementary Figures SM2 to 6. The results of NanoSIMS analyses of apatite for Cl isotopic compositions and H$_2$O and Cl abundances are listed in Table 2. In addition F abundances for apatite in some samples are listed in Table 2.

4.1. 14053,19

In sample 14053,19 eight analyses were carried out in seven apatite crystals occurring in four separate areas (Fig. SM2A-D). Apatite crystals in this sample are all associated with mesostasis. Here, mesostasis regions were identified by the breakdown of fayalite into Fe metal (often described as ‘spongy’ Fe in the literature (Taylor et al., 2004)) and silica-rich glass, as well as the presence of a diverse range of phases with relatively small grain sizes (<20 µm in the longest dimension; Potts et al., 2016). All of the apatite grains measured here were subhedral to anhedral, >10 µm in the longest dimension, and were found associated with quenched K-rich glass. The majority of apatite grains in this section were also found in contact with plagioclase, except Ap#4a and Ap#4b.
The volatile abundances of apatite in 14053 overlap with those of Mg- and alkali-suite rocks (Fig. 1), which are fluorapatite with greater amounts of Cl than H$_2$O. The $\delta^{37}$Cl values of apatite in 14053,19 range from $+15.6 \pm 2.2$‰ to $+34.3 \pm 2.9$‰. H$_2$O abundances of apatite in this sample range from 89 ± 4 ppm to 1662 ± 80 ppm (Fig. 2A; Table 2). The Cl concentrations of apatite in this sample range from 1569 ± 2 ppm to 16054 ± 17 ppm (Fig. 2B; Table 2). Apatite 4a shows the highest $\delta^{37}$Cl value ($+34.3 \pm 2.9$‰) whilst having the lowest H$_2$O content (89 ± 4 ppm) and highest Cl content (16054 ± 17 ppm) of any apatite measured from this sample. In contrast, Ap#1 has the lowest $\delta^{37}$Cl value ($+15.6 \pm 2.2$‰) measured from this sample and the highest H$_2$O content (1662 ± 80 ppm) and lowest Cl content (1569 ± 2 ppm).

Both apatite crystals Ap#4a and Ap#1 are found within mesostasis regions although there appears to be significantly more fayalite reduction surrounding Ap#4a than Ap#1. Overall, there are strong correlations between increasing $\delta^{37}$Cl values and (a) decreasing H$_2$O abundances and (b) increasing Cl abundances for apatite in 14053,19 (Fig. 2A-B). There is little intra-region variation, in terms of $\delta^{37}$Cl, in this section except for Area #1 in which the two analyses yielded a difference of ~12 ‰. The two heaviest values (> $+32$‰) in this section are from two apatite grains within the same region (area 4), which displays the highest proportion of reduction-related texture. Apatite grains in this region also display resorbed edges compared to apatite within areas 1 and 5 that are characterized by $\delta^{37}$Cl values around +23 to +28 ‰ (except Ap#1). Apatite grains within area 8 also appear to have resorbed edges, and have $\delta^{37}$Cl values of between +21 and +24 ‰. The subhedral apatite grains within areas 1 and 5 have higher H$_2$O contents (>500 ppm) compared to the andehral apatite grains within area 4 (<200 ppm). The highest Cl contents have been measured in the subhedral grains found in area 4.
In sample 14072,13 five analyses were carried out in five distinct apatite crystals occurring in four different areas (Fig. SM3A-E where B and C are both part of one larger area). All apatite crystals were found within mesostasis regions that were texturally similar to those in 14053,19, although mesostasis regions in 14072,13 generally contained a larger fraction (>30 modal %) of spongy Fe. Large (> 20 µm) euhedral to sub-euhedral apatite yielded δ\(^{37}\)Cl values ranging from +16.3 ± 2.9 ‰ to +40.0 ± 2.9 ‰, with Cl and H\(_2\)O abundances ranging from 4167 ± 5 to 14759 ± 15 ppm and 117 ± 6 to 189 ± 9 ppm, respectively (Figs. 2A-B; Table 2).

The volatile abundances of apatite in this thin-section overlap with those of Mg- and alkali-suite rocks (Fig. 1). Unlike sample 14053,19, there is no clear correlation between apatite Cl or H\(_2\)O abundance and the associated δ\(^{37}\)Cl values in 14072,13 (Fig. 2). All of the apatite grains, except in area 7, are in contact with spongy Fe- and K-rich glass, while the mesostasis pockets are surrounded by plagioclase. The lower δ\(^{37}\)Cl values of around +16 to +20 ‰ have been measured in euhedral apatite grains, while the heaviest δ\(^{37}\)Cl values (+28.8 ± 2.9 ‰ and +40.0 ± 2.9 ‰) are associated with anhedral crystals. This relationship is broadly consistent with what we observed in sample 14053,19.

In sample 14321,1482 four analyses were carried out in three apatite crystals occurring in three different areas (Fig. SM4A-C). Apatite crystals in 14321,1482 are euhedral to subhedral, > ~10 µm in the longest dimension, and were located in mesostasis regions, which contain spongy Fe in areas 3 and 5, fayalite, silica, and K-rich glass.
The apatite $\delta^{37}$Cl values range from $+20.1 \pm 0.9$ ‰ to $+28.6 \pm 1.1$ ‰ and are associated with Cl abundances of ~5000-8000 ppm and very low H$_2$O contents < 150 ppm (Figs. 2A-B; Table 2). Although limited in number, the analyses of 14321,1482 are consistent with the ranges of Cl abundances and $\delta^{37}$Cl values measured in most of the apatite grains from samples 14053 and 14072. The lowest $\delta^{37}$Cl value in this sample has been measured in area 5 on an anhedral apatite grain in this section, opposite to observations for 14053 and 14072. This grain also is in direct contact with spongy Fe. The other apatite grains within this sample have $\delta^{37}$Cl values between ~ +24 and +29 ‰ and are all euhedral to subhedral.

4.4. 14073,9

In sample 14073,9 fifteen analyses were carried out on nine apatite crystals occurring in five different areas (Fig. SM5A-E). All apatite grains in this sample were located in mesostasis regions, identified by the presence of K-rich glass. The mesostasis regions in 14073, however, are texturally and compositionally different from those in 14053 and 14072, as they do not contain spongy Fe, but interstitial K-rich glass associated with K-feldspar. The apatite grains analyzed here are subhedral, up to 50 µm in the longest dimension, and are all in contact with K-rich glass, with some containing melt inclusions.

The analyzed apatite grains are H$_2$O-poor and Cl-rich compared to typical mare basalts (Fig. 1). The $\delta^{37}$Cl values of apatite from sample 14073,9 display a large range from $+16.5 \pm 2.2$ ‰ to $+36.9 \pm 2.1$ ‰, most of them clustering between ~ +21 and +28 ‰ (Fig. 2A-B). The Cl and H$_2$O abundances of these apatite range from 580 ± 1 ppm to 16149 ± 18 ppm and
291 ± 14 ppm to 1081 ± 52 ppm, respectively. Generally, the higher δ^{37}Cl values correspond to low to moderate H\textsubscript{2}O contents, while there is no strong correlation between δ^{37}Cl values and Cl abundances (Fig. 2). In some mesostasis areas, such as area 11 (a cluster of apatite crystals) in which 5 analyses were carried out, apatite crystals are fairly homogeneous in terms of abundances of H\textsubscript{2}O (317 ± 15 ppm to 419 ± 20 ppm) and Cl (1241 ± 2 ppm to 1648 ± 2 ppm) and Cl isotopic composition (+21.0 ± 2.2 ‰ to 27.5 ± 2.6 ‰). In other areas, the intra-region variations of δ^{37}Cl are large, ranging from +16.5 ± 2.2 ‰ to +27.7 ± 2.0 ‰ within a single apatite grain (Ap#12), and between +25.7 ± 1.9 ‰ and +36.9 ± 2.1 ‰ in a single grain analyzed in area 19.

4.5. 14310,171

Seven analyses were made across four apatite crystals in three areas (Figs. SM6A-C) in thin section 14310,171. Generally apatite was found in mesostasis regions in this sample, although these areas noticeably lack the large amount of K-rich glass observed in other Apollo 14 mesostasis regions, particularly 14073,9. The apatite grains in 14310,171 are euhedral to subhedral, with the size varying from >~30 μm to ~10 μm in the longest dimension. Apatite is associated with pyroxene, plagioclase, K-feldspar, merrillite, and ilmenite. The δ^{37}Cl values for apatite in this sample range from +14.6 ± 1.6 ‰ to +25.3 ± 2.0 ‰, and apatite Cl and H\textsubscript{2}O abundances range from 4597 ± 8 ppm to 11256 ± 19 ppm and 95 ± 3 to 354 ± 11 ppm, respectively (Table 2). Similarly to apatite in sample 14073,9, elevated δ^{37}Cl values tend to be associated with lower H\textsubscript{2}O abundances (Fig. 2A). In this sample, the higher δ^{37}Cl values also tend to be associated with higher Cl abundances (Fig. 2B). As in sample 14073,9, the degree of intra-region heterogeneity in δ^{37}Cl values varies across the sample, particularly in area 4. The euhedral apatite grains in this section have the lower δ^{37}Cl values (< +18 ‰), while the
heavier Cl isotope values are associated with a smaller (<10 μm) subhedral apatite grain, apart from those in area 1.

5. Discussion

This study provides a comprehensive dataset on the chlorine isotopic compositions of apatite from Apollo 14 samples, including both igneous high-Al basalts and impact melt rocks. As shown in Figure 3, the δ^{37}Cl values measured here mostly cluster within a range of between +15 and +35 ‰, which is consistent with the upper end of the range of δ^{37}Cl values measured in high- and low-Ti mare basalts and with those obtained on KREEP-rich samples (Barnes et al., 2016; Boyce et al., 2015; Sharp et al., 2010a; Tartèse et al., 2014a; Treiman et al., 2014). The heaviest δ^{37}Cl values, of around +35 to +40 ‰, were measured in apatite from samples 14053, 14072, and 14073 and are comparable to the heaviest δ^{37}Cl values reported for KREEP-rich basalts (Sharp et al., 2010a; Barnes et al., 2016) and KREEP-rich intrusive rocks of the Mg-suite (Treiman et al., 2015; Barnes et al., 2016). The unique petrogeneses of the Apollo 14 samples studied here provide an opportunity to evaluate the potential mechanisms for Cl isotope fractionation under lunar magmatic conditions.

5.1. Linking assimilation of KREEP to the Cl isotope composition of magmatic apatite

Magmatic degassing of chlorine from the LMO, in the form of metal chlorides, has been invoked to explain the elevated chlorine isotopic compositions of lunar samples (Boyce et al., 2015; Barnes et al., 2016). This hypotheses results in an enrichment of ^{37}Cl in the KREEP-rich residual melts of the LMO, and is supported by the positive correlations observed between bulk-rock incompatible trace element contents (REE, Th) and apatite δ^{37}Cl values (Fig. 4). Our analyses of apatite in five Apollo 14 samples, however, do not show any correlation between
KREEP component (e.g. elevated La/Lu ratios in bulk samples) and elevated $\delta^{37}\text{Cl}$ values (Fig. 4). Petrologically, the high-Al pristine basalts 14053, 14072, and 14321,1482 are all believed to have assimilated an evolved KREEP-rich component even though they are not sensu stricto KREEP-basalts (Hui et al., 2011; Neal et al., 1988; Neal and Kramer, 2006). The impact melt samples 14073 and 14310 also contain a significant KREEP component (El Goresy et al., 1971; McKay et al., 1979) but are thought to have formed via the melting of feldspathic regolith or anorthosite material (Hui et al., 2011; Schonfeld et al., 1972). The Apollo 14 samples studied here thus suggest that additional magmatic and/or post-crystallization processes can modify apatite $\delta^{37}\text{Cl}$ values.

5.2. *Volatile abundances in Apollo 14 apatite*

All of the apatite analyzed here are F-rich, with compositions clustering around the F apex of the apatite volatile ternary (Fig. 1). Volatile compositions of apatite in samples 14072, 14310, and 14321,1482 plot almost exclusively along the F-Cl binary, in the field typically occupied by apatite from lunar highland samples. Apatite compositions for 14053 and 14073 have a greater H$_2$O component, consistent with the apatite compositions of KREEP-rich basalts and relatively H$_2$O-poor mare basalts (Barnes et al., 2014, 2013; Boyce et al., 2010; Greenwood et al., 2011; McCubbin et al., 2015b, 2011, 2010a, 2010b; Tartèse et al., 2014; Tartèse et al., 2013; Tartèse et al., 2014b).

The range of measured water contents within apatite in high-Al basalt 14053 (~90 - 1660 ppm H$_2$O) is similar to the range obtained in previous studies of this sample, from around 200 ppm up to ~2400 ppm H$_2$O (Greenwood et al., 2011; Boyce et al., 2010; McCubbin et al., 2010; Pernet-Fisher et al., 2014). Similarly, previously measured apatite Cl contents of ~0.17 to 0.47
wt.% in 14053 (Boyce et al., 2010; McCubbin et al., 2010) are within the range of apatite Cl abundances measured here (~0.16 to 1.6 wt.%).

Determining the volatile content of the melt from which apatite crystallized, based on the measured volatile contents of apatite, is not trivial given that F, Cl, and OH (reported here as H$_2$O) share the crystallographic X-site within the apatite crystal lattice. As such, volatiles are essential structural components, meaning that simple Nernst partitioning behavior cannot be applied (Boyce et al., 2014; McCubbin et al., 2015). Apatite, however, is generally considered a major sink for F in crystallizing melts (McCubbin et al., 2015) as crystal chemistry favors preferential incorporation of F, over OH and Cl, into apatite (Boyce et al., 2014; Kusebauch et al., 2015). As F is incorporated into apatite and/or lost via degassing (Ustunisik et al., 2015; Ustunisik et al., 2011), total F in the melt would decrease with crystallization, meaning primary apatite would have higher F contents than later grown apatite. If all the samples began with similar F melt content and Cl isotope ratios, this could suggest that apatite with greater F abundances record the initial $\delta^{37}$Cl values of their respective melts. Apatite grains with lower F abundance would, therefore, have grown later and record the $\delta^{37}$Cl isotopic compositions of the melt at the more advanced stages of crystallization. There is a vague correlation between increasing $\delta^{37}$Cl values and decreasing F abundance of apatite (Fig. 5). In sample 14321,1482 there are very few F measurements, so we cannot ascertain whether we have analyzed early growing apatite, there is only one stage of apatite growth, or there is no change in apatite F contents (and Cl isotope signatures) with melt evolution. For 14310, there is some correlation between F abundances and $\delta^{37}$Cl values (Fig. 5). Overall, the rough trend displayed by most apatite analysis in samples 14053, 14072, and 14073 could suggest that the initial $\delta^{37}$Cl values of the Apollo 14 melts were around $\sim20 \pm 5$‰ and that subsequent melt evolution has imparted heavier $\delta^{37}$Cl signatures. It is important to stress that this interpretation is only valid if F
contents and Cl isotope ratios were similar throughout different melts. The different petrogeneses of these samples also suggests it is unlikely they began with the same volatile abundance and isotope signatures. Importantly, however, if crystal chemistry controls dominateapatite compositions, then the chlorine isotopic compositions of apatite can only be explained by increasing the $^{37}\text{Cl}/^{35}\text{Cl}$ of the melt, or apatite after crystallization.

5.3. Solar-wind implantation

Apollo 14 sample 14053 is thought to have crystallized as a typical high-Al basalt, but the outer sections were later affected by solar-wind H implantation during its residence in the lunar regolith (Taylor et al., 2004). Subsequently, subsolidus thermal metamorphism (likely induced from ejecta blanket heat) facilitated the permeation of solar-wind H into the rock and led to reduction of localized areas, characterized by reduction-breakdown textures of fayalite to Fe-metal and silica, identified by the below reaction (Taylor et al., 2004).

$$\text{Fe}_2\text{SiO}_4 + 2\text{H}_2 = 2\text{Fe}^0 + \text{SiO}_2 + 2\text{H}_2\text{O}↑$$

These reduction-breakdown textures, identified by the presence of Fe-metal and silica, are shown in Figures SM2A, 2B, and 2D. Reduction-breakdown textures are also seen in 14072, and to a smaller extent in 14321, 1482. It has also been suggested that La$_2$O$_3$ and Ce$_2$O$_3$ contents in apatite from 14053, in contact with reduced areas, may have undergone secondary alteration as a consequence of H-reduction (Taylor et al., 2004). If such metamorphism occurred then it is conceivable that the volatile abundances and isotopic composition of apatite in these samples may have been modified (Boyce et al., 2010; Greenwood et al., 2011).
The lack of reduction textures in 14310 and 14073 is important given that these rocks formed from impact melt processing of the lunar regolith, indicating that either (i) such a signature was erased during impact melting or (ii) that these samples did not undergo the surface reduction process, unlike the other samples studied. The second scenario would support late alteration of 14053 (and potentially 14072, as well as 14321,1482) and negligible solar-wind alteration of 14310 and 14073.

5.4. The role of volatile degassing from lunar magmas

Chlorine is incompatible in the major silicate minerals that crystallize from basaltic melts (e.g. Webster et al., 2009). When Cl reaches saturation it will partition into the vapor phase, and degas from basaltic melts (Boyce and Hervig, 2008; Patiño Douce and Roden, 2006; Shinohara, 2009; Ustunisik et al., 2011; Ustunisik et al., 2015; Webster et al., 1999). Sharp et al. (2010b) suggested that under anhydrous lunar magmatic conditions the bonding potentials of both isotopes ($^{35}\text{Cl}$ and $^{37}\text{Cl}$) are similar. The kinetic loss of $^{35}\text{Cl}$ is not cancelled out by the loss of $^{37}\text{Cl}$ via bond incorporation (e.g. HCl$_{(g)}$). The melt is then enriched in $^{37}\text{Cl}$ explaining the heavy $\delta^{37}\text{Cl}$ values acquired by late-crystallizing apatite. Theoretical modeling of Cl isotope fractionation during degassing of metal chloride species indicates that a $\delta^{37}\text{Cl}$ increase of up to 20 ‰ is expected for 95% Cl loss as FeCl$_2$ (Sharp et al., 2010a; Ustunisik et al., 2015), which could explain the range in $\delta^{37}\text{Cl}$ values exhibited by apatite from most mare basalt samples (Barnes et al., 2016; Boyce et al., 2015; Sharp et al., 2010a; Tartèse et al., 2014a). It is important to note that the H $\ll$ Cl conditions required in the Sharp et al. (2010a) model does not necessarily imply that lunar melts were dry, but it does require melt H $\ll$ Cl at the time of Cl degassing. It should also be noted that other lines of evidence for magmatic degassing from lunar melts is recorded in the literature, through coatings on glass beads (McKay et al., 1972),
fractionations of H (Hauri et al., 2015 and references therein), and C (Wetzel et al., 2015) isotope systems. The large inter- and intra-sample $\delta^{37}\text{Cl}$ variations measured in apatite across Apollo samples, with vastly different petrogenesis seem difficult.

5.5. Vapor-phase interactions

Near-surface fractionation of Cl isotopes via Cl evaporation (as HCl, as well as organic and metal compounds) has been suggested as a potential mechanism to induce fractionation in terrestrial systems (Gola et al., 2005), which is supported by modelling (Richet et al., 1977), as well as experimental work (Huang et al., 1999; Liebscher et al., 2006), and thought to be responsible for elevated signatures (~32 ‰) in lunar granulite 79215 (Treiman et al., 2014). It is, therefore, conceivable that a volatile-rich vapor, enriched in $^{37}\text{Cl}$, interacted with the late-stage Apollo 14 basaltic and impact melts, similar to what has been proposed by Treiman et al. (2014) to account for elevated apatite $\delta^{37}\text{Cl}$ values in granulite 79215. Vapor phase crystallization of a variety of minerals, including oxides, halides, iron, and alkali, has been reported in vugs within Apollo 14 breccias (McKay et al., 1972). This vapor phase, noted to have contained chlorides, has been attributed to thermal metamorphism immediately following the deposition of the Fra Mauro ejecta blanket from the Imbrium Basin (McKay et al., 1972), the source of which would be a volatile-rich rock in the shallow crust. Thermal metamorphism has also been attributed to Apollo 14 volcanic rocks 14053 and 14072 undergoing subsolidus alteration, as mentioned above (Taylor et al., 2004).

Vapor-phase metasomatism could have enriched individual mesostasis regions in Cl with minimal effect on their $\text{H}_2\text{O}$ budgets (if the metasomatic agent was low in H for example), and, at the same time, increased apatite $\delta^{37}\text{Cl}$ values. Such mechanism could, therefore, induce
heterogeneous increase of apatite $\delta^{37}\text{Cl}$ values and Cl contents depending on the timing and degree of interaction. No strong correlation between apatite Cl and H$_2$O abundances and $\delta^{37}\text{Cl}$ values is expected in this scenario since measured abundances would be variable depending on the initial apatite volatile contents. Such a process could also create variations of apatite volatile abundances and isotopic compositions from grain to grain and from mesostasis area to mesostasis area in a single sample depending on the apatite size or the local permeability, for example. In the case of granulite 79215, Treiman et al. (2014) suggested that the addition of P and halogens due to vapor-phase metasomatism triggered growth of large apatite crystals characterized by homogeneous, elevated $\delta^{37}\text{Cl}$ values. Although in this same sample, 79215, Barnes et al. (2016) found variations in $\delta^{37}\text{Cl}$ values on the order of ~10‰. Furthermore, the Treiman et al. (2014) study suggested apatite crystallization in 79215 was induced from P-rich vapor. Recent work, on S abundances in lunar apatite, has also suggested that metasomatic alteration by a S-Cl-bearing volatile phase is responsible for Cl-S zoning observed in apatite in some mare basalts (Konecke et al., 2017). During the final stages of solidification of the studied Apollo 14 samples, a metasomatic agent could have interacted with the melt, altering Cl isotope ratios and abundances. The large variation in $\delta^{37}\text{Cl}$ values could thus suggest that some apatite formed prior to interaction with a metasomatic agent, while others grew after variable metasomatism. It is also plausible that the high-Al basalts assimilated vapor phase products during lava flow on the lunar surface, in a similar way to how variable amounts of KREEP material were assimilated to these basalts (Hui et al., 2011; Hui et al., 2013). This variability in assimilation, and in the original Cl isotope signatures of vapor phase products, could account for the large inter- and intra-sample heterogeneity of Cl isotopes observed in these samples.
It has been suggested that lunar ejecta blankets, such as the Fra Mauro unit, could have initiate non-volcanic fumarole activity (McKay et al., 1972). Vapors released during crystallization within hot zones (~ 1000 °C) percolate up through colder zones where non-condensable gases (i.e. Cl) may escape through the ejecta blanket forming fumaroles (Fig. 6; Shearer et al., 2014). This process has also been identified in ‘rusty-rock’ 66095 (Shearer et al., 2014) and is similar to the mechanism proposed to explain crystallization of large apatite with elevated δ³⁷Cl values in granulite 79215 (Treiman et al., 2014). Vapor condensation has also been proposed as a mechanism to explain volatile contents in lunar glass beads (74220, 15426) and 66095 (Day et al., 2017). The two samples, 66095 and 79215, have yielded dates around 3.9 Ga (Fischer-Gödde and Becker, 2012; Norman et al., 2006; Snape et al., 2017), similar to the Apollo 14 samples studied here (Table 1). Altogether, these samples hint at the widespread occurrence of vapor-related metasomatism during a period when the impact flux on the lunar surface may have been particularly high (Gomes et al., 2005; Morbidelli et al., 2012; Tera et al., 1974). As samples 66095 and 79215 are from landing sites on the western limb of the nearside, this work extends the geographical occurrence of vapor-rich metasomatism on the lunar surface to include the Apollo 14 site on the mid-eastern section of the nearside, hinting at large-scale volatile release during this period, possibly related to the Imbrium impact event.

6. Conclusions

Understanding processes that have affected the volatile contents and isotopic compositions of lunar samples is important for constraining the volatile budget of the lunar interior. The Apollo 14 samples studied here have provided an opportunity to explore the various processes that can fractionate Cl isotopes in lunar magmatic and surface environments. The interaction
with a KREEP component, during the Apollo 14 samples petrogenesis, is expected to have
imprinted an elevated $\delta^{37}$Cl signature. Instead, other process(es) must be responsible for the
wide-range, elevated, $\delta^{37}$Cl values of the Apollo 14 samples investigated. We propose that
magmatic degassing, as first suggest by Sharp et al. (2010) could explain the elevated $\delta^{37}$Cl
signature of Apollo 14 melts but that this process alone could not account for the variability of
isotopic signatures observed in these rocks. The mechanism we ultimately favor, to explain the
large intra- and inter-sample variability in $\delta^{37}$Cl isotope values measured, is variable interaction
of late-stage melts with a Cl-rich vapor-phase. The presence of vapor-induced metasomatism
in these samples points to the presence of wide-spread fumarolic activity on the nearside of the
Moon at $\sim$ 4 Ga.

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Figure Captions

Figure 1: Ternary diagram of apatite X-site occupancy (mol%), assuming that X-site is completely filled with F + Cl + H₂O. F was calculated by difference for all analyses expect those with F abundances reported in Table 3. Literature data from McCubbin et al., (2015), and references therein.

Figure 2: δ³⁷Cl data for volcanic samples (see text) 14053, 14072, and 14321,1482 plotted against (A) Cl and (B) H₂O abundances, and for impact melt samples (see text) 14073 and 14310 plotted against (C) Cl concentration (D) H₂O abundances.

Figure 3: All available δ³⁷Cl data plotted against (A) H₂O (ppm), and (B) Cl (ppm) with fields for literature data.. Literature data from Barnes et al. (2016), Boyce et al. (2015), Tartèse et al. (2014a), Treiman et al. (2014), and Sharp et al. (2010). NWA refers to KREEP-rich clast in NWA4472 from Tartèse et al. (2014b). Note the difference in VHK and granulite fields between A and B result from the highest δ³⁷Cl values for each rock type not having H₂O abundance associated with them.

Figure 4: All available δ³⁷Cl data for Apollo samples plotted against bulk rock La/Lu. La and Lu abundances averaged from data taken from Lunar Sample Compendium. References are given in SM1 Table 1. Literature data from Barnes et al. (2016), Boyce et al. (2015), Treiman et al. (2014), and Sharp et al. (2010). ‘14321’ refers to 14321,1482.

Figure 5: F abundance of apatite (wt.%) plotted against δ³⁷Cl values for samples in this study. F contents are those either measured (see Table 2) or calculated by difference assuming the X-site is completely filled with F + Cl + H₂O. ‘14321’ refers to 14321,1482.

Figure 6: Schematic diagram of vapor-release metasomatism following impact-events or emplacement of lava flows. After an impact-event or volcanic eruption, a hot zone (~1000 °C) develops underneath the ejecta blanket/lava flow. As crystallization occurs in this hot zone, vapors are released. These vapors travel up through the solidifying ejector blanket/lava flow allowing for vapor interaction with warmed-up/solidifying rock. Cartoon after Shearer et al. (2014) and McKay et al. (1972).
Figure 1

A ternary plot showing the distribution of Cl, H₂O, and F concentrations. Different symbols and colors represent various samples:
- Diamonds: 14053
- Purple diamonds: 14072
- Orange diamond: 14321, 1482
- Pink diamonds: 14073
- Green diamonds: 14310
- Gray circles: mare basalts
- Gray squares: KREEP basalts
- Gray downward triangles: Mg- and alkali-suite
- Gray upward triangles: VHK
Figure 4
Table 1: Radiometric dates obtained for Apollo 14 samples studied here and their geochemical grouping. All dates are in Ga. Data from a) Husain et al. (1971), b) Papanastassiou and Wasserburg (1971), c) York et al. (1972), d) Compston et al. (1972b), e) Dasch et al. (1987), f) Turner et al. (1972), g) Mark et al. (1974), and h) Tatsumoto et al. (1972). *Rb-Sr data re-processed with updated decay constant, all dates from Hui et al. (2013). **14072 does not belong to any group of high-Al basalts but is geochemically intermediate between Group A and C. Note a crystallization age of 3905 ± 8 Ma has also been determined for 14072 from Pb/Pb dating by Snape et al. (2016).

<table>
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<th>Sample</th>
<th>40Ar/39Ar</th>
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<th>Rb-Sr*</th>
<th>Group</th>
<th>Crystallization</th>
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<td>3.96 ± 0.04^b</td>
<td>3.94 ± 0.03</td>
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<td>14072</td>
<td>4.04 ± 0.05^c</td>
<td>3.99 ± 0.09^d</td>
<td>3.98 ± 0.15, 3.98 ± 0.09</td>
<td>A – C**</td>
<td>open</td>
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<tr>
<td>14321,1482</td>
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<td></td>
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<tr>
<td>14073</td>
<td>3.88 ± 0.05^e</td>
<td>3.88 ± 0.04^a</td>
<td>3.86 ± 0.02</td>
<td>impact melt</td>
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<td>14310</td>
<td>3.88 ± 0.05^f</td>
<td>3.94 ± 0.03^g</td>
<td>3.85 ± 0.02, 3.92 ± 0.06, 3.90 ± 0.19</td>
<td>impact melt</td>
<td>closed</td>
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Table 2: Measured Cl isotopic values (‰), and background corrected Cl (ppm), H$_2$O (ppm), and F (wt.%) abundances of apatite in the Apollo 14 samples analyzed in this study. (B) and (C) refer to Fig.2 panel for 14072,13.

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<th>$2\sigma$ (‰)</th>
<th>Cl (ppm)</th>
<th>$2\sigma$ (ppm)</th>
<th>H$_2$O (ppm)</th>
<th>$2\sigma$ (ppm)</th>
<th>F (wt.%)</th>
<th>$2\sigma$ (%)</th>
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