# Early loss, fractionation, and redistribution of chlorine in the Moon as revealed by the low-Ti lunar mare basalt suite

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A B S T R A C T

The relative abundances of chlorine isotopes measured in low-Ti basalts from the Moon appear to reflect mixing between two reservoirs: One component representing the urKREEP—the final product of the crystallization of the lunar magma ocean—with $\delta^{37}Cl = +25‰$ (relative to Standard Mean Ocean Chlorine), the other representing either a mare basalt reservoir or meteoritic materials with $\delta^{37}Cl \sim 0‰$. Using the abundances of other KREEP-enriched elements as proxies for the abundance of Cl in low-Ti mare basalts—which is difficult to constrain due to magmatic processes such as fractional crystallization and degassing—we find that the urKREEP contains $\sim28$ times higher Cl abundance (25–170 ppm Cl) as compared to the low-$\delta^{37}Cl$ end member in the observed mixing relationship. Chlorine—with an urKREEP/C.I. ratio of 0.2 to 1.5—is 500 to 3400 times less enriched than refractory incompatibles such as U and Th, and is consistent with incomplete loss of Cl species taking place during or prior to the magma ocean phase. The preservation of multiple, isotopically distinct reservoirs of Cl can be explained by: 1) Incomplete degassing pre- or syn-giant impact, with preservation of undegassed chondritic Cl and subsequent formation of an enriched and isotopically fractionated reservoir; or 2) Development of both high-concentration, high-$\delta^{37}Cl$ and low-concentration, low-$\delta^{37}Cl$ reservoirs during the degassing and crystallization of the lunar magma ocean. A range of model bulk lunar Cl abundances from 0.3–0.6 ppm allows us to place Cl in the context of the rest of the elements of the periodic table, and suggests that Cl behaves as only a moderately volatile element during degassing. Chlorine isotope fractionation resulting from loss syn- or pre-magma ocean is characterized by $1000 \bullet \ln[\alpha] = -3.96$ to $-4.04$. Abundance and isotopic constraints are consistent with the loss of Cl being limited by vaporization of mixtures of Cl salts such as HCl, $ZnCl_2$, $FeCl_2$, and NaCl. These new constraints on the chlorine abundance and isotopic values of urKREEP make it a well-constrained target for dynamic models aiming to test plausible conditions for the formation of the Earth–Moon system.

## 1. Introduction

The systematic depletion of volatile elements in lunar rocks and estimates of bulk lunar abundances based on those rocks is a fundamental constraint on the formation and evolution of the Earth–Moon system (Barr, 2016 and references therein; Day and Moynier, 2014; Hauri et al., 2015; McCubbin et al., 2015a). The loss of moderately to highly volatile elements is also associated with measurable—in some cases quite large—isotopic fractionations

(Day and Moynier, 2014; Day et al., 2017; Herzog et al., 2009; Kato and Moynier, 2017; Paniello et al., 2012; Pringle and Moynier, 2017; Wang and Jacobsen, 2016a). One such example is Cl, which has two stable isotopes ($^{35}Cl$ and $^{37}Cl$) that are fractionated tens of per mille (‰; parts per thousand) more in lunar rocks than in their terrestrial equivalents (Sharp et al., 2010a). There are two kinds of chlorine isotope data available for lunar basalts: 1) High-precision ($<1‰$ $2\sigma$) conventional mass spectrometry measurements, sometimes reported with separate $\delta^{37}Cl$ measurements on soluble and insoluble portions of bulk samples, and 2) Lower-precision (1–3‰ $2\sigma$), *in situ* secondary ion mass spectrometry (SIMS) measurements of the Cl-rich phase apatite, a mineral that

is present in most lunar basalts. For variations of the magnitude observed on the Moon (from $-4‰$ to $+81‰$; Boyce et al., 2015; Wang et al., 2012), both techniques can provide useful but different information about the rocks sampled.

Early models (Sharp et al., 2010a) based on a combination of SIMS and conventional mass spectrometry data suggested that these highly fractionated basalts could only form by anhydrous degassing of metal chloride such as NaCl, $FeCl_2$, or $ZnCl_2$ during eruption. However, this model is inconsistent with experimental data showing large fractionations during evaporation of HCl (Sharp et al., 2010b), the presence of hydrogen in samples with elevated $\delta^{37}Cl$ (Boyce et al., 2010, 2015; Greenwood et al., 2011; McCubbin et al., 2010; Potts et al., 2018), and the observation that the highest Cl abundances are associated with elevated $\delta^{37}Cl$ (Barnes et al., 2016; Boyce et al., 2015).

An alternative model was presented by Boyce et al. (2015) and later by Barnes et al. (2016) in which elevated $\delta^{37}Cl$ measurements were attributed to mixing between light and heavy isotopic reservoirs of Cl within the Moon: The light reservoir ($\delta^{37}Cl \leq 0‰$) was suggested to be the uncontaminated signal of mare basalts, whereas the heavy reservoir ($\delta^{37}Cl > +25‰$) was attributed to the urKREEP—the last vestige of the lunar magma ocean. The fractionation mechanisms proposed by Sharp et al. (2010a) are consistent with the model of Boyce et al. (2015) with the caveat that the timing of degassing was different with the latter model attributing the degassing and related fractionation to the magma ocean following the giant impact that formed the Earth–Moon system. Incompatible elements—including Cl—are assumed to be concentrated into the urKREEP during the crystallization of the lunar magma ocean (Warren and Wasson, 1978, 1979). Correlations between these abundances and $\delta^{37}Cl$ are the primary evidence for the urKREEP being the source of heavy Cl on the Moon (Boyce et al., 2015).

Here, we continue this line of thinking to use chlorine isotopes in lunar basalts to further constrain the planet-scale chemical evolution of the early Earth–Moon system.

### 1.1. Relationship between chlorine isotopes and incompatible elements

Elevated $\delta^{37}Cl$ values are observed in apatite crystals that are rich in Cl, consistent with a reservoir enriched in Cl, and relatively enriched in $^{37}Cl$ over $^{35}Cl$ (Boyce et al., 2015). Chlorine isotope ratios are also observed to increase with increasing bulk Th and La/Lu, both indicators of an urKREEP component in the basalt (Neal and Taylor, 1989; Warren and Wasson, 1978). Barnes et al. (2017) noted that this relationship only appears to hold for low-Ti and KREEP-rich basalts (which are also low in Ti), but that high-Ti basalts do not appear to define the same $\delta^{37}Cl$-trace element relationship. This is consistent with overall petrogenetic relationships of the low-Ti and high-Ti basalts, which are thought to derive from different source regions within the lunar mantle, possibly at different depths (Krawczynski and Grove, 2012; Longhi, 1992; Shearer et al., 2006). It is also consistent with the "neuKREEP" hypothesis of Jerde and Taylor (Jerde et al., 1993; Jerde and Taylor, 1993), who suggested that the high-Ti basalts derived their trace element systematics by incorporating a different material than did the low-Ti basalts. The recent work of Barnes et al. (2017) supports this hypothesis, although more work is needed to determine and subsequently evaluate the systematics of the high-Ti basalts, which are not described in detail here.

In order to test the hypothesis that the urKREEP is the source of elevated $\delta^{37}Cl$ in low-Ti and KREEP basalts, we have expanded the analysis of Boyce et al. (2015) comparing in situ $\delta^{37}Cl$ measured in apatite and bulk trace elements to include a larger number of samples. When considering any $\delta^{37}Cl$-trace element relationship, one concern is that the elements correlating positively with $\delta^{37}Cl$

are all compatible in apatite (Cl, Th, REE), which might implicate apatite itself as the culprit in generating these relationships. One possibility would be that there is an unidentified lithology with $^{37}Cl$-rich, Cl-rich apatites that can generate mixing arrays via contamination. In order to address this we have also considered a wider range of elements with different geochemical affinities including large ion lithophile (K, Ba) and high field strength (Zr, Hf) elements, which do not partition favorably into apatite. This choice of elements with diverse geochemical behavior—saving for their incompatibility in the phases crystallizing from the lunar magma ocean—uniquely tests the hypothesis that the urKREEP is the source of elevated $\delta^{37}Cl$ in the low-Ti suite of lunar mare basalts.

### 1.2. Mixing models

Ideally, one would use hyperbolic mixing relationships to constrain the isotopic composition of the two end members (in this case $\delta^{37}Cl_{mare}$ and $\delta^{37}Cl_{urKREEP}$), as well as the elemental abundances ($Cl_{mare}$ and $Cl_{urKREEP}$, with the former representing the KREEP-free abundance in mare basalts, and the latter representing the Cl content of the urKREEP). This would be a valuable contribution to our understanding of the Moon, as Cl is a volatile element and the volatile budget of the Moon is an important and active field of study (Hauri et al., 2015). However, the aforementioned analysis requires knowledge of the Cl content of the basalts studied. This is a problem because the three methods we have for constraining the Cl content of mare basalts—bulk measurements; melt inclusions; apatite volatile barometry—are flawed (see supplemental information). The almost certainty with which the assertions of any $\delta^{37}Cl$–$Cl_{apatite}$ model that relies on Cl estimates are violated would make any result suspect at best. In the following paragraphs we outline a more robust strategy.

### 1.3. Modeling Cl isotopic mixing by proxy

The concomitant enrichment of all incompatible elements in the urKREEP provides an alternative to using Cl abundances in bulk rocks or apatites to constrain $Cl_{mare}$ and $Cl_{urKREEP}$. We can use other elements for which more robust bulk estimates are available as proxies for Cl, and build mixing models with those elements taking the place of Cl. For mixtures with component moles of Cl here labeled $Cl_A$, $Cl_B$, (etc.), and isotopic compositions $\delta^{37}Cl_A$, $\delta^{37}Cl_B$, (etc.), the canonical equation for mixtures where the components have small differences is given by

$$\delta^{37}Cl_{Total}Cl_{Total} \approx \delta^{37}Cl_A Cl_A + \delta^{37}Cl_B Cl_B + \delta^{37}Cl_C Cl_C + \cdots \quad (1)$$

this simplifies in the binary case to solve for a magma contaminated by urKREEP to be:

$$\delta^{37}Cl_{Total} \approx \frac{(\delta^{37}Cl_{mare}Cl_{mare} + \delta^{37}Cl_{urKREEP}Cl_{urKREEP})}{Cl_{Total}} \quad (2)$$

It should be noted that the approximation used above differs slightly from the exact solution—which treats moles of $^{35}Cl$ and $^{37}Cl$ as separate species instead of relying on $\delta^{37}Cl$ values—by $\leq 0.04‰$ for these scenarios. In our case, $Cl_{mare}$ and $Cl_{urKREEP}$ in Eq. (2) are unknown. We can use other elements for which more robust bulk estimates are available as proxies for Cl, and build mixing models with those elements taking the place of Cl:

$$\delta^{37}Cl_{Total} \approx \frac{(\delta^{37}Cl_{mare}X_{mare} + \delta^{37}Cl_{urKREEP}X_{urKREEP})}{X_{Total}} \quad (3)$$