

THE CHLORINE ISOTOPIC COMPOSITION OF LUNAR URKREEP. J. J. Barnes^{1,*}, R. Tartèse^{1,2}, M. Anand^{1,3}, F. M. McCubbin⁴, C. R. Neal⁵, and I. A. Franchi¹, ¹ Planetary and Space Sciences, The Open University, Milton Keynes, MK7 6AA, UK, *Jessica.barnes@open.ac.uk, ²IMPMC, Muséum National d'Histoire Naturelle, Paris, 75005, France, ³Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK, ⁴NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, Texas 77058, USA, ⁵Department of Civil & Environmental Engineering & Earth Science, University of Notre Dame, IN, 46556, USA.

Introduction: Since the long standing paradigm of an anhydrous Moon [1] was challenged there has been a renewed focus on investigating volatiles in a variety of lunar samples (e.g., [2-9]). Numerous studies have examined the abundances and isotopic compositions of volatiles in lunar apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$ [3-7]. In particular, apatite has been used as a tool for assessing the sources of H_2O in the lunar interior (e.g., [3-5]). However, current models for the Moon's formation have yet to fully account for its thermal evolution in the presence of H_2O and other volatiles [10-11]. For example, in the context of the lunar magma ocean (LMO) model, it is anticipated that chlorine (and other volatiles) should have been concentrated in the late-stage LMO residual melts (i.e., the dregs enriched in incompatible elements such as K, REEs, and P, collectively called KREEP, and in its primitive form – urKREEP, [12]), given its incompatibility in mafic minerals like olivine and pyroxene, which were the dominant phases that crystallized early in the cumulate pile of the LMO (e.g., [13]). When compared to chondritic meteorites and terrestrial rocks (e.g., [14-15]), lunar samples have exotic chlorine isotope compositions (Figure 1, [7,16-19]), which are difficult to explain in light of the abundance and isotopic composition of other volatile species, especially H, and the current estimates for chlorine and H_2O in the bulk silicate Moon (BSM) [2,20].

In order to better understand the processes involved in giving rise to the heavy chlorine isotope compositions of lunar samples, we have performed a comprehensive *in situ* high precision study of chlorine isotopes in lunar apatite from a suite of Apollo samples covering a range of geochemical characteristics and petrologic types.

Samples: The polished thin-sections of Apollo lunar samples investigated in this study were 10044, 10058, 14304, 15386, 15555, 70035, 76535, 78235 and 79215. Twenty nine apatite grains were identified as being suitable for analysis by ion probe. Our sample set includes low-Ti, high-Ti, KREEP and very high potassium (VHK) basalts, and selected plutonic highlands rocks from the magnesian suite.

Methods: The Cl content and Cl isotopic composition of lunar apatite grains were measured using the Cameca NanoSIMS 50L at the Open University following a protocol modified after Tartèse et al. [18]. A

primary Cs^+ beam of ~ 50 pA was used. Negative secondary ions of $^{16}\text{O}^1\text{H}$, ^{18}O , ^{35}Cl , and ^{37}Cl were collected simultaneously on electron multipliers, and $^{40}\text{Ca}^{19}\text{F}$ was used to locate apatite using real time isotope imaging. Typically, areas of $\sim 5 \times 5 \mu\text{m}$ were analyzed and electronic gating was applied to collect data from the inner 25% of each analysis area.

Results and discussion: Figure 1 shows the results obtained during this study [19]. The Cl isotopic composition of apatite from low- and high-Ti mare basalts are consistent with previous studies [7,16], with $\delta^{37}\text{Cl}$ values from $\sim +2$ to $+18$ ‰ and Cl contents from ~ 0.01 to 0.4 wt.% Cl.

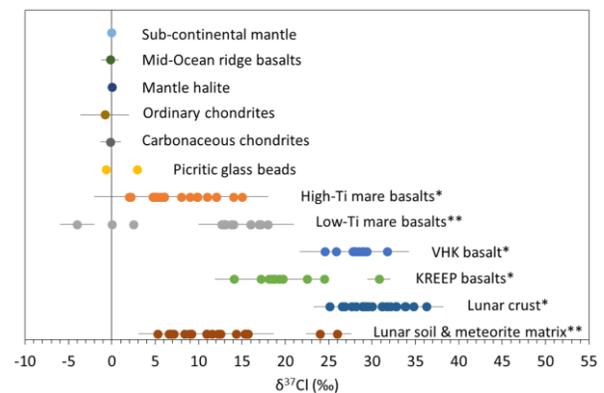


Figure 1. The chlorine isotopic compositions of different objects in the Solar System. All of the data available for lunar samples [7,16-19] have been plotted together with their individual uncertainties. The other data are from Sharp et al. [14-15]. *data from the *in situ* analyses of apatite and **data included from both *in situ* analyses of apatite and bulk Cl measurements.

In contrast, apatite from KREEP-rich basalts such as KREEP basalt 72275 [16] and very high potassium (VHK) basalt 14304 have distinctly heavier Cl isotopic compositions than apatite found in mare basalts (Figure 1). Similarly apatite from highlands samples display very heavy Cl isotopic compositions ($>+20$ ‰) and have >0.5 wt.% Cl.

Magmatic degassing. H_2O in apatite from mare basalts is generally characterized by H-isotopic compositions that are elevated ($>+500$ ‰) relative to Earth (e.g., [3-4]). One of the explanations put forward for this is the degassing of H_2 from mare magmas which had starting H isotopic compositions similar to Earth's

mantle (~ 0 ‰, [4]). Degassing has also been proposed to explain the heavy Cl isotope values of lunar samples, provided that low H/Cl ratios prevailed in the parent magma to permit degassing of metal chlorides [16,21]. However, it is difficult to reconcile both the H & Cl isotopic compositions and OH-rich nature of apatite in some mare basalts with a Cl degassing model [16] given the partitioning relationships for volatiles between apatite and melt [22]. Samples 72275 and 78235 are considered to have escaped degassing and their apatite contain H₂O with lower H isotopic compositions [5-6], which are simultaneously characterized by elevated Cl isotopic compositions (Figure 1). Therefore, these rocks are particularly good candidates with which to understand the primordial signatures of H and Cl in the Moon.

Relating Cl-isotopes to KREEP assimilation. We investigated whether the heavy Cl isotope compositions of lunar rocks could be related to the proportion of KREEP component they contain, by comparing the Cl isotope compositions of apatite with bulk-rock incompatible trace element data. Figure 2 shows that there is a strong positive correlation between apatite $\delta^{37}\text{Cl}$ values and La/Sm ratios, which strongly indicates mixing between a mantle source with low Cl isotopic composition (~ 0 ‰) and a KREEP-rich component characterized by a $\delta^{37}\text{Cl}$ value $\sim +30$ ‰.

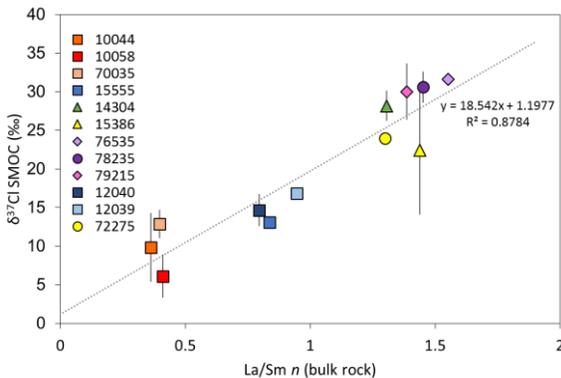


Figure 2. New Cl isotope data for lunar apatite (averages) compared to carbonaceous chondrite-normalized La/Sm bulk-rock ratios from the literature. Uncertainties represent the standard deviation in the $\delta^{37}\text{Cl}$ values of apatite for each sample. The Cl isotope data for 12039 and 12040 are from Boyce et al. [7], and 72275 is from Sharp et al. [16].

How did urKREEP obtain a heavy Cl isotopic composition? The internal differentiation of the Moon via a LMO predicts a volatile-rich urKREEP layer dominated by Cl, containing at least 1350 ppm Cl [2]. Boyce et al. [7] have proposed that degassing of Cl from the LMO would account for the fractionation of Cl isotopes and $\delta^{37}\text{Cl}$ values $\sim +30$ ‰ in the residual

urKREEP layer. Whilst the LMO model provides an elegant mechanism for concentrating Cl in the Moon, the solubility of Cl in basaltic silicate liquids is high (e.g., [23]) and the confining pressure beneath the 30-40 km of lunar crust [24] would be sufficient to prevent the loss of Cl by degassing.

Therefore, in order to explain the fractionated Cl isotopic composition of urKREEP, we envisage a scenario in which, during the latter stages of LMO crystallization (>95 %), a large bolide punctured the lunar crust [25] to a depth sufficient to expose the urKREEP layer to the vacuum of space, which drastically decreased the solubility of Cl in the residual LMO magmatic liquids and enabled degassing of metal chlorides [16] into a vacuum, leading to the fractionation of Cl isotopes. If such an event was restricted to the nearside of the Moon, i.e., the Procellarum KREEP Terrane, then one would expect rocks from outside of this region to have relatively unfractionated Cl isotope compositions. Additionally, important insights into the processes operating to fractionate chlorine isotopes could be gleaned from studies of other reduced, airless, and differentiated bodies [26].

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