CHLORINE IN LUNAR BASALTS.

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Introduction: 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, [1]), 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., [2]).

When compared to chondritic meteorites and terrestrial rocks (e.g., [3-4]), lunar samples often display heavy chlorine isotope compositions [5-9]. Boyce *et al.* [8] found a correlation between $\delta^{37}Cl_{Ap}$ and bulk-rock incompatible trace elements (ITEs) in lunar basalts, and used this to propose that early degassing of Cl (likely as metal chlorides) from the LMO led to progressive enrichment in remaining LMO melt in ^{37}Cl over ^{35}Cl – the early degassing model. Barnes *et al.* [9] suggested that relatively late degassing of chlorine from urKREEP (to yield $\delta^{37}Cl_{urKREEP} >+25‰$) followed by variable mixing between KREEPy melts and mantle cumulates (characterized by $\delta^{37}Cl \sim 0‰$) could explain the majority of Cl isotope data from igneous lunar samples.

In order to better understand the processes involved in giving rise to the heavy chlorine isotope compositions of lunar samples, we have performed an *in situ* study of chlorine isotopes and abundances of volatiles in lunar apatite from a diverse suite of lunar basalts spanning a range of geochemical types.
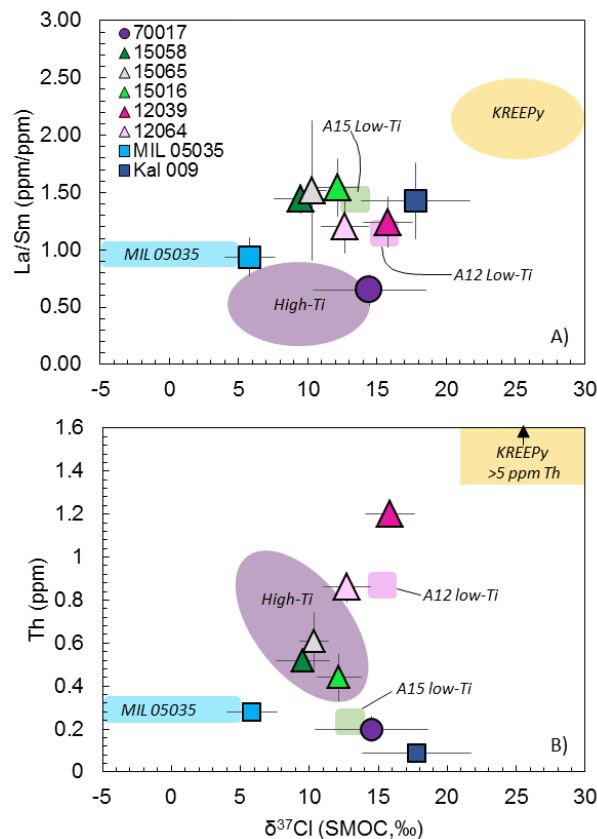
Samples studied: Two Apollo 12 basalts, 12039 a coarse-grained pigeonite basalt and 12064 a coarse-grained sub-ophitic ilmenite basalt, were studied. They have crystallization ages of between ~3.1 and 3.2 Ga [10-11]. Of the Apollo 15 basalts studied, 15016 is a vesicular, medium-grained, olivine-normative basalt, 15058 is a sub-ophitic pigeonite basalt, and 15065 is a coarse-grained, low-Ti basalt. These samples have crystallization ages of between ~3.3 and ~3.5 Ga [11]. 70017 is a medium-grained, vesicular, 'unclassified' high-Ti basalt from Apollo 17 that has a crystallization age of ~3.7-3.8 Ga [11]. Miller Range (MIL) 05035 is an ITE depleted lunar gabbroic meteorite of low-Ti bulk-composition that has a crystallization age of between ~3.8 and 3.9 Ga [12]. Kalahari 009 is a fragmental basaltic meteorite containing very low-Ti lunar basalt components [13-14]. It is one of the most ITE de-pleted and oldest lunar basalts (crystallization age of ~4.35 ± 0.15 Ga, [13]) available for study.

Methods: Isotopic analyses of apatite were acquired using the Open University NanoSIMS 50L following a procedure similar to that of Barnes *et al.* [9]. The NanoSIMS was operated in multicollection mode and negative secondary ions of ^{16}OH, ^{18}O, ^{19}F, ^{35}Cl, ^{37}Cl were measured simultaneously with electron multipliers. A primary beam of ~30 pA was rastered over the sample across areas ~25 μm^2, no electronic gating was used. Standardization was performed with standards of known isotopic compositions and abundances.

Results: We acquired forty measurements from thirty one apatite crystals from the eight samples investigated. For the Apollo 12 low-Ti basalts (12039 and 12064) the $\delta^{37}Cl$ value varied from +10.3 ± 3 to +19.4 ± 2.6 ‰ (2σ), and Cl content from 0.04 to 0.26 wt.%. The Apollo 15 low-Ti basalts (15016, 15058, and 15065) gave apatite $\delta^{37}Cl$ values ranging from +7.4 ± 1.6 to +13.7 ± 2.0 ‰ (2σ), and Cl contents from 0.01 to 0.52 wt.%. Apollo 17 high-Ti basalt 70017 contained apatite with an average Cl isotopic composition of +14.5 ± 8.2 ‰ (2 SD), and an average Cl content of 0.36 ± 1.24 wt.% (2 SD). Lunar basaltic meteorites, MIL 05035 and Kalahari 009, gave average $\delta^{37}Cl_{Ap}$ values of +5.8 ± 3.6 ‰ and +17.8 ± 7.9 ‰ (2 SD), respectively. The chlorine content of apatite in MIL 05035 ranged from 0.66 to 0.95 wt.% and in Kalahari 009 from 0.08 to 0.54 wt.%.

Volatiles in lunar basalts: The H_2O contents of lunar apatite obtained in this study are comparable to what has been published previously for these samples [7,15-16], as are the apatite Cl abundances [8,13,15,17]. In addition, our new Cl isotope data for apatite in 12039 are comparable to those reported by Boyce *et al.* [8]. The results for apatite in MIL 05035 are not as depleted in ^{37}Cl as those reported by Boyce *et al.* [8] (-4 ± 2 ‰) but are very similar to the numerous data points presented by Wang *et al.* [18] (+3.8 ± 3.1 ‰). There is no discernable correlation, outside of analytical uncertainty, between $\delta^{37}Cl$ and Cl content of apatite within individual samples. Apatite in the high-Ti basalts show large intra-sample variations (6 to 8 ‰ (2 SD)) for samples in which more than 4 analyses were acquired [8-9], as well as inter-sample ranges in $\delta^{37}Cl$ (Fig. 1). In contrast, the low-Ti basalts show relatively restricted intra-sample variations (2 to 4 ‰, 2 SD) in $\delta^{37}Cl$.

Figure 1: Average Cl isotopic composition of apatite from lunar basalts (errors represent 1 standard deviation among measured values) versus average bulk (A) La/Sm and (B) Th abundances (uncertainties 1 SD level [11,14,17-20]). $\delta^{37}Cl$ data in the fields for MIL 05035, high-Ti, and KREEPy basalts come from [5,7-9,18]. The data used to construct the lunar low-Ti basalt fields comes only from samples not studied in the current work [5,8-9]. A12 and A15 refer to Apollo 12 and 15, respectively.

Is the Cl in all mare basalts related to KREEP contamination? Overall most of the samples from this study fit within the ranges defined by previous studies for the different geochemical types of lunar basalts (Fig. 1). The Apollo 12 mare basalts appear to have slightly heavier average $\delta^{37}Cl$ values than Apollo 15 mare basalts whilst having slightly lower La/Sm ratios and higher Th contents compared to basalts from Apollo 15. Crucially, the results from MIL 05035 and the low-Ti mare basalts fit on a crude mixing trend between a hypothetical mantle Cl reservoir (~0‰) and urKREEP (>+25‰) (denoted by the KREEPy basalts field in Fig. 1).

The current dataset, including new data from 70017, hints that the high-Ti basalts do not strictly conform to this trend (e.g., Fig. 1, [21]). This is not surprising given that current petrogenetic models for the formation of the high-Ti mare basalts favor source re-

gion heterogeneity over assimilation (of KREEP) to explain the geochemical characteristics of these basalts [e.g., 22]. If the high-Ti basalts as a group did not acquire their REEs (and other ITEs, including highly volatile elements) from urKREEP, then we should not expect them to plot on the mixing trend formed by the other lunar basaslts (Fig. 1), and that other magmatic processes and or geochemical reservoirs of Cl need to be considered when interpreting the $\delta^{37}Cl$ of the high-Ti mare basalts.

The results for Kalahari 009 are interesting since this is reported to be one of the most KREEP-poor basalts available for study, based on its low Th content (~0.09 ppm, [14]) and low abundances of La and Sm (0.8 and 0.56 ppm, respectively [14]), and yet Kalahari 009 has an average $\delta^{37}Cl_{Ap}$ value akin to the low-Ti basalts (Fig. 1). It is possible that Kalahari 009 sampled a portion of the lunar mantle Cl budget not yet recognized/sampled in the Apollo sample collection or by nearside mare basalts; alternatively it is possible that fractionation of chlorine isotopes occurred during the magmatic and subsquent history of this suspected 'cryptomare' [13].

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