

# THE CHLORINE ISOTOPIC COMPOSITION OF THE MOON AS REVEALED BY MELT INCLUSIONS.

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**Introduction:** Almost all known lunar samples exhibit heavier chlorine isotopic compositions ( $\delta^{37}\text{Cl}$ ) compared to the Earth. Several hypotheses have been put forward to explain this difference, based mostly on analyses of apatite in lunar samples complemented by some bulk-rock data. The earliest hypothesis argued for Cl isotope fractionation during the degassing of anhydrous basaltic magmas on the Moon [1]. Subsequently, an alternative scenario was proposed to explain the elevated  $\delta^{37}\text{Cl}$  in lunar basalts, which includes mixing between 2 potential reservoirs: a lighter one ( $\sim 0\text{‰}$ ), representative of mare-basalt source regions and an elevated one ( $\sim 25\text{--}30\text{‰}$ ), associated with a KREEP component. The heavier Cl isotopic composition of the KREEP component is thought to have been acquired either during the incremental degassing of the LMO [2] or by the degassing of the urKREEP layer exposed to the vacuum of space during crust-breaching impact event(s) [3].

A potential shortcoming with lunar Cl measurements to date, with the exception of few bulk measurements on lunar glasses [1], is that they have been performed on lunar apatite [1-4]. During the crystallization of mare magmas, apatite typically forms after >95% fractional crystallization and as such, it is not possible to confirm whether the Cl isotope fractionation occurs prior to or during the crystallization of the parent magma. In order to evaluate the possibility of isotopic fractionation during crystallization and eruption of lunar basalt, and explore other alternatives, a more pristine, early-crystallized phase should be targeted in the same samples from which apatite are also analyzed. Here we analyzed the Cl abundance and its isotopic composition in 38 olivine- and pyroxene-hosted melt inclusions (MI) in five Apollo basalts.

**Samples:** The samples investigated are low-K ilmenite basalt 10020, low-Ti basalts 12004, 12040 and 15016, and high-Al basalt 14072. We selected these samples from four Apollo landing sites, in order to ensure a broad regional coverage of the Moon as well as to document any lateral heterogeneity for Cl in the lunar mantle as sampled by mare magmas. We also selected these samples as Cl abundances of 10020, 12040 and 15016 were previously measured in olivine-hosted MI [5]; while Cl isotopic compositions and abundances have been reported for apatite in mare basalts 12040 [1-2], 15016 [3] and 14072 [4].

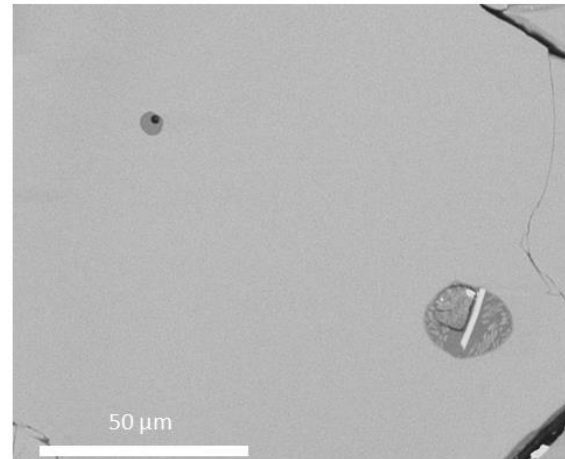


Figure 1: Glassy and crystallized olivine-hosted MI in Apollo section 12040,44.

**Analytical methods:** *Identification.* Olivine and pyroxene phenocrysts containing MI were identified by optical microscopy and the FEI Quanta 200 3D Dual Beam scanning electron microscope (Fig. 1) at The Open University (OU). Samples were also analyzed using a Jobin-Yvon Horiba LabRam HR Raman microprobe at the OU.

*Chlorine concentration and isotopic composition.* Cl abundance and its isotopic composition were measured using the Cameca NanoSIMS 50L at OU. A 300-500 pA  $\text{Cs}^+$  primary current ( $\sim 1\mu\text{m}$  spatial resolution) was rastered over the sample on areas ranging between  $10\mu\text{m} \times 10\mu\text{m}$  to  $30\mu\text{m} \times 30\mu\text{m}$ , depending on the sizes of MI. Secondary negative ions of  $^{18}\text{O}$ ,  $^{29}\text{Si}$ ,  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$  and  $^{27}\text{Al}^{16}\text{O}$  were imaged by scanning ion imaging. Regions of interest were determined on each image based on the  $^{27}\text{Al}^{16}\text{O}/^{18}\text{O}$  and  $^{35}\text{Cl}/^{18}\text{O}$  images to locate the MI and exclude any cracks, voids or Cl-rich hotspots associated with extraneous contamination (Fig. 2).

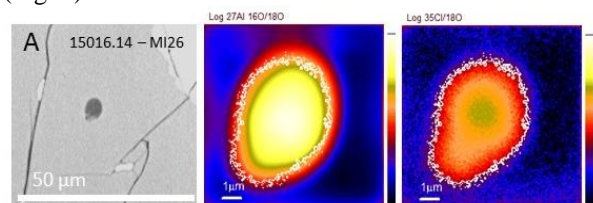


Figure 2: Back Scattered Electron image,  $^{27}\text{Al}^{16}\text{O}/^{18}\text{O}$  and  $^{35}\text{Cl}/^{18}\text{O}$  NanoSIMS images of olivine MI in sample 15016,14.

**Results:** Olivine-hosted MIs have a Cl concentration ranging from  $1.3 \pm 0.5$  ppm to  $28.2 \pm 6.4$  ppm (corrected from post-entrapment crystallization), with an average of  $3.3 \pm 1.4$  ppm. Higher Cl abundances (from  $2.9 \pm 0.5$  ppm to  $78.4 \pm 14.1$  ppm) are measured for pyroxene-hosted MI. In terms of  $\delta^{37}\text{Cl}$  values, olivine MIs in the 5 Apollo samples range from  $+6.6 \pm 9.0$  ‰ to  $+26.3 \pm 8.9$  ‰ (Fig. 3A), while pyroxene hosted-MIs range from  $+4.5 \pm 4.6$  ‰ to  $+33 \pm 4.2$  ‰ (Fig. 3B). No systematic differences are observed among the 5 samples and overall, olivine-hosted MIs and pyroxene-hosted MIs have weighted averages of  $+12.8 \pm 2.4$  ‰ and  $+10.1 \pm 3.2$  ‰, respectively, which are statistically indistinguishable.

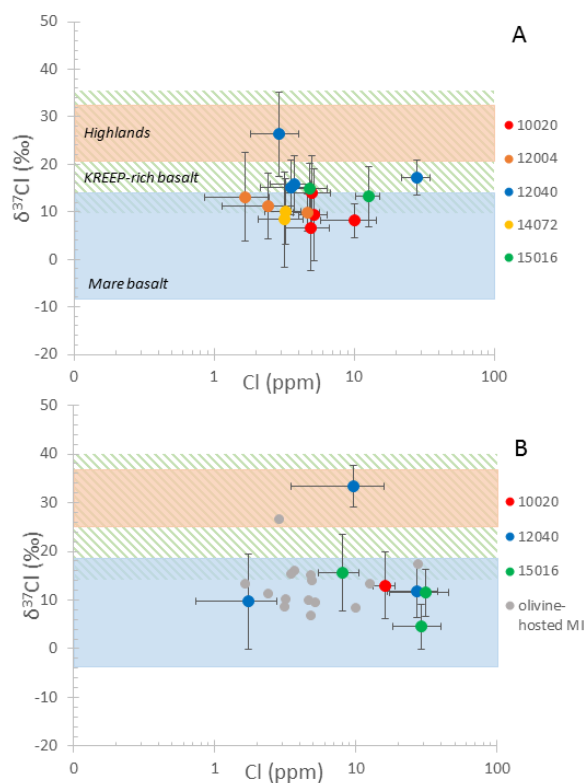


Figure 3:  $\delta^{37}\text{Cl}$  (‰) vs Cl (ppm) for olivine-hosted MI (top - A) and pyroxene-hosted MI (bottom - B) in 10020,31, 12004,51, 12040,44, 14072,13 and 15016,14 mare basalts. Colored bands represent data on apatites from major lunar lithologies [1-4]

**Discussion:** Chlorine concentration in lunar mantle. Cl concentration average of  $3.3 \pm 1.4$  ppm for olivine-hosted MI is in good agreement with previous measurements on Apollo 11, 12, and 15 lunar basalts (0.1-6 ppm) [5]. From our olivine MI results, we estimated a range of 0.1-1.4 ppm of Cl for the lunar mantle (for 5% to 30% partial melting), which is similar to the estimate of 0.14-0.83 ppm [6] and 0.4 ppm [1].

**Comparison with apatite data.** The chlorine isotopic compositions of 12040 and 15016 in both olivine and pyroxene-hosted MIs are similar to those measured in apatites [1-2;7]. However, this is not the case for sample 14072 [4] where the apatites are enriched in  $\delta^{37}\text{Cl}$  (+16.3 to +40.0‰) [4] compared to silicate MIs (+8.3‰ to +10.1‰). This feature is not observed in any other lunar basalt from Apollo 11, 12 or 15 and seems specific of Apollo 14 high-Al basalts. As explained by [4], Apollo Al-rich basalts, such as 14072, may have experienced post-crystallization processes, possibly metasomatism, resulting in additional Cl isotopic fractionation recorded by apatites but not melt inclusions.

For the four others basalts, the similarity between both olivine and pyroxene-hosted MI, and also apatite  $\delta^{37}\text{Cl}$  confirm that there is no Cl isotopic fractionation associated with crystallization or any other magmatic processes that would result in a preferential loss of the  $^{35}\text{Cl}$ . As such, it appears more likely that the primary magma of lunar basalts were already enriched in  $^{37}\text{Cl}$  relative to  $^{35}\text{Cl}$ , either an inherent pre-eruptive signature of mare magmas or that of their mantle source-regions, and that these signatures weren't altered in any significant manner during crystallization and eruption of the magma. Moreover, as MI measured in this study include samples collected from four separate geographical locations on the Moon, it is possibly indicative of a widespread enrichment in  $^{37}\text{Cl}$  relative to  $^{35}\text{Cl}$  in the basaltic lunar reservoirs, at least on the near side of the Moon. Interestingly, despite differences in bulk-rock trace-element compositions, the similarities in  $\delta^{37}\text{Cl}$  between 10020, 12004, 12040, 14072 and 15016 silicate MIs suggest that heavier Cl isotopic signatures are not directly correlated with KREEP signature and perhaps additional processes may have also played a role.

Overall, our findings are compatible with the hypothesis that in the majority of the cases the heavy Cl isotopic signature of the Moon was acquired during the earliest stages of Lunar Magma Ocean (LMO) evolution.

**References:** [1] Sharp Z.D. et al. (2010) *Science*, 329, 1050-1053. [2] Boyce J.W. et al. (2015) *Science Advances*, 1, 8. [3] Barnes J.J. et al. (2016) *EPSL*, 447, 84-94. [4] Potts N. et al., *GCA*, 230, 46-59. [5] Chen Y. et al. (2015) *EPSL*, 427, 37-46. [6] Hauri E.H. et al. (2011) *Science*, 333, 213-215. [7] Barnes J.J. et al. (2019) *GCA*, in press.