Chlorine in Brecciated Lunar Meteorite Nwa 12593: Implications for Lunar Volatile History

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CHLORINE IN BRECCIATED LUNAR METEORITE NWA 12593: IMPLICATIONS FOR LUNAR VOLATILE HISTORY.

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Introduction: Pristine lunar samples returned by the Apollo and Luna missions in the 1960s and 1970s have significantly broadened our understanding of the geological history of the Moon. The material these missions returned to Earth, however, were collected from an area that represents only a small proportion (~5 %) of the entire lunar surface [1]. Until new lunar material is returned from the upcoming Artemis, Luna and Chang'e missions, lunar meteorites are the only samples that may have originated from outside of the Apollo and Luna-sampled regions. These samples, therefore, provide less biased representation of the lunar surface's chemical and lithological diversity.

Northwest Africa (NWA) 12593, is a lunar fragmental breccia [2]. The rock is clast-rich, with mineral and lithic clasts embedded in a fine-grained vesicular impact melt matrix. Within the lithic clast population are crystalline impact-melt breccias, highlands, and basaltic clasts. The main minerals comprising this rock, in both clastic and isolated matrix mineral populations are anorthite, pigeonite, augite, olivine, with minor amounts of chromite, ilmenite, zircon, apatite and merrillite. The apatite grains in this sample are of considerable size (up to 70 µm in the longest dimension) and in texturally pristine condition within both lithic clasts and the matrix. As a major volatile-bearing phase in lunar samples, apatite in this sample could reveal new insights into the distribution and isotopic composition of volatile elements in areas of the Moon not sampled previously. Of the highlands lithologies preserved in NWA 12593, a number of them show affinities to ferroan anorthosites (FAN) sampled during the Apollo missions, but with slight chemical variance (more Ca-rich plagioclase (An$_{98}$) and Mg-rich mafic silicates (Mg# = ~73). There are also highlands-type clasts compositionally distinct from Apollo highlands sampled material, re-affirming a greater compositional diversity in lunar crustal rocks [3]. In this context, chlorine in the apatites of NWA 12593 could potentially be used to explore the heterogeneity in the distribution and isotopic composition of volatiles, as has been highlighted through recent work on Apollo samples [4].

Methods: Apatite grains in NWA 12593 were identified using an FEI Quanta 200 Scanning Electron Microscope (SEM) fitted with an Oxford Instruments Energy Dispersive X-ray detector, with an accelerating voltage of 20kV and beam current of 0.60nA. The chlorine content (Cl wt. %) and isotopic composition (δ^{37}Cl) of the apatites were then measured using the CAMECA NanoSIMS 50L at The Open University, using a 20pA probe current. Following a protocol adapted from [5-10], negative secondary ions of ^{13}C, ^{18}O, ^{35}Cl, ^{37}Cl and ^{40}Ca^{19}F were acquired simultaneously on electron multipliers in scanning ion imaging mode. Regions of interest (ROIs) were selected within the acquired images based on greater Cl abundance and homogeneity in ^{18}O and Cl images . The isotopic ratio of ^{37}Cl/^{35}Cl of the ROIs were then used to calculate the δ^{37}Cl and Cl abundances. For calibration of Cl content and isotopic ratios three terrestrial apatite standards Ap004, Ap005, Ap018 were used [11]. The isotopic composition of Ap020 standard, which has the lowest chlorine content among all the standards used [11] was analysed to assess reproducibility of the results for apatite with low Cl abundances (see [8]). This was found to be within error of typical terrestrial values reported for Ap004. There is, consequently, no evidence of an extreme background isotopic composition of the SIMS. Background Cl abundances of the system were considered the same as those measured in San Carlos olivine (~1ppm). The lack of an extreme isotopic composition and low abundance of background Cl would result in an inappreciable difference in the measured isotopic composition of apatite grains in NWA 12593, and therefore no correction for background contribution was applied.

Results: There appears to be two groups of Cl isotopic composition in NWA 12593 apatite: a heavy δ^{37}Cl group (of ~+55‰) and a lighter δ^{37}Cl group (ranging between +10‰ and +24‰) (Fig. 1). It should be noted that most of these apatites are present within the matrix as isolated grains, with the majority of these displaying δ^{37}Cl values between +10‰ and +24‰ and, therefore, are assumed to represent a similar source region. There is no correlation between measured δ^{37}Cl and Cl contents.

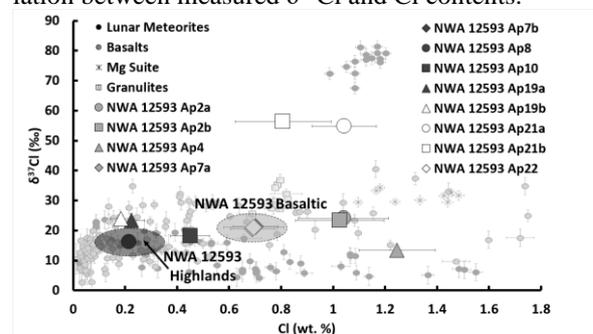**Fig. 1: Cl abundances (wt. %) vs δ37Cl (‰) of apatites in NWA 12593 compared to literature data [5-7, 12-15]. 2σ errors on δ37Cl are smaller than the symbol sizes.**

Discussion: Given the elevated Cl contents of the heavier δ^{37}Cl group (Ap21a, b in Fig. 1), magmatic degassing is unlikely to be the primary fractionation

mechanisms. Since Ap21 is not associated with any clast, and occurs as an isolated grain in the matrix, its geological context is not known. Although such heavy Cl isotopic compositions have not yet been reported from Apollo material, much heavier δ^{37}Cl values have been measured in apatite in lunar meteorite Dhofar 458 [12] (Fig. 1). This large isotopic fractionation was attributed to the giant impact which formed the Moon, followed by an extensive evaporation of the lunar magma ocean [12, 15]. The Moon coalesced from an enriched vapor, as ^{35}Cl would be preferentially lost from the vapor phase by Rayleigh distillation [12, 17], followed by an extended LMO liquidus phase that persisted for 10 – 200 Myr, inducing further isotopic fractionation by metal chloride evaporation [12]. It is possible that the isotopic composition of Ap21 is indicative of its source region, which may have recorded this process. The influence of shock effects on the Cl isotopes of the apatite grains in NWA 12593 should be further assessed (e.g. using Raman spectroscopy [12]), as petrographic analysis that has concluded the sample is moderately shocked. Notably, Ap21 exhibits irregular outlines indicating some degree of high-temperature interaction with an external melt/fluid source, possibly during shock events which formed the impact melt matrix. Similarly ^{37}Cl-enriched values (up to ~+40‰) in Apollo 14 rocks have been attributed to vapor metasomatism associated with an impact event [14], and it may therefore be reasonable to suggest a similar process is responsible for the heavy signature in NWA 12593. Further work is required to test these hypotheses further.

Of lithic-clast associated apatites, there is a clustering of values for basaltic apatites around +21‰, whereas highlands-type clasts record lower values (+16‰) (see ellipses in Fig. 1). The basaltic apatites are consistent with the literature data (which range from +2‰ to +40‰ [5, 7, 14-15], whereas typical highlands rocks are known to have heavier δ^{37}Cl (+25‰ to +36‰ [5] than those in NWA 12593 (Fig. 1). The matrix associated apatites mainly show lighter δ^{37}Cl values (+13‰ to +24‰). Some of these apatites plot very close to those with highlands clastic associations (see Fig. 1), which could indicate that these isolated apatites may represent the same highlands signature, with the difference in isotopic composition (~+24‰ compared to +16‰ for matrix- and clast-associated, respectively) resulting from magmatic crystallization or source heterogeneity. Other isolated apatites have similar δ^{37}Cl values to those mentioned above (+13‰ to +18‰), but with elevated chlorine contents (0.69 to 1.25 wt. % vs ~2000pm). Further analysis of the mineral chemistry of the lithic clast with which some of the apatites are associated is required to define which highlands lithology this signature represents.

Apatite grains associated with a basaltic clast have Cl abundances of ~7000 ppm and δ^{37}Cl values of +20‰ to +22‰. A number of isolated apatites show comparable δ^{37}Cl (+23‰ to +24‰) but greater Cl abundances (1.02 to 1.04 wt. %). Cl concentration variation likely reflects partitioning behavior in the source region of these apatites, with a limited δ^{37}Cl range reflecting the isotopic composition of this region.

Conclusion: The measured δ^{37}Cl and Cl contents of apatites in lunar meteorite NWA 12593 indicate the possibility of multiple fractionation events and lithologies recorded in this rock. Possible highlands apatites show lighter δ^{37}Cl than previously recorded. Further investigations are ongoing to better constrain the nature of the heavy δ^{37}Cl reservoir on the Moon.

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