Chlorine and hydrogen in brecciated lunar meteorites: implications for lunar volatile history

Conference or Workshop Item

CHLORINE AND HYDROGEN IN BRECCIATED LUNAR METEORITES: IMPLICATIONS FOR LUNAR VOLATILE HISTORY. T. S. Hayden[1], T. J. Barrett[1], X. Zhao[1], G. Degli-Alessandrini[1], M. Anand[1], I. A. Franchi[1] [1]The Open University (School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK) (Email: tara.hayden@open.ac.uk)

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]. While progress is being made on returning lunar samples from previously unsampled regions of the Moon (e.g. Chang'e-5), lunar meteorites potentially provide a diverse geographical sampling of the Moon and a less-biased representation of the lunar surface's chemical and lithological diversities. Furthermore, lunar meteorites appear to provide a wider sampling of the lunar interior, in terms of greater heterogeneity in the nature and distribution of lunar volatiles (e.g. H, Cl) than observed in Apollo samples [e.g. 2-9].

Apatite is the primary volatile bearing mineral in lunar samples and is ubiquitous in all lithologies excluding the ferroan anorthosites (FAN) [10]. The preservation of apatite in brecciated samples (within lithic clasts and as isolated grains in the matrix) has broadened the sample set for analysis of volatiles.

Samples: The samples selected for this study are four lunar brecciated meteorites with various lithic clast populations (e.g. basaltic and highlands-type, and symplectite clasts). Northwest Africa (NWA) 12593 and Arabian Peninsula (AP) 007 are fragmental breccias containing highlands and basaltic-type clasts, and Dominion Range (DOM) 18666, 18262 [11] and Elephant Moraine (EET) 96008 [12] are classified as basaltic breccias. The two DOM meteorites are thought to be paired [11].

Methods: The Cl content and isotopic composition (δ^{37}Cl) of apatite were measured using the Cameca NanoSIMS 50L at The Open University, following a modified protocol of Stephant et al. [13]. 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 primarily within ^{35}Cl/^{18}O images.

Hydrogen isotopes (δD) and water content (reported as equivalent H_2O) were collected on top of existing Cl isotope image pits using the NanoSIMS 50L in multicollection mode, refining an established protocol [3-4, 14] acquiring negative secondary ions of ^{13}C, ^{1}H, ^{2}H and ^{18}O. Measured D/H ratios were corrected for spallation in EET 96008, which has a reported CRE age of 10 ± 1 Ma [15].

Results: A total of 53 Cl measurements from 33 individual apatite grains were collected, with a total of 36 H measurements collected on top of Cl pits in 25 apatites grains.

Apatite in the fragmental breccias NWA 12593 and AP 007 show a range in Cl contents from ~ 1430 ppm to 1.6 wt.%. Some analyses yielded Cl contents > 5000 ppm, with a number of them yielding > 1 wt.% Cl. NWA 12593 apatite show a larger variation in Cl contents than AP 007 (Fig. 1). The higher Cl contents in NWA 12593 (~ 1.0 to 1.2 wt.%) are similar to Apollo 14 high Al basalts [8] and Apollo 17 Mg-suite samples [5]. Apatite in the basaltic breccias DOM 18666, DOM 18262 and EET 96008 show a range in Cl content from ~ 20 ppm to 3.65 wt.%. Chlorine > 1 wt.% was measured in several apatite grains in DOM 18666 (~ 1.1 to 3.7 wt.%).

The δ^{37}Cl values for apatite in fragmental breccias NWA 12593 and AP 007 (~ + 10 ‰ to + 55 ‰) mostly fall within the range of literature values reported for pristine lunar material and basaltic lunar meteorites [3-9] (Fig. 1). The isotopically heavier population (~ + 45 ‰ to + 55 ‰) is represented by four analyses across both samples. NWA 12593 is more variable in δ^{37}Cl than the other fragmental breccia.

The δ^{37}Cl values for apatite in basaltic breccias DOM 18666, DOM 18262, and EET 96008 (~ - 1 ‰ to + 26 ‰) are similar to Apollo 11 high Ti, Apollo 12 low-Ti [5, 9] and Apollo 14 high Al basalts [8] (Fig. 1). The lighter population (~ - 1 ± 0.2 ‰, n = 1) is resolvable from the light values reported from MIL 05035 (- 4 ± 2 ‰) [9].

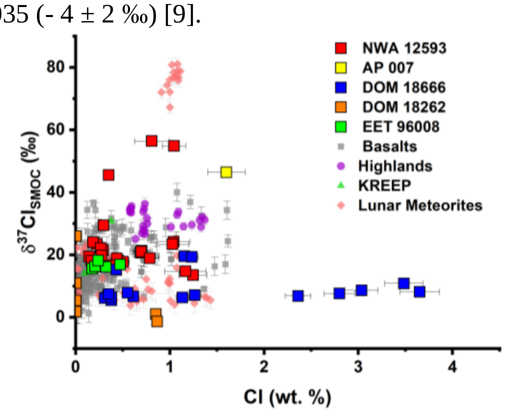

Fig. 1: Cl (wt. %) vs δ^{37}Cl (‰) of apatite in the studied lunar meteorites compared with the literature data [3-9].

Water abundances for apatite in NWA 12593 and exhibit a large variation (from ~ 135 to 4490 ppm) (Fig. 2). DOM 18666 has higher H_2O abundances in apatite compared with the other meteorites (~ 1210 to 3970 ppm), while DOM 18262 has a more restricted range in water contents (~ 250 to 310 ppm). EET 96008 shows a similar variation to NWA 12593 in H_2O abundance (~ 150 to 3750 ppm) (Fig. 2).

The δD values for apatite in NWA 12593 (~ - 370 ‰ to + 1030 ‰) are similar to Apollo 11 and 12 low-Ti and high-Ti basalts [9, 16-18]. The δD values for apatite in DOM 18666, DOM 18262 and EET 96008, however, vary from ~ - 940 ‰ to + 860 ‰ (Fig. 2).

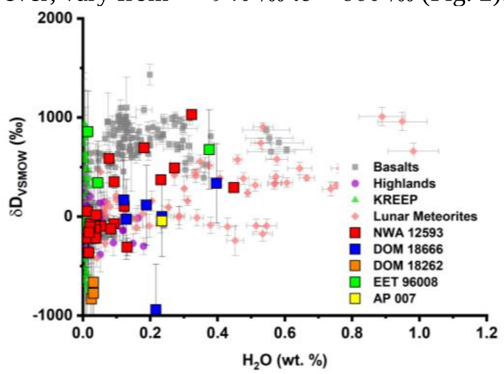

Fig. 2: H_2O (wt.%) vs δD (‰) of apatite in studied lunar meteorites compared with literature data [2-4, 7, 9, 16-24].

Discussion: The heavy Cl isotopes measured in NWA 12593 and AP 007 are associated with high Cl contents (~ 8080 to 16000 ppm). Magmatic degassing is unlikely to cause this heavy signature without significant depletion in Cl contents. There appears to be two clusters of heavier δ^{37}Cl values, at ~ + 45 ‰ and ~ + 55 ‰ respectively. There is limited geological context for the matrix-associated apatite which has δ^{37}Cl of + 55 ‰. Although such heavy Cl isotope values have not yet been reported for Apollo material, much heavier δ^{37}Cl (up to + 81 ‰) values have been measured in apatite in lunar meteorite Dhofar 458 [6] (Fig. 1). These authors attributed the large isotopic fractionation to the giant impact formation of the Moon, and extensive evaporation of the lunar magma ocean which followed [6, 9]. It is possible that the heavy Cl isotopes are indicative of the source regions, which could have recorded this process. One of the apatite grains exhibit irregular outlines indicating some degree of high temperature interaction with an external fluid source/melt, possibly during shock events which formed the impact melt matrix of this rock. Similarly ^{37}Cl-enriched values (up to ~ + 40 ‰) in Apollo 14 rocks were attributed to vapor metasomatism associated with an impact event [8], and it may therefore be reasonable to assume that a similar process might have been responsible for the heavy signatures in these samples. Further work is required to test these hypotheses further.

The extremely light H isotopes of DOM 18666 (~ - 940 ‰) are similar to solar wind values (< - 988 ‰) [25]. Analyses in DOM 18262 show similarly light values (~ - 830 ‰ to - 630 ‰). Solar wind penetrates < 1 μm depth in grains, meaning direct implantation of solar wind H into apatite grains is unlikely [2]. As these are basaltic breccias, solar wind could have been incorporated into the parental melt upon eruption at the Moon's surface through assimilation of lunar regolith [26]. The texture of the lithic clasts in these meteorites closely resemble lunar quartz-monzodiorites (QMDs) which have been observed to show very low δD (~ – 750 ‰) [2]. The possibility that these are indigenous lunar interior values cannot be discounted.

Conclusion: The measured δ^{37}Cl, δD, Cl and H_2O contents of apatites in selected brecciated lunar meteorites indicate the possibility of multiple fractionation events and lithologies recorded in these rocks. Further investigations are ongoing to better constrain the nature of the light δD and heavy δ^{37}Cl reservoirs in the Moon. An indigenous origin for these compositions may indicate the lunar interior is more heterogenous, and lunar volatile history is more complex than previously thought.

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