THE ISOTOPIC COMPOSITION OF CHLORINE IN APATITE FROM EUCRITES. T. J. Barrett[1], J. J. Barnes[1], M. Anand[1,2], I. A. Franchi[1], R. C. Greenwood[1], B. L. A. Charlier[1], and M. M. Grady[1,2]. [1]Department of Physical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK (Email: thomas.barrett@open.ac.uk), [2]Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK.

Introduction: Chlorine is an important element being incompatible in nearly all silicates, extremely volatile and strongly hydrophilic [1]. The Cl isotope composition ($^{37}Cl/^{35}Cl$) of meteorites, therefore, can provide useful information regarding the isotopic reservoirs that were present in the early Solar System and any secondary processes that may have occurred on different parent bodies [2, 3]. There is relatively a narrow range in the Cl isotope compositions of terrestrial rocks, and martian and chondritic meteorites ($\delta^{37}Cl \sim$ -4 to +1 ‰) [2-4], with an exception to this rule being the Moon. It has recently been demonstrated that lunar samples display a significant range in Cl isotopic composition, especially lunar apatite [$Ca_5(PO_4)_3(F,Cl,OH)$], which is a common accessory mineral that can contain abundant Cl, and which shows $\delta^{37}Cl$ values ranging from typical terrestrial values of $\sim$ -4 ± 2 ‰ to extremely enriched values of +81 ± 2 ‰ [5-11].

The Howardite-Eucrite-Diogenite (HED) suite of meteorites represents the largest suite of crustal and sub-crustal rocks available from a differentiated basaltic asteroid (most probably 4 Vesta) [12-13]. The eucrites are also some of the oldest igneous rocks in the Solar System, typically with crystallization ages from 4547 Ma to 4559 Ma [14-15]. Therefore, characterizing the volatile inventories of eucrites can help us understand the processes operating on asteroid parent bodies early in the Solar System history. In order to investigate the history of volatiles in eucrites, we have measured Cl isotopic composition of apatite from the cumulate eucrite Moore County and the basaltic eucrite Dar al Gani 945 (DaG 945). Apatite grains in these two samples were previously analyzed for their H isotopic composition [16].

Methods: The Cl content and isotopic compositions were measured using the Cameca NanoSIMS 50L at The Open University in multi-collection mode based upon the protocol of Tartèse et al. [9] and Barnes et al. [10], acquiring negative secondary ions of $^{16}O^1H$, ^{18}O, ^{35}Cl, ^{37}Cl and $^{40}Ca^{19}F$, simultaneously on electron multipliers. A primary current of ~50 pA (in Cs+ mode) was used for the analyses. Typically a 3 × 3 μm area was analyzed, however for some larger grains this area was increased to 5 × 5 μm. No electronic gating was used.

Results: A total of 12 measurements from nine individual apatite grains were obtained. Apatite in both samples is typically located within mesostasis regions (Fig. 1).
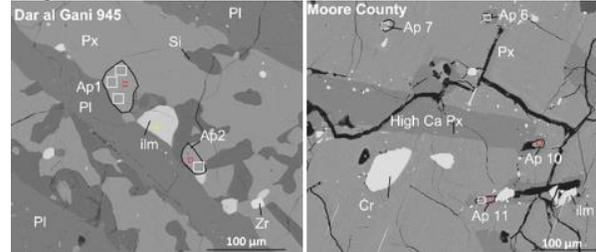

Figure 1. Representative Back Scattered Electron (BSE) images of each eucrite. Pl = plagioclase, Px = pyroxene, Ap = apatite, ilm = ilmenite, Cr = chromite, Si = silica phase, Zr = zircon. Red boxes represent the approximate locations of the sputter pits corresponding to the analyses of Cl isotopes. White boxes represent the approximate locations of H isotope measurements [16].

Apatite grains from Moore County display a large range in Cl content, from ~ 70 to 700 ppm Cl which is consistent with the results of previous studies [17]. Considerable intra-grain variability in Cl abundance is also observed in Moore County with a single grain having a range of ~ 360 ppm. Apatite crystals from DaG 945 display a more restricted variation (both inter as well as intra-grain) with values ranging from ~ 25 to 60 ppm Cl (Fig. 2).

The $\delta^{37}Cl$ values obtained for apatite from Moore County (~ +0.7 ± 2.7 ‰ to ~ +3.6 ± 1.8 ‰) are typically within error of terrestrial values and chondrites, with the exception of two grains which are more enriched (~ +6.6 ± 3.4 ‰ and +13.1 ± 3 ‰). DaG 945, however, shows a significant enrichment in $\delta^{37}Cl$ with values ranging from ~ +27 ± 4.4 ‰ to ~ +35 ± 6.2 ‰. The results we have obtained form two distinct populations one with a weighted average of +4.1 ± 3.4 ‰ (95 % confidence level, n = 7) (Moore County) and the other with an average of +31 ± 4.4 ‰ (95 % confidence level, n = 5) (DaG 945).

Discussion: In both samples apatite display consistent δD values (Fig. 3). There is no correlation between $\delta^{37}Cl$ and δD values (Fig. 3), in keeping with the conclusions drawn from lunar rocks [7]. The apatite in these meteorites are also characterized by low H_2O contents (typically < 200 ppm), with DaG 945 showing more variability than Moore County in terms of H_2O content [16].
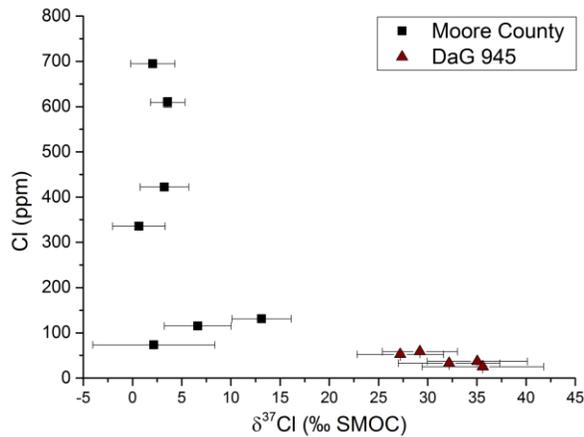
Figure 2. Plot of Cl content (ppm) versus $\delta^{37}Cl$ value (‰) for individual measurements of apatite. Uncertainties are reported at the 2σ level.

The model put forward by Sharp et al. [5] suggests that $\delta^{37}Cl$ enrichment in lunar basalts could be the product of isotopic fractionation during extensive outgassing of Cl from a magma sufficiently poor in H, such that the magma degassed Cl in the form of metal chlorides. If the H_2O content of apatite in the meteorites studied here reflect, relatively, the melt composition then this mechanism [5] could provide a viable explanation. Furthermore, DaG 945 is a basalt whose parental magma may have erupted under similar degassing conditions as in the models proposed by Sharp et al. [5] and Ustunisik et al. [18], and could have produced the heavy Cl isotopic compositions observed in the apatite from this sample. However, Moore County, which is a cumulate eucrite and likely to have formed at depth, is unlikely to have suffered significant magmatic degassing. It is, therefore, possible that Moore County retained its original Cl isotopic composition (~ +4 ‰).

A different model, put forward by Boyce et al. [7], shows that in the case of lunar basalts the heavy $\delta^{37}Cl$ values are likely to have been inherited from a residual magma ocean reservoir in the Moon (urKREEP) which had undergone Cl isotope fractionation early in the Moon's history. Currently no urKREEP-like component has been proposed for Vesta although any body that has undergone differentiation via a magma ocean is likely to have a similarly incompatable element rich residuum [19]. In the eucrites studied here, however, the La/Yb ratios do not show a relationship consistent with the heavy Cl isotope signature being attributable to assimilation of an incompatible element enriched melt [20-21].

Conclusions: The isotopic composition of Cl recorded by apatite from the eucrites show a similar range in $\delta^{37}Cl$ values to those reported for lunar apatite [e.g., [7, 10]. The results obtained here form two distinct

populations with weighted averages of +4.1 ± 3.4 ‰ and +31 ± 4.4 ‰, for Moore County and DaG 945, respectively. The mechanism of ^{37}Cl isotope enrichment on Vesta is likely to have been the degassing of Cl in the form of metal chlorides. In order to establish fully whether or not degassing of Cl played a role in the magmatic histories of the eucrites, however, the analyses of an expanded sample set is required.
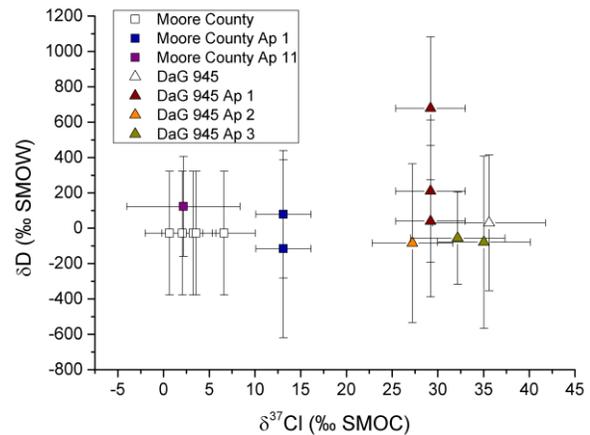

Figure 3. Plot of δD value versus $\delta^{37}Cl$ value for eucritic apatite. Where possible apatite grains that have been analyzed for both $\delta^{37}Cl$ and δD values are separated out. White symbols indicate in-situ $\delta^{37}Cl$ measurements plotted with the mean δD value for that meteorite (H isotope data are taken from [16]).

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