Chlorine and hydrogen degassing in Vesta's magma ocean

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Abstract:

The hydrophilic nature of halogens makes these elements ideal for probing potential hydrous geologic processes. Generally, in magmatic settings the stable isotopes of Cl may fractionate when H is in low concentrations and little fractionation occurs when the H concentration is high. We determined the Cl isotope composition and halogen content (F, Cl, Br, and I) of apatite and merrillite in seven basaltic eucrites, which are meteorites linked to the asteroid 4-Vesta, by using secondary ion mass spectrometry. We compare our halogen results with H isotope data, existing bulk rock concentrations, and petrologic models. The inferred Cl isotope composition of eucrites from this study, expressed in standard $\delta^{37}\text{Cl}$ notation, which ranges from -3.8 to 7.7‰, correlates with the bulk major- and trace-element content, e.g., the Cl isotope composition positively correlates with Mg and Sc, while Cl isotope composition negatively correlate with K, V, and Cr. Here we suggest that eucrites preserve evidence of a degassing magma ocean as evidenced by the decreasing bulk rock K content with increasing $\delta^{37}\text{Cl}$. If the eucrite

parent body, 4-Vesta, accreted with a negative $\delta^{37}\text{Cl}$ of $-3.8 \pm 1.1\%$, at least some parts of the solar nebula would have been isotopically light compared to most estimates of the Earth, which on average is close to 0%.

1. Introduction:

Eucrites are differentiated meteorites that group together with howardites and diogenites to form a genetically linked suite of rocks, the HED group of meteorites. Eucrites can be further subdivided into basaltic or cumulate rocks, which sample some of the some of the oldest asteroidal crusts in the solar system (e.g. Touboul et al., 2015). Most eucrites are thought to derive from the asteroid 4-Vesta (McSween et al., 2012 and refs. therein), but some eucrites probably sample other geochemically similar asteroids (Sarafian et al., 2014, 2013,; Scott et al., 2009; Takeda and Graham, 1991). Here we will use the asteroid 4-Vesta as a proxy for all eucrite parent bodies. Basaltic eucrites can be classified into three geochemical groups by plotting proxies for fractional crystallization, such as Mg# (molar $\text{Mg}/(\text{Mg}+\text{Fe})$) or Sc content ($[\text{Sc}]$) vs. an incompatible element, e.g., $[\text{Ti}]$ or $[\text{Hf}]$ (Fig. 1). Main group eucrites define a trend consistent with fractional and/or equilibrium crystallization (Fig. 1; Mandler and Elkins-Tanton, 2013; Warren and Jerde, 1987), although their petrogenesis is subject to some debate. Some models require partial melting of the mantle (Stolper, 1977), while most models predict direct extraction from a magma ocean (Mandler and Elkins-Tanton, 2013; McSween et al., 2012; Barrat et al., 2007;). The most recent and quantitative geochemical modeling suggest that eucrites originate directly from a crystallizing magma ocean (Mandler and Elkins-Tanton, 2013; McSween et al., 2012). The Stannern trend eucrites are characterized by an enrichment in

incompatible elements, independent of their crystallization index, e.g., Mg# or [Sc] (Fig. 1). This trend was likely generated by contamination of a main group magma with a crustal partial melt (Yamaguchi et al., 2009; Barrat et al., 2007;), but could have been generated by low degrees of partial melting of the vestan mantle (Stolper, 1977). The third group of basaltic eucrites are residual eucrites, which are depleted in incompatible trace elements and likely represent a residual crustal rock that was partially melted (Yamaguchi et al., 2009). Thermal alteration among eucrites is nearly ubiquitous. Eucrites can be classified into seven types on the basis of increasing thermal alteration, type 1 eucrites are extremely rare and represent no evidence of thermal alteration, whereas type 7 eucrites exhibit evidence of partial melting (Takeda and Graham, 1991; Yamaguchi et al., 2009).

Eucrites contain two phosphates, merrillite ($\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$) and apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$), whilst the latter is mostly F-rich apatite (Sarafian et al., 2013). In eucrites apatite and merrillite generally occur in late stage melt pockets, i.e., mesostasis (Sarafian et al., 2013) since basaltic melts have a high solubility of P (Harrison and Watson, 1984). , Similar to other incompatible elements, P becomes enriched during the late stages of fractional crystallization, resulting in precipitation of apatite and/or merrillite. In planetary basalts, apatite is the main carrier of halogens and H, while merrillite is nearly devoid of H, F, and Cl. Several studies have examined H, F, and Cl exchange between apatite and melt (McCubbin et al., 2015), as well as the partitioning of halogens between apatite and fluid (Kusebauch et al., 2015a). Thus, the apatite H, F, Cl, Br, and I content can be related to the magmatic and hydrothermal conditions apatite formed under and/or equilibrated with.

81 Euclites are systematically depleted in volatile elements compared to
82 carbonaceous chondrites and the Earth. For example, the geochemically similar pair Ga
83 (volatile) and Al (refractory) should remain invariant during magmatic processes, yet the
84 Ga/Al of euclites, Earth and carbonaceous chondrites are 0.32, 1.7, 11, respectively (
85 McDonough and Sun, 1995; Warren et al., 2009). While euclites are depleted in volatile
86 elements, there are multiple lines of evidence that fluids may have interacted with the
87 euclitic crust. For example, fluids may have precipitated observed quartz veins (Treiman
88 et al., 2004), apatite veins (Sarafian et al., 2013), Fe-rich olivine veins (Roszjar et al.,
89 2011), and Fe-enrichment along pyroxene grain boundaries (Barrat et al., 2011; Roszjar
90 et al., 2011). The source of magmatic water has been determined to have a carbonaceous
91 chondrite signature (Barrett et al., 2016; Sarafian et al., 2014), but the source of water for
92 fluid-generated features, such as the quartz, apatite, and Fe-rich olivine veins, are
93 unknown.

94 The Cl isotope composition of planetary basalts is extremely variable compared to
95 magmatic rocks on Earth (Halldórsson et al., 2016; Williams et al., 2016; John et al.,
96 2010; Sharp et al., 2010b). Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl , with natural
97 abundances of 75.77% and 24.23%, respectively. Chlorine isotope ratios can be
98 represented in standard delta notation, as: $\delta^{37}\text{Cl} = (^{37}\text{Cl}/^{35}\text{Cl}_{\text{sample}}/^{37}\text{Cl}/^{35}\text{Cl}_{\text{SMOC}} - 1) \times$
99 1000, where SMOC is standard mean ocean chloride, with a $\delta^{37}\text{Cl}$ value defined as zero.
100 Multiple studies of $\delta^{37}\text{Cl}$ of lunar and martian rocks are widely used to decipher
101 interactions between lithospheric, atmospheric and hydrospheric components. For
102 example, $\delta^{37}\text{Cl}$ has been used to show crustal/fluid assimilation processes on Mars (Sharp
103 et al., 2016; Williams et al., 2016) and degassing processes on the Moon (Barnes et al.,

2016; Boyce et al., 2015; Sharp et al., 2010b). Delta ^{37}Cl is an extremely sensitive indicator of crustal contamination in martian rocks, as crustal fluids on Mars are thought to be extremely saline (Knauth and Burt, 2002) and have an elevated $\delta^{37}\text{Cl}$ (Sharp et al., 2016; Williams et al., 2016). Chlorine isotope ratios in some lunar samples are extremely enriched in ^{37}Cl , which is thought to be due to metal-chloride degassing (Barnes et al., 2016; Boyce et al., 2015; Sharp et al., 2010b). The latter could be due to in-situ degassing of low H content of lunar magmas (Sharp et al., 2010b), or from degassing of a magma ocean (Barnes et al., 2016; Boyce et al., 2015). If a magma ocean on 4-Vesta existed and degassed, then $\delta^{37}\text{Cl}$ should correlate with key bulk rock indicators of magma ocean crystallization.

Here, we report the H, F, Cl, Br, and I content of eucritic apatite and merrillite as well as the $\delta^{37}\text{Cl}$ and H-isotope composition of eucritic apatite. We show that the Cl isotopic composition of apatite in eucrites strongly correlate with bulk rock major and trace element concentrations. We determined a light $\delta^{37}\text{Cl}$ signature for 4-Vesta that is similar to that of the unequilibrated chondrites Parnallee and NWA 8276 (Sharp et al., 2016; 2013b; Williams et al., 2016), the former was confirmed by *in-situ* analysis of apatite grains. We suggest that 4-Vesta accreted a light Cl isotope reservoir that may be distinct from other solar system bodies, like the Earth and Moon.

2. Sample description:

We chose seven samples (Cachari, GRA 98098, Juvinas, NWA 1908, NWA 5073, Pasamonte, and Stannern) to evaluate the halogen (F, Cl, Br, and I) concentrations and stable Cl isotopes in apatite and merrillite and two samples (GRA 98098 and NWA 1908)

to measure apatite D/H and water contents. Our samples are selected from the main group and Stannern trend, and represent a wide range of thermal alteration types (types 2–6). In the following sections we provide relevant petrographic descriptions of our selected samples.

2.1 Cachari:

Cachari (N513, NHM Vienna) is a heavily-shocked monomict basaltic eucrite that has vesicular glass veins attributed to shock melting by impact (Bogard et al., 1985). It is mainly composed of fractured and mosaicised pyroxenes of 0.2–2.5 mm, i.e., orthopyroxene and augite and each containing exsolution lamellae of each other, and plagioclase of 0.2–2 mm in size and with mottled extinction when viewed in cross-polarized light. Apatite and merrillite are 10–150 μm in apparent diameter and typically occur adjacent or interstitial to pyroxene, plagioclase, chromite, and zircon. Apatite grains are larger and more abundant compared to merrillite. Sarafian et al. (2014) measured H isotopes in Cachari and found this sample to have a H isotope composition similar to other measured eucrites.

2.2 GRA 98098:

Graves Nunataks (GRA) 98098 is an unbrecciated coarse-grained type 4 main group eucrite. Our thick section of GRA 98098,65 has 0.2–1 mm laths of plagioclase with rounded edges and 0.2–1 mm blocky exsolved pyroxene. Graves Nunataks 98098 is absent of any late stage melt pockets and merrillite, but it does contain abundant and

large apatite often 100 μm in the long direction. The sample has distinctive tridymite veins throughout the main mass that are associated Cl-rich apatite (Sarafian et al., 2013).

2.3 *Juvinas*:

Juvinas is a main group type 5 monomict basaltic eucrite. We analyzed two thin sections of *Juvinas*, WWU Münster (apatite measurements) and *Juvinas* AMNH 466-2 (merrillite measurements). Our sections of *Juvinas* have lathy plagioclase up to ca. 2 mm in the long direction and large blocky pigeonite >4 mm in some cases. The late stage melt regions of *Juvinas* are also relatively coarse grained and contain ulvöspinel, troilite, pigeonite, plagioclase, merrillite and apatite.

2.4 *NWA 1908*:

Northwest Africa 1908 is a monomict and thermally metamorphosed basaltic eucrite with exsolved pyroxenes of ~0.1–1 mm in the long direction and subhedral to anhedral plagioclase intergrowths ca. 100–800 μm in the long direction. Apatite is typically 10–60 μm in apparent size and occurs in late stage melt pockets along with ilmenite, troilite, pigeonite, plagioclase, SiO_2 polymorph, and merrillite, or interstitial to silicates.

2.5 *NWA 5073*:

NWA 5073 is a rare member of an unbrecciated Stannern trend eucrite and represent one of the least thermally-metamorphosed eucrite basalts. It is mainly composed of elongated, zoned pyroxene phenocrysts up to 1.2 cm, and plagioclase laths

up to 0.3 cm in length, and rich in mesostasis (Roszjar et al., 2011). Abundant late-stage melt pockets are rich in (terrestrial weathered) metal, troilite, tridymite, apatite, merrillite, zircon and baddeleyite. Apatite and merrillite grains are typically 20–100 μm and either occur adjacent to or exsolved from each other.

2.6 Pasamonte:

Pasamonte is a monomict eucrite with thermal alteration type 2 (Takeda and Graham, 1991), meaning that pyroxenes maintain their magmatic Fe and Mg zonation and absent of exsolution lamellae. Pasamonte is geochemically similar to main group eucrites, but has a distinct O isotope composition (Scott et al., 2009). Based on O isotope compositions Pasamonte likely derived from different parent body, which has similar geochemical characteristics as 4-Vesta (Scott et al., 2009). Our section of Pasamonte on loan from the University of New Mexico (UNM-221) contains rounded basaltic clasts made up of subhedral lathes of plagioclase ca. 100–1000 μm in the long direction with blocky pigeonite 100–500 μm long. Abundant late-stage melt pockets contain ulvöspinel, troilite, pigeonite, plagioclase, merrillite and apatite. While it is difficult to determine petrographically which phosphates crystallized first, merrillite and apatite are present as late crystallizing phases.

2.7 Stannern:

Stannern is a type 4 Stannern trend brecciated basaltic eucrite. Our thin section of Stannern, AMNH 554-1 exhibit plagioclase lathes 0.2–3 mm in length with intergrown pyroxenes 0.1–2 mm in the long direction. In addition, some regions have dendritic

intergrown plagioclase and pyroxene, which could indicate quench growth. Late stage melt regions in Stannern are abundant and contain ilmenite, troilite, pigeonite, plagioclase, SiO₂ polymorph, chromite, merrillite, apatite and zircon. Apatite and merrillite are in the range of 10–100 µm in the long direction.

2.8 Parnallee:

Parnallee is an unequilibrated ordinary chondrite. Apatites occur interstitial to matrix olivine and adjacent to metal grains and range in size from 15–100 µm in the long direction. The bulk $\delta^{37}\text{Cl}$ of Parnallee and NWA 8276 were previously measured and are considered to represent the unprocessed original solar system value of ca -4‰ (Sharp et al., 2016; 2013b; Williams et al., 2016).

3. Methods:

3.1 Scanning electron microscope:

We used the JEOL JSM 6610-LV scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS) at the Natural History Museum Vienna, Austria and a Hitachi TM3000 SEM equipped with an EDS at the Woods Hole Oceanographic Institution for petrographical observations and location of phosphate grains. Low beam currents and fast acquisition times were used to ensure apatites were not electron beam damaged.

3.2 Secondary ion mass spectrometry:

3.2.1 Cl isotopes and halogen concentrations: Halogen concentrations (F, Cl, Br, and I) and stable Cl isotopic compositions were measured using a CAMECA IMS1280 large-geometry secondary ion mass spectrometer at the NordSIMS facility at the Swedish Museum of Natural History. The procedures used here closely follow those of (Kusebauch et al., 2015a; 2015b). Cleaned samples were coated with 30 nm of Au. Prior to spot analyses, the analytical positions were pre-sputtered for 120 s over a $25 \times 25 \mu\text{m}^2$ raster area to remove the Au coating and any remaining surface contamination. For both concentration and isotope analysis, secondary ions of halogens species were sputtered from the surface using a 2 nA Cs^+ Gaussian focused beam and a $15 \times 15 \mu\text{m}^2$ raster with an impact energy of 20 kV. An electron gun was used in conjunction with the primary Cs^+ beam to counteract any charging effects on the surface of the sample. Secondary ions were then centered in a 2000 μm field aperture, which provides a ca. $25 \times 25 \mu\text{m}^2$ field of view on the sample that is smaller than the combined spot and pre-sputter area, thus precluding admission of surface contaminant halogens to the mass spectrometer. For halogen concentration measurements, secondary ions were filtered at a mass resolving power (MRP; $M/\Delta M$ at 10% peak height) of 5000 and species of $^{19}\text{F}^-$, $^{37}\text{Cl}^-$, $^{127}\text{I}^-$, and a matrix peak of $^{40}\text{Ca}^{31}\text{P}^-$ were then measured in either an electron multiplier ($<10^6$ cps) or Faraday cup ($>10^6$ cps) in mono-collection mode using a peak hopping routine. In order to measure $^{81}\text{Br}^-$, which has complex molecular interferences, a combined $^{81}\text{Br}^- + ^{44}\text{Ca}^{35}\text{Cl}^- + ^{46}\text{Ca}^{37}\text{Cl}^-$ peak was measured and during data reduction stripped of its CaCl interferences using the measurement of the most abundant $^{40}\text{Ca}^{37}\text{Cl}^-$ species and assuming the natural isotopic abundances of Ca and Cl. Ratios of $^{19}\text{F}^-$, $^{37}\text{Cl}^-$, $^{81}\text{Br}^-$ and $^{127}\text{I}^-$ to the matrix $^{40}\text{Ca}^{31}\text{P}^-$ species were used to calculate concentrations using relative

sensitivity factors determined by analyses of the Durango apatite standard during the same session, which has F, Cl, Br, and I contents of 33500, 4099, 0.84, and 0.73 $\mu\text{g/g}$ respectively (Kusebauch et al., 2015b).

Chlorine isotopic compositions were measured in adjacent spots in the same grains as the halogen concentrations where possible or in adjacent grains where necessary. The secondary ions $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ were filtered at a mass resolution of 2500 and measured simultaneously on two Faraday cups equipped with $10^{11} \Omega$ low noise amplifiers in four blocks of ten integrations, resulting in an overall counting time of 160 s. Secondary magnet stability was maintained using an nuclear magnetic resonance (NMR) field sensor in regulation mode. Measurements of two different apatite standards, Durango and a pure, synthetic Cl-apatite of known composition, i.e., $\delta^{37}\text{Cl}$ of 0.5‰ and 2.0‰, respectively from Kusebauch et al. (2015b), were interspersed with analyses of unknowns. To account for matrix dependent variations in instrumental mass bias (IMF) resulting from variable Cl content(s), a linear correction based on drift-corrected measured Cl intensities was made to eucrite isotopic compositions relative to intensity and isotopic composition of the bracketing apatite standards. This IMF bias correction was not made for Parnallee because those apatites were Cl-rich.

3.2.2 D/H and water content: The isotopes of H (deuterium, D and H) and H_2O concentrations were measured in apatite grains from GRA 98098 and NWA 1908. According SIMS measurements were conducted on a CAMECA IMS1280 ion probe at the Woods Hole Oceanographic Institution. Prior to measurements, sample mounts were cleaned with distilled water and ethanol and dried in a vacuum chamber with a pressure

less than $\sim 6.6 \times 10^{-5}$ Pa (5×10^{-7} Torr). The samples were then taken out of the vacuum chamber and gold coated. After gold coating, the sample was placed into the instrument to obtain a pressure of lower than 1.3×10^{-7} Pa ($\sim 5 \times 10^{-9}$ Torr) in the analysis chamber.

We followed the methods given in Sarafian et al. (2014) to measure D/H in apatite. Briefly, a focused 1 nA Cs^+ primary beam was rastered to produce a $15 \times 15 \mu\text{m}^2$ sputter crater. During our analysis we used a physical field aperture was used, such that ions from the central $8 \times 8 \mu\text{m}^2$ of the SIMS pit were counted. Prior to analysis of unknowns the production rate of $^{16}\text{O}^1\text{H}^1\text{H}^-$ was determined using JD17H reference material, i.e., a natural glasses with 2.49 wt% H_2O . A MRP of 12,000 (MRP of 11,632 needed to separate $^{16}\text{O}^2\text{H}^-$ for $^{16}\text{O}^1\text{H}^1\text{H}^-$) was used for the $^{16}\text{O}^1\text{H}^1\text{H}^-$ production rate test. We found the $^{16}\text{O}^1\text{H}^1\text{H}^-$ peak is lower than our electron multiplier (EM) background (~ 0.01 counts per second), meaning the production of $^{16}\text{O}^1\text{H}^1\text{H}^-$ is less than 1‰ of $^{16}\text{O}^2\text{H}^-$. For our analyses MRP was nominally 10,000, which separates $^{17}\text{O}^1\text{H}^-$ from $^{16}\text{O}^2\text{H}^-$. Using mono-collection mode, we counted mass $^{17}\text{O}^-$, $^{16}\text{O}^1\text{H}^-$, and $^{16}\text{O}^2\text{H}^-$. Background $^{17}\text{O}^1\text{H}^-$ / $^{17}\text{O}^-$ measured throughout the session was ca. 4.5×10^{-2} , which translates to ca. 19 $\mu\text{g/g}$ H_2O . Background was corrected by subtracting counts of $^{17}\text{O}^1\text{H}^-$ and $^{17}\text{O}^2\text{H}^-$ of our low water reference material, Suprasil 3002 (1 $\mu\text{g/g}$ H_2O , provided by Heraeus Quarzglas, Switzerland) from our apatite measurements. All uncertainties were propagated from background and analytical uncertainty.

4. Results:

4.1 Halogen concentrations:

The F, Cl, Br, and I content of apatite and/or merrillite was measured in all eucrite samples and representative analyses are presented in Tables S1. The merrillite F, Cl, Br, and I content vary considerably for all samples, 5.8 – 3532 $\mu\text{g/g}$, 2.73 – 546.36 $\mu\text{g/g}$, 0.28 – 78.14 $\mu\text{g/g}$, and 0.11 – 14.1 $\mu\text{g/g}$, respectively (Fig. 2). Our measurements of F and Cl in apatite from Stannern, Pasamonte, and GRA 98098 agree with previous measurements (Sarafian et al., 2013). Bromine and I concentrations positively correlate with Cl content, but not F. External precision (1σ , $n=35$) for F, Cl, Br, and I for Durango apatite were 4%, 5%, 12%, and 3%, respectively.

4.2 $\delta^{37}\text{Cl}$:

The Cl isotopic composition of single apatite grains in all measured eucrites vary from -4.6‰ in NWA 5073 to +11.9‰ in NWA 1908 (Table 1). This large variation is similar to the variation seen on Mars (Sharp et al., 2016; Williams et al., 2016), but less than the variation observed on the Moon (Barnes et al., 2016; Boyce et al., 2015) and mantle-derived magmatic rock of the Earth (Halldórsson et al., 2016; John et al., 2010). Apatite $\delta^{37}\text{Cl}$ from each eucrite sample correlate with its bulk rock major- and trace-element composition, e.g., Sc, Mg, V, Cr, and K content (Fig. 3A-D). Additionally, apatite $\delta^{37}\text{Cl}$ correlate with apatite Br/Cl (Fig. 3E), apatite I/Cl (Table S1), and bulk rock $\delta^{66}\text{Zn}$ (Fig. 3F). External precision on Durango apatite and the synthetic apatite were 0.17‰ ($n=159$) and 0.32‰ ($n=40$), respectively.

4.2.1 $\delta^{37}\text{Cl}$ -Parnallee: We measured apatite grains interstitial to olivine and associated with metal grains in the ordinary chondrite Parnallee. The mean of all analyses

is $-4.7 \pm 1.5\text{‰}$ (2 sd, n=32), which is in excellent agreement with the structurally bound Cl determined by bulk measurements, $-4.1 \pm 0.3\text{‰}$ (Sharp et al., 2013b).

4.3 δD :

The hydrogen isotopic composition was measured in two eucrites, GRA 98098 and NWA 1908 (Table 2). No spallation correction was made because (1) no cosmic-ray exposure ages exist for GRA 98098 and NWA 1908 and (2) the H-rich nature of apatite and the render the spallation correction negligible (Sarafian et al., 2014). For example, an apatite with ca. 56 $\mu\text{g/g}$ H (500 $\mu\text{g/g}$ H_2O) and exposure age of 30 Myr would have a spallation correction of ca. -20‰ (Sarafian et al., 2014). Graves Nunataks 98098 and NWA 1908 show elevated D/H relative to Cachari, Juvinas, Pasamonte (Barrett et al., 2016; Sarafian et al., 2014). With the exception of Stannern, the elevated in δD corresponds to elevated $\delta^{37}\text{Cl}$ (Fig. 4).

5. Discussion:

5.1 Phosphate saturation:

The halogen content of apatite and merrillite can help determine the limiting element(s) in apatite saturation. Beside OH, F and Cl are major structural constituents in the mineral apatite, but trace elements in merrillite. Therefore, these key characteristics of halogen geochemistry can be used to determine the crystallization sequence of phosphates in eucrites. We observe the F and Cl content of merrillite vary according to

the power function $F = 1.8 \times Cl^{(0.915)}$ (Fig. 2). At a F and Cl content of greater than 300 $\mu\text{g/g}$ the slope steepens, i.e., F becomes enriched compared to Cl (Fig. 2). The steepening of the slope in F vs. Cl space could be the merrillite structure switching to the apatite structure, where F is extremely compatible and Cl is moderately compatible (Kusebauch et al., 2015b). Therefore, merrillite coexisting with apatite suggest that F, or any other anion compatible in apatite, is the limiting element in apatite saturation in eucrite basalts, not P.

5.2 The H content of eucrite magmas:

The bulk water content of eucrite magmas can be evaluated in two ways. (1) Apatite-melt hygrometry (McCubbin et al., 2016, 2015), which uses an apatite-melt OH-F exchange coefficient (K_d) that were mostly determined at the C-CO buffer at 1 GPa, bulk F content (see supplementary material), and apatite OH and F contents (this study and Sarafian et al., 2013). Apatite-melt hygrometry, while a useful tool, is only an approximation of the melt water content, especially at low oxygen fugacity when H_2 is present in the melt. This approach assumes a closed system during crystallization, similar partition coefficients for H and F between the major crystallizing phases, i.e., plagioclase and pyroxene, and melt, and no pressure dependence on the K_d , extrapolating from 1 GPa to $\sim 10^0 - 10^7$ Pa - the potential pressure of crystallization for eucrite basalts. A closed system implies that no degassing took place prior to apatite crystallization, which means magmas must have crystallized under pressure and/or melts were extremely water-poor. However, this may not be the case for eucrite magmas. Additionally, the partition coefficients for H and F between the silicate crystallizing phases and melt are different (

Dalou et al., 2012; Hauri et al., 2006) and poorly characterized at low pressure. Nevertheless, we provide the first estimate for the water content of a eucritic melt. Using the OH-F exchange coefficient and F content of the bulk rock, which likely represents a melt composition, we can estimate the H content of a primitive melt (McCubbin et al., 2016):

$$C_{H_2O}^{PM} = \frac{X_{H_2O}^{ap} \times X_F^{Melt}}{K_{d_{OH-F}}^{ap-melt} \times X_F^{ap}} \quad (1)$$

Where $C_{H_2O}^{PM}$ is the concentration of H₂O in the primitive melt, $X_{H_2O}^{ap}$ is the H₂O content of apatite, X_F^{ap} is the concentration of F in apatite, X_F^{Melt} is the concentration of F in the melt, which is assumed to be equal to that of the bulk rock, and $K_{d_{OH-F}}^{ap-melt}$ is the exchange coefficient determined by McCubbin et al (2015). The estimated water content of the Juvinas, Pasamonte, and Stannern primitive melts are 53 ± 14 , 52 ± 13 , 5 ± 1 µg/g H (470 ± 121 , 460 ± 120 , 40 ± 7 µg/g H₂O), respectively. These estimates should be considered minima if F is more compatible than H in pyroxene and plagioclase, if degassing took place prior to apatite crystallization, and/or if abundant H₂ was present in the melt. The large uncertainties in the calculated H₂O contents are due to the sizable variations in measured F contents in the literature. However, the eucrite melt water contents fit into petrologic models for eucrite genesis and our isotope measurements, where Pasamonte and Juvinas have similar H, major and trace element contents, and isotopic signatures (Fig. 4). The elevated δD of Stannern (Fig. 4) suggests that H degassing took place during either magma cooling or crustal interaction (Barrat et al., 2007) and low calculated H content of the Stannern primitive melt further support the

degassing hypothesis. We would like to emphasize that these are estimates of eucrite parent melt H contents and determining the H content of 4-Vesta is beyond the scope of this contribution.

(2) An alternate method to estimate the bulk H₂O content of 4-Vesta is to use bulk rock volatile-refractory elemental ratios, extrapolating them to a 4-Vesta composition. We can assume a maximum initial preserved eucrite melt H content of ca. 112 µg/g (1000 µg/g H₂O), by extrapolating the volatile element depletion of eucrites based on the K/U of Earth, the Moon and eucrites (Fig. S1; Hauri et al., 2015; Sarafian et al., 2013 Marty, 2012; Hirschmann and Dasgupta, 2009). This approach fundamentally assumes that K and U are not fractionated from one another, which may not be the case if a magma ocean was present. We also must assume a constant depletion factor from K to H. For Earth, this assumption holds true for many elements (Lodders, 2003), except for some, e.g., Cl (Sharp and Draper, 2013). Therefore, we would like to emphasize that this is a crude estimate for the H content of eucrite melts.

The solubility of H is pressure dependent (Berndt et al., 2002; Dixon et al., 1995;). Using previously established H solubility models (Berndt et al., 2002; Dixon et al., 1995;), our upper H content limit of 112 µg/g H as OH in a vestan magma ocean is soluble at a pressure of 2.29 MPa, or at ~3 km deep; less overburden is needed for ca. 22.4 µg/g H dissolved as OH. At a depth of 6 km, ~2000 µg/g H₂O is soluble (Berndt et al., 2002; Dixon et al., 1995). If we choose the initial preserved H content of 22.4–112 µg/g based on our above hygrometry calculations, and assume the vestan magma ocean crystallized 50%, then the magma ocean must be under at least 2.5 km to 11 km of crust to allow for our observed H₂O contents, which agrees with other recent crustal thickness

models (Mandler and Elkins-Tanton, 2013) and chronological constraints (Roszjar et al., 2016).

5.3 Possible Cl and H isotope fraction processes:

Apatite in eucrites display an extremely wide range of $\delta^{37}\text{Cl}$ values that correlate with the bulk rock major- and trace-element content and apatite halogen content (Fig. 3A-E). Processes that can fractionate the Cl isotopes include (a) perchlorate formation (Farley et al., 2016; Jackson et al., 2010), (b) distillation (Sharp et al., 2010a), and (c) degassing of metal chlorides (Sharp et al., 2010b). (a) Perchlorate (ClO_4^-) forms by UV irradiation of Cl and generally affects samples in desert environments due to low water flux, and can impart a wide range of Cl isotopic compositions, both heavy and light (Bellucci et al., in press; Farley et al., 2016; Jackson et al., 2010). If perchlorate caused the wide range of observed $\delta^{37}\text{Cl}$ values, then surface contamination of basalts would be the primary process driving the variation in $\delta^{37}\text{Cl}$. In this case, we may expect a correlation between $\delta^{37}\text{Cl}$ and halogen content as well as exposure age or solar wind derived noble gas content (Cartwright et al., 2013). However, regolithic eucrites do not exist in the meteorite collection and regolithic howardites are rare (Cartwright et al., 2013). Additionally, our sample with the most elevated $\delta^{37}\text{Cl}$ is an unbrecciated rock, meaning that it was likely not part of a regolith on the surface of 4-Vesta. Therefore, the observed range in $\delta^{37}\text{Cl}$ cannot be explained by perchlorates.

(b) Volcanic fumaroles produce vapors with high $\delta^{37}\text{Cl}$ values (Sharp et al., 2010a). In these fluid dominated systems, chloride ions evaporate to form HCl vapor causing $\delta^{37}\text{Cl}$ fractionation where the heavy isotope resides in the vapor, and the light

isotope remains in the liquid (Sharp et al., 2010a). The vapor phase is isotopically heavy because the bond strength of HCl_g is stronger than the Cl^- dissolved in the liquid (Sharp et al., 2010a). The H isotopes also fractionate during evaporation (Horita and Wesolowski, 1994). There is a strong temperature-dependence on the D/H fractionation, but at temperatures less than 230 °C the vapor is isotopically light and at temperatures between 230-360 °C the vapor is slightly heavy, <10‰. If boiling/distillation fractionated the Cl isotopes, then apatite with the most elevated $\delta^{37}\text{Cl}$ signature should be associated with the lowest D/H if the apatite equilibrated with a low-temperature fluid, or no measurable variation in D/H if the boiling/distillation event was at high temperature. Boiling/distillation was likely not the mechanism to cause $\delta^{37}\text{Cl}$ variation because we observe the highest $\delta^{37}\text{Cl}$ associated with elevated D/H (Fig. 4). Additionally, if all of the studied eucrites were the product of intense hydrothermal alteration secondary phases, e.g., clays and other phyllosilicates, would likely be pervasive.

5.3.1 Magma ocean degassing: (c) Degassing of high-temperature magmas causes the loss of many volatile species, including K^+ , KOH, KCl, HCl, H_2O , H_2 (Schaefer and Fegley, 2004). Degassing of HCl causes little if any Cl isotope fractionation (Sharp et al., 2013b), but degassing of metal chlorides, like KCl causes a significant increase in $\delta^{37}\text{Cl}$ (Fig S2; Sharp et al., 2010b). Additionally, Br/Cl and I/Cl likely decreases during crystallization (Kusebauch et al., 2015a).

As stated above, eucrites are a sampling of the asteroid 4-Vesta and geochemically similar asteroids. The eucrite main group likely formed via extraction from an equilibrium crystalizing magma ocean into magma chambers by fractional

crystallization (Mandler and Elkins-Tanton, 2013). Therefore, less evolved eucrites, e.g., low [Sc] or high [Mg], were extracted from the magma ocean earlier than evolved eucrites e.g., high [Sc] or low [Mg]. Systematic trends can be observed across many major and trace elements when plotted against $\delta^{37}\text{Cl}$ (Figs. 3A-D). One trend shows K, an incompatible element in mafic/ultramafic systems, decreases with increasing Sc and $\delta^{37}\text{Cl}$ (Figs. 3A & 3D). This correlation suggests that K either acts compatibly during magma ocean crystallization, or degassed during 4-Vesta's magma ocean phase (Mittlefehldt, 1987). The latter is more likely, as K degases from high-temperature magmas (Schaefer and Fegley, 2004). Additionally, the Br and I content of apatite decreases by a factor of ca. 3.5 and 2.3 (Tables 1, S2), respectively, from the lowest to highest $\delta^{37}\text{Cl}$ value measured. This decrease is expected, as first-order high-temperature volatility scales with atomic number (Bunsen, 1866). The decrease in Cl content does not follow the Br and I trend, which could be because Cl is a major structural component in apatite, meaning Cl partition between apatite and melt is non-ideal, or more likely, degassing of Cl may have been rate-limited due to its high solubility in melts. Here, we suggest that the correlation between major and trace elements, and halogens with $\delta^{37}\text{Cl}$ are related to degassing of the 4-Vesta magma ocean, where increasing $\delta^{37}\text{Cl}$ with decreasing K is observed. Alternatively, the degassing event(s) could have occurred during magmatic emplacement or eruption after a magma ocean stage. This hypothesis is supported by the large variation in H isotope composition observed in apatite, but is inconsistent with the excellent correlation between bulk rock $\delta^{66}\text{Zn}$ and apatite $\delta^{37}\text{Cl}$ of the eucrites investigated (Fig 3F; Paniello et al., 2012b), as stable Zn isotopes do not fractionate during magmatic emplacement (Paniello et al., 2012a). Therefore, we suggest that while some of the

isotopic variation (including Cl) are related to magmatic emplacement processes, the large-scale Cl isotope fractionation occurred during degassing of the magma ocean. In addition, the decreasing Br/Cl and I/Cl may be due to magma ocean degassing too, but also could be due to incompatible nature of Br and I relative to Cl.

During the magma ocean stage of lunar formation, it has been hypothesized that metal chloride degassing occurred because some apatite were found to have a relative enrichment of ^{37}Cl (Barnes et al., 2016; Boyce et al., 2015). Likewise, we suggest that during the magma ocean stage of 4-Vesta, while eucrite magmas were segregating and erupting, degassing of metal chlorides (or metal halides) occurred. Degassing of the magma ocean could have been enhanced by impacts breaking through the crust (Barnes et al., 2016), or degassing may have occurred despite the presence of a crust due to the low pressure environment on 4-Vesta. Our degassing models, which assume Rayleigh fractionation, show that a ~60% loss of Cl as KCl will evolve the $\delta^{37}\text{Cl}$ from -3.8‰ (average NWA 5073 $\delta^{37}\text{Cl}$) to 7.7‰ (average GRA 98098 $\delta^{37}\text{Cl}$; Fig. S2). Therefore, the large range in Cl isotope compositions observed in basaltic eucrites can be explained by a simple metal chloride degassing model (Fig. 3).

It can be assumed that Cl and H species were likely degassing at the same time. The H isotope fractionation between melt and vapor is controlled by (1) the isotope fraction factor of the degassing species, H_2 and H_2O , and (2) the abundance ratio of the two species (Fig. S3). The isotope fractionation factors (α) commonly used for H_2 and H_2O are 0.816 and 1.049 (Newman et al., 1988), but the α for H_2O between melt and vapor is likely a function of melt composition and pressure and has not been fully parameterized (Newman et al., 1988). The abundance ratio, $\text{H}_2:\text{H}_2\text{O}$, is controlled by the

oxygen fugacity of the system (Hirschmann et al., 2012). At the oxygen fugacity of eucrite formation, IW-1 (McSween et al., 2012; where IW-1 is 1 log unit below the Fe $\rightarrow$ FeO oxygen buffer), low pressure and low H₂O content, the molar H₂:H₂O ratio is ~5:95 (Hirschmann et al., 2012). If the concentrations of H₂ and H₂O in the magma ocean are above saturation, a mixture of H₂ and H₂O will degas, although H₂ may degas more rapidly than H₂O (Sharp et al., 2013a). Degassing will stop when the volatile species is no longer saturated in the melt. At low oxygen fugacity, the H₂ fugacity is much higher than the H₂O fugacity, meaning that H₂O will become soluble in the melt before H₂ (Sharp et al., 2013a). If degassing took place at a lower oxygen fugacity (Pringle et al., 2014), or if H₂ degasses more efficiently than H₂O (Sharp et al., 2013b), then one would expect to generate greater H isotope fractionation than observed here. 4-Vesta likely accreted and underwent core formation at a very low oxygen fugacity, however this was likely prior to any volatile accretion 4-Vesta experienced (Pringle et al., 2014).

We model the vestan magma ocean by first degassing H₂, H₂O, and metal chlorides for a period, followed by degassing of only H₂ and metal chlorides (Fig. 4). The system can switch from a mixed H₂–H₂O species, which causes little H isotope fractionation (Fig. S3) to only H₂, which causes massive H isotope fractionation, for two reasons, (1) H₂O can become soluble due to low concentrations of H₂O in the magma ocean, or (2) H₂O becomes soluble due to an increase of pressure (Berndt et al., 2002; Dixon et al., 1995). Our model shows that mixed-phase degassing can explain the variations seen in the data (Fig. 4) and requires an early-formed crust at least 3-11 km in thickness, which generally agrees with recent physicochemical models of 4-Vesta (Mandler and Elkins-Tanton, 2013) and chronological constraints (Roszjar et al., 2016).

The location of the inflection point (where Juvinas sits, Fig. 4) is a function of absolute H₂O content and crustal thickness (pressure).

5.4 Stannern, the outlier:

Stannern is enriched in incompatible elements relative to $\delta^{37}\text{Cl}$ compared to the other eucrites studied here (Figs. 1, 3D). Apatite in Stannern also has an elevated δD relative to other eucrites (Barrett et al., 2016; Sarafian et al., 2014), yet has unfractionated Cl isotopes (Fig. 3). Stannern, the namesake of the Stannern trend, was likely generated by mixing small degree crustal partial melts with main group-type magmas (Yamaguchi et al., 2009; Barrat et al., 2007). The partial melt generated would be enriched in the incompatible elements, including H and Cl, and likely degassed H₂. A loss of at least 60% of total H can account for the enrichment of D, if no H₂O degassing took place at the time of crystallization. The NWA 5073 sample is another member of Stannern trend eucrites, but likely samples a relatively primitive magma ocean. We suggest that Stannern received its Cl isotope signature from the magma ocean but underwent further processing, e.g., interaction with a crustal melt.

5.5 The $\delta^{37}\text{Cl}$ of 4-Vesta:

Here we have shown that magma ocean degassing of mixed species (KCl, HCl, H₂O, H₂) is the likely mechanism that caused the observed enrichments in $\delta^{37}\text{Cl}$ and δD . Our best estimate for the primordial $\delta^{37}\text{Cl}$ of 4-Vesta derives from the eucrite with the lowest measured $\delta^{37}\text{Cl}$, NWA 5073, $-3.8 \pm 1.1\text{‰}$ (2 sd, n=23) based on our bulk rock major- and trace-element content and apatite halogen content trends (Fig. 3). Our

estimate (1) would be an upper limit for 4-Vesta, because magma ocean degassing increases the $\delta^{37}\text{Cl}$ of segregated magmas and we probably did not sample the most primitive lava possible (such as the primitive eucrite Sioux County); (2) is within error of some unequilibrated chondrites (Williams et al., 2016; Sharp et al., 2016; 2013b). The similarly low $\delta^{37}\text{Cl}$ of 4-Vesta and the chondrites Parnallee and NWA 8276 (Sharp et al., 2016; 2013b) may suggest a primordial light Cl isotope reservoir existed, but was extremely difficult to preserve.

5.6 The volatile element accretion/processing in the inner solar system:

4-Vesta, with a fast accretion history (Touboul et al., 2015), likely avoided any potential isotopically heavy HCl hydrate ices (Sharp et al., 2016), which condenses around 140–160 K (Zolotov and Mironenko, 2007). If 4-Vesta did not receive HCl hydrate ices, then it may not have received other hydrous- and carbon-bearing ices, as H and C condense at ca. 180 and 40 K, respectively (Lodders, 2003), meaning 4-Vesta would be relatively depleted in H, C, Cl, and other elements contained in ice, compared to bodies with a $\delta^{37}\text{Cl}$ of 0‰. Consequently, 4-Vesta could have avoided the delivery/and or accumulation of HCl hydrate ice because the ices probably were lost once “wet” material crossed an ice line, presumably in the early inner solar system, or 4-Vesta finished primary accretion prior to ice injection into the inner solar system. Interestingly, the terrestrial mantle likely has a $\delta^{37}\text{Cl}$ value of ca. 0‰ (Sharp et al., 2013b), although some mantle reservoirs are as light as -3‰ (Halldórsson et al., 2016; John et al., 2010). Therefore, if the source of H is the same between Earth, the Moon and 4-Vesta (Barrett et al., 2016; Sarafian et al., 2014; Clog et al., 2013; Saal et al., 2013), then some processes

that affected the Earth and possibly the Moon must have fractionated the Cl isotopes without fractionating the H isotopes, or 4-Vesta is missing a heavy-Cl component independent of the other volatile elements.

6. Conclusions:

Here we have shown that F is a phase-limiting element for apatite growth in eucrite basalts. Using apatite hygrometry we have shown that the Juvinas/Pasamonte primitive melt contained ~200–600 $\mu\text{g/g}$ H_2O . We have also shown large variations in apatite Br/Cl and I/Cl, and $\delta^{37}\text{Cl}$ were preserved in eucrite meteorites. Large-scale geochemical trends, interpreted to be evidence of a magma ocean on 4-Vesta, were related to apatite Br/Cl and $\delta^{37}\text{Cl}$. 4-Vesta likely had a magma ocean that degassed many volatile species, including KCl, H_2 , H_2O , Br, and I. We confirm that Parnallee has a $\delta^{37}\text{Cl}$ of $-4.7 \pm 1.5\%$, which suggests that some chondrite parent bodies and 4-Vesta accreted a depleted Cl isotope signature compared to Earth and possibly the Moon. Either these bodies are missing a heavy Cl isotope volatile-element component, or Earth accreted from material that had been geochemically processed or was isotopically distinct from the start.

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Table 1. Cl isotope composition of measured apatite

	$\delta^{37}\text{Cl}$	2σ	Sample	$\delta^{37}\text{Cl}$	2σ	Sample	$\delta^{37}\text{Cl}$	2σ
Cachari			Juvinas					
Ap3	5.58	0.54	Ap4	-0.05	0.78	GRA 98098		
Ap3	6.25	0.54	Ap4	0.36	0.91	Ap2	7.66	0.31
Ap3	6.41	0.50	Ap5	1.27	0.94	Ap2	7.65	0.31
Ap3	5.12	0.44	Ap5	1.06	0.83	Ap3	6.77	0.31
Ap3	4.82	0.48	Ap2	-0.50	1.31	Ap9	8.29	0.31
Ap4	5.09	0.45	Ap2	1.22	0.90	Ap9	8.29	0.31
Ap4	5.06	0.43	Ap2	-0.94	1.22	Average	7.73	1.25
Ap4	6.00	0.58	Ap3	-1.18	1.80	Stannern (AMNH)		
Ap4	3.56	0.42	Average	0.16	1.96	Ap8	1.48	0.32
Ap5	4.38	0.51	NWA 5073			Ap8	1.08	0.35
Ap5	4.84	0.61	Ap7	-3.10	0.54	Ap4	-0.31	1.82
Ap5	6.02	0.56	Ap7	-3.08	0.54	Ap3	1.26	0.32
Ap5	4.99	0.77	Ap6	-3.37	0.56	Ap3	0.15	0.37
Ap1	4.15	0.44	Ap15	-2.94	0.56	Ap1	0.01	0.42
Ap1	6.13	0.44	Ap15	-2.26	0.70	Ap1	1.11	0.31
Ap1	4.90	0.44	Ap3	-3.70	0.51	Ap7	1.08	0.39
Ap1	4.74	0.44	Ap3	-3.22	0.56	Stannern (WWU)		
Ap6	4.53	0.41	Ap4	-3.91	0.56	Ap10	2.84	0.38
Ap6	2.35	0.45	Ap4	-3.51	0.53	Ap10	-0.37	0.36
Ap6	2.42	0.41	Ap2	-4.09	0.56	Ap10	2.03	0.36
Average	4.87	2.25	Ap2	-4.21	0.59	Ap10	2.03	0.34
NWA 1908			Ap10	-3.67	0.42	Ap11	2.32	0.42
Ap16	7.90	1.11	Ap10	-4.38	0.41	Ap11	2.76	0.52
Ap16	6.61	0.92	Ap11	-4.15	0.34	Ap11	3.18	0.34
Ap18	4.97	0.85	Ap11	-4.61	0.38	Ap11	3.44	0.46
Ap18	4.82	0.87	Ap11	-4.36	0.35	Ap11	2.67	0.36
Ap18	11.93	0.88	Ap12	-3.61	0.35	Ap11	2.45	0.42
Ap19	8.25	0.77	Ap12	-4.25	0.52	Ap17	2.82	0.40
Ap13	4.77	0.75	Ap12	-3.96	0.36	Ap17	1.74	0.40
Ap13	5.43	0.68	Ap13	-4.14	0.37	Ap17	3.26	0.38
Ap6	7.35	0.73	Ap13	-4.31	0.35	Ap13	0.92	0.36
Ap8	8.94	1.15	Ap13	-3.94	0.33	Ap13	0.15	0.40
Average	7.10	4.57	Ap13	-3.50	0.34	Ap13	1.93	0.42
Pasamonte			Average	-3.75	1.14	Ap13	2.27	0.44
Ap5	1.70	0.37				Average	1.69	2.30
Ap4	1.41	0.34						
Ap7	1.67	0.39						
Average	1.60	0.32						

602 Table 2. Hydrogen isotope composition and water concentration of measured
 603 apatite.

Sample	δD	2σ	[H ₂ O]	2σ	Sample	δD	2σ	[H ₂ O]	2σ
GRA 98098					NWA 1908				
Ap1	-124	21	2182	45	Ap14	-147	20	2672	55
Ap2	-45	29	988	20	Ap15	-83	20	2505	51
Ap3	-50	67	177	4	Ap16	-78	20	2622	54
Ap4	-65	77	143	3	Ap17	-157	15	9090	186
Ap5	-238	15	7183	147	Ap17	-97	20	2706	55
Ap6	-76	25	1460	30	Ap13	-207	24	1514	31
Ap7	-77	62	250	5	Ap6	-84	20	2975	61
Ap8	-206	27	1353	28					
Ap9	-133	44	417	9					
Ap10	-145	21	2110	43					
wtd avg	-126	139			wtd avg	-121	97		

Figure 1. Bulk rock Hf vs. Sc concentrations. Note that Stannern trend eucrites (Stannern and NWA 5073) are enriched in Hf compared to main group eucrites.

642 Figure 2. Fluorine vs. Cl in eucrite apatite and merrillite.

Figure 3. A) bulk rock Sc vs. $\delta^{37}\text{Cl}$; note the increase of Sc with $\delta^{37}\text{Cl}$, implying olivine instead of pyroxene was a major phase crystallizing during magma ocean crystallization. B) bulk rock Mg vs. $\delta^{37}\text{Cl}$ note decrease of Mg with increasing $\delta^{37}\text{Cl}$, implying olivine was a major phase crystallizing during magma ocean crystallization. C) bulk rock Cr vs. $\delta^{37}\text{Cl}$; note negative relationship between Cr and $\delta^{37}\text{Cl}$, implying spinel was crystallizing during magma ocean crystallization. D) bulk rock K vs. $\delta^{37}\text{Cl}$; note negative relationship between K and $\delta^{37}\text{Cl}$, implying loss of K during magma ocean crystallization. E). Apatite Br/Cl vs. $\delta^{37}\text{Cl}$; note negative relationship between Br/Cl and $\delta^{37}\text{Cl}$, degassing of Br and Cl during magma ocean crystallization. F) bulk rock $\delta^{66}\text{Zn}$ vs $\delta^{37}\text{Cl}$ are positively correlated. Stable Zn isotope do not fractionate during magma emplacement. Therefore, Cl and Zn must be fractionating during magma ocean cooling. Graves Nunataks 98098 gives a minimum value for $\delta^{66}\text{Zn}$ due to Antarctic weathering removing heavy Zn (Paniello et al., 2012b). See Supplementary information for references for bulk rock concentrations.

Figure 4. Hydrogen isotope composition vs. Cl isotope composition. Note positive correlation between the two isotope systems, which suggest that H and Cl were degassing contemporaneously.

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