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The abundance and isotopic composition of water in eucrites

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Abstract—Volatile elements play a key role in the dynamics of planetary evolution. Extensive work has been carried out to determine the abundance, distribution, and source(s) of volatiles in planetary bodies such as the Earth, Moon, and Mars. A recent study showed that the water in apatite from eucrites has similar hydrogen isotopic compositions compared to water in terrestrial rocks and carbonaceous chondrites, suggesting that water accreted very early in the inner solar system given the ancient crystallization ages (~4.5 Ga) of eucrites. Here, the measurements of water (reported as equivalent H\(_2\)O abundances) and the hydrogen isotopic composition (\(\delta D\)) of apatite from five basaltic eucrites and one cumulate eucrite are reported. Apatite H\(_2\)O abundances range from ~30 to ~3500 ppm and are associated with a weighted average \(\delta D\) value of ~34 ± 67\%\(_o\). No systematic variations or correlations are observed in H\(_2\)O abundance or \(\delta D\) value with eucrite geochemical trend or metamorphic grade. These results extend the range of previously published hydrogen isotope data for eucrites and confirm the striking homogeneity in the H-isotopic composition of water in eucrites, which is consistent with a common source for water in the inner solar system.

INTRODUCTION

Asteroids formed early within the solar nebula (~10\(^5\)–10\(^7\) years after CAIs; Chambers and Wetherill 2001; O’Brien et al. 2014) and are likely to have retained information regarding the very earliest processes occurring in the proto-planetary disk. They are, therefore, crucial for understanding how the solar system formed and evolved. Furthermore, because of their antiquity, composition, and heliocentric distance, asteroids may also provide clues to the delivery of water and other volatiles to the early Earth, the Moon, and more generally to the inner solar system, which is of prime importance in the context of development of habitable environments on the early Earth.

The howardite–eucrite–diogenite (HED) meteorites are a group of basaltic achondrites derived from a common parent body believed to be the asteroid 4 Vesta (McCord et al. 1970; Consolmagno and Drake 1977; Binzel and Xu 1993). The HED meteorites comprise the largest suite of crustal rocks available from a differentiated asteroid, and account for 3% of all meteorites collected globally, ~5% of all falls, and ~70% of all achondrites (Meteoritical Bulletin http://www.lpi.usra.edu/meteor/metbull.php; Janots et al. 2012). Since HED meteorites are some of the oldest achondrites, typically with crystallization ages from 4547 to 4559 Ma (Misawa et al. 2005; Zhou et al. 2013), determining their water inventory may provide crucial insights into the processes involved in the early water delivery to the inner solar system.

The volatile inventories of volatile-depleted bodies such as the Moon or Vesta have been poorly constrained until recently because of the limitations in analytical techniques. However, recent analytical advances in secondary ion mass spectrometry (SIMS) techniques have permitted the successful in situ detection of H in volcanic glasses and minerals such as
apatite from a variety of lunar and eucrite samples (Saal et al. 2008; Greenwood et al. 2011; Hauri et al. 2011; Barnes et al. 2013; Tartèse et al. 2013; Sarafian et al. 2014). Similar to lunar and Martian samples, eucrites contain two major phosphate minerals—apatite and merrillite. Apatite (Ca$_5$[PO$_4$]$_3$[F, Cl, OH]) is a widely distributed accessory phase in planetary materials, and has been used as a recorder of the relative abundances of the volatile species OH, F, and Cl in magmas and magmatic source regions (Patiño Douce and Roden 2006; McCubbin et al. 2011, 2014; Patiño Douce et al. 2011; Barnes et al. 2013; Sarafian et al. 2013, 2014; Tartèse et al. 2013, 2014b). In contrast, the phosphate merrillite ([Mg,Fe]$_2$REE$_2$Ca$_{16}$P$_{14}$O$_{56}$) does not incorporate significant volatiles, but is a major reservoir of rare-earth elements (REEs) (20,000–30,000 times chondrite, compared to apatite at 500–1000 times chondrite for light REEs; Delaney et al. 1984). In this study, we focus on apatite as it is the only known volatile-bearing mineral in eucrites (Delaney et al. 1984; Sarafian et al. 2013). Apatite contains hydrogen in the form of structurally bound OH, but in this contribution the measured OH abundance is converted to its weight equivalent H$_2$O for the purposes of comparing the data with those in the literature.

Currently the water inventory and isotopic composition of eucrites is poorly understood partly owing to a limited number of studies (Sarafian et al. 2013, 2014). Here, we present a comprehensive data set for the H$_2$O abundance and H isotopic composition of apatite in a suite of basaltic eucrites, representative of the principal geochemical trends and metamorphic grades, as well as for cumulate eucrites, which have not been analyzed previously. The isotopic signatures of water in eucritic apatite are assessed and processes, such as volatile degassing, which could have affected these signatures, are explored. By combining these new results with published data, the origin of volatiles in the inner solar system and the mechanisms/processes of volatile transport across the solar system are investigated.

**CRITERIA FOR SAMPLE SELECTION AND PETROLOGY OF THE STUDIED SAMPLES**

Based on their petrographic textures, monomict and unbrecciated eucrites are subdivided into cumulate and noncumulate (basaltic) groups (Stolper 1977; B.V.S.P. 1981; Mayne et al. 2009). The basaltic eucrites can be further subdivided geochemically into the Main Group-Nuevo Laredo and Stannern trends based on their magnesium numbers, Mg#$ ($or their Fe$_{\text{total}}$/MgO weight ratio), Ti content, and incompatible trace element abundances (Stolper 1977; Hsu and Crozaz 1996; Hutchison 2004; Barrat et al. 2007). The Main Group-Nuevo Laredo trend comprises the majority of the eucrites and is widely regarded as representing a fractional crystallization trend, where incompatible element abundances increase with Fe enrichment (Stolper 1977; Warren and Jerde 1987; Mittlefehldt and Lindstrom 2003). The Stannern trend eucrites are very similar to the main group for major elements. However, they contain greater abundances of Ti and incompatible trace elements (Barrat et al. 2000, 2007; Hutchison 2004). Barrat et al. (2007) suggested that contamination of Main Group-Nuevo Laredo trend eucrites by crustal melts can explain both the elevated incompatible element concentrations and the distinctive Eu, Sr, and Be anomalies exhibited by the Stannern trend eucrites when normalized to a representative Main Group eucrite. This crustal partial melt would leave behind a residual melt associated with LREE depletion, which Yamaguchi et al. (2009) observed in several eucrites and assigned them to a potential third geochemical trend.

The samples studied here are broadly representative of eucrites as a whole since they represent each of the five criteria listed below (see Table 1 for more details):

1. Samples were selected to represent the different geochemical trends, the Main Group-Nuevo Laredo trend, Stannern trend, residual, and cumulate eucrite.
2. To ensure both a representative sampling and to enable comparisons with the existing data set, both falls and finds were studied. To reduce the potential influence of terrestrial contamination on measured values, however, eucrite falls were preferred where possible.
3. Eucrites with a variety of metamorphic grades, between type 4 and 6 on the pyroxene thermal scale (Takeda and Graham 1991; Yamaguchi et al. 1996), were selected in order to examine whether a relationship exists between metamorphic grade and volatile composition.
4. A range of breccia types was chosen in order to assess any lithological-volatile patterns.
5. Samples with a range of cosmic ray exposure (CRE) ages were selected.

The amount of water reported by previous studies of apatite in eucrites ranges between ~80 to 7800 ppm H$_2$O (Sarafian et al. 2013). Sarafian et al. (2014) expanded on their initial study by reporting the $^{18}$H isotope composition of the water in five eucrites using the standard $\delta D$ (per mil, $\%_o$) notation whereby:

$$\delta D = \left\{ \frac{D_{\text{sample}}}{D_{\text{VSMOW}}} - 1 \right\} * 1000 \tag{1}$$

The reference used is VSMOW with a $D/H$ ratio of $155.76 \times 10^{-6}$ (Hagemann et al. 1970). The average $\delta D$
value of water measured in apatite from five eucrites was $-162 \pm 127_{\text{oo}}^\circ (2\sigma)$ (Sarafian et al. 2014).

**Samples**

Representative BSE images illustrating the textural and petrological context of the apatite grains analyzed in this study are given in Fig. 1.

**Dar al Gani 844**

Dar al Gani (DaG) 844 is a highly fractured, polymict breccia composed of large coarse-grained clasts supported in a fine-grained matrix. The lack of Ca zonation in pyroxene and inversion of pigeonite to orthopyroxene suggests that it is a type 6 eucrite (Takeda and Graham 1991). Minor phases include apatite, troilite, ilmenite, chromite, zircon, and merrillite. Apatite occurs as subhedral to anhedral crystals within fine-grained mesostasis areas, typically ranging in length from 5 to 20 µm, and is associated with other late-stage minerals. Apatite and merrillite were found together only in one area of this sample (Fig. 1).

**Dar al Gani 945**

Dar al Gani (DaG) 945 is a coarse-grained granulitic eucrite mainly composed of subhedral type 4 pyroxene and plagioclase, with some fine-grained relict mesostasis regions. The sample shows well-defined 120° triple junctions indicative of significant recrystallization (Yamaguchi et al. 2009). Minor phases include apatite, zircon, ilmenite, a silica polymorph, and chromite, all of which usually occur within the late-stage mesostasis areas. Apatite grains in this sample are abundant and subhedral, ranging in size from ~10 to 50 µm in the longest dimension (Fig. 1).

**Millbillillie**

Millbillillie is a polymict breccia comprising type 6 pyroxene; an indicator of significant thermal metamorphism (Takeda and Graham 1991; Yamaguchi et al. 1994, 1996). The sample consists of two dominant rock types. The first lithology displays areas with a fine-grained subophitic, basaltic texture, in which the interstitial pyroxene has recrystallized to a fine-grained granoblastic texture. This first lithology may have formed as a fast-cooling lava, possibly near the surface of the parent body. The second lithology is a coarse-grained granulitic breccia (Bobe et al. 1989; Yamaguchi et al. 1994, 1996). Minor phases occur in both lithologies and include chromite, apatite, ilmenite, a silica polymorph, troilite, merrillite, and zircon. Apatite grains in both lithologies range from ~10 to 100 µm in the longest direction. In the coarse-grained granulitic lithology apatite is typically anhedral. Apatite has also been found within the finer grained lithology. Only apatite grains from the coarser grained (granulitic) region were analyzed in this study (Fig. 1).

**Sioux County**

Sioux County is a heavily fractured, coarse-grained breccia. Pyroxene crystals are mainly type 5. According to the Meteoritical Bulletin Database, Sioux County is monomict; however, Yamaguchi et al. (1997) suggested that there are also minor amounts of type 4 and type 6 pyroxene within the sample, suggestive of a polymict breccia. Plagioclase occurs as a mixture of large fractured grains (~a few mm), or as fine-grained crystals interstitial to the coarser grains. Minor phases include apatite, troilite, zircon, ilmenite, merrillite, and a silica polymorph. Apatite grains are mainly subhedral, ranging in size from 10 to 60 µm, occurring interstitially between the larger silicate minerals (Fig. 1).

**Stannern**

Stannern is a type 4 monomict breccia displaying medium-grained subophitic texture. Late-stage fine-grained mesostasis pockets typically occur interstitially between the large (several mm in the longest axis) plagioclase laths. Minor phases include apatite, ilmenite, troilite, a silica polymorph, merrillite, and zircon.
Fig. 1. Representative backscatter electron (BSE) images of each of the eucrite samples. Pl = plagioclase, Px = pyroxene, Ap = apatite, Mrl = merrillite, ilm = ilmenite, Cr = chromite, Tr = troilite, Si = silica phase, Zr = zircon. Solid white squares represent approximate location of SIMS raster area.
Apatite in Stannern occurs as subhedral to anhedral crystals, which range in size from ~10 to 100 μm in length and are associated with relict mesostasis (Fig. 1). In one region of Stannern (discussed later), apatite appears to have cococrystallized with pyroxene, whereas apatite in other areas appears to have crystallized later, along with other late-stage phases such as ilmenite and troilite. Moore County

Moore County is a coarse-grained, unbrecciated cumulate eucrite. The meteorite consists of large, mm-sized euhedral to subhedral pyroxene grains with coarse augite exsolution features (~15–100 μm) and granular plagioclase. Minor phases include tridymite, ilmenite, chromite, troilite, Fe-Ni metal, and apatite (Hess and Henderson 1949; Mayne et al. 2009). Apatite primarily occurs as subhedral or acicular grains typically 10–50 μm in longest dimension (Fig. 1).

METHODS

Secondary Electron Microscopy

Each polished thin-section was carbon-coated using an EMITECH K950X Turbo carbon sputter coater and examined at The Open University using a Quanta 3-D Focused Ion Beam Scanning Electron Microscope (FIB SEM) fitted with an Oxford Instrument INCA energy dispersive X-ray detector. An electron beam with an acceleration voltage of 20 kV and a beam current of 0.6 nA was used for the acquisition of all the backscattered electron (BSE) images and X-ray maps. The latter were acquired for the entirety of each section to locate phosphates, which could be achieved readily on account of their elevated and concordant Ca and P X-ray counts.

Once located, high-resolution BSE and secondary electron (SE) images of the phosphates were collected. Rapid energy dispersive X-ray spectroscopy (EDS) spot analyses (~30 s exposure) were then acquired to distinguish apatite from merrillite (short exposure at low beam currents does not affect the water contents or δD values of apatite; Barnes et al. 2013). Apatite grains suitable for further analysis were then selected based on their dimensions (>10 μm × 10 μm) and relative lack of fractures and inclusions.

NanoSIMS Protocol

Prior to ion-probe analyses, the carbon coat used for SEM analysis was removed and replaced with a ~30 nm gold coat. Samples were stored in a vacuum oven at ~55 °C for at least 24 h. Once in the airlock, the sample was left to degas under vacuum at ~55 °C for at least a day before transferring it to the vessel chamber. Analyses were conducted using a Cameca NanoSIMS 50L at the Open University following a well-established protocol (Barnes et al. 2013, 2014; Tartièse et al. 2013). Prior to analysis, areas (typically 12 μm × 12 μm) containing target apatite grains were presputtered to remove surface contamination, using a large Cs+ primary beam of ~600 pA current with an acceleration voltage of 8 kV, the sample surface being at ~8 kV. The instrument was set up in multicollection mode, measuring negative secondary ions of 1H, D, 12C, and 18O on electron multipliers with a mass resolving power of ~4300 (Cameca definition) sufficient to resolve 1H2 from D2. An electron flood gun was used to compensate for charge build up. For analysis, the beam current was lowered to ~250 pA and the raster area was reduced to a 10 μm × 10 μm area, with a 25% electronic gating set in order to collect only secondary ions emitted from the central zone (5 μm × 5 μm) of the analysis area. Secondary ion images of 1H and 12C were monitored in real time during presputtering to ensure that the area to be analyzed was free of cracks or hotspots indicative of contamination. Monitoring the 1H and 12C ion beam intensities during analyses allowed the identification of cracks originally hidden beneath the surface. In such cases, only portions of the secondary ion signals corresponding to analysis of pristine material were considered and isolated using the NanoSIMS DataEditor software (Frank Gyngard, Washington University). In cases where apatite grains showed extensive cracks or were particularly small, the raster size was reduced to as small as 4 μm × 4 μm. The D/H and 12C/16O ratio of standards analyzed at smaller raster sizes are comparable to those obtained during typical standard measurements. Analysis rasters were divided into 64 × 64 pixels and the counting time was set to 132 μs/pixel, corresponding to 0.54 s/cycle. Each analysis consisted of 2000 cycles, corresponding to a total analysis time of about 18 min. Typical counts per second of 1H and 2D were 9.3 × 104 and 1.9, respectively, for samples with ~1000 ppm H2O and 8.5 × 102 and 1.9 × 10−1, respectively, for ~100 ppm H2O samples. Terrestrial apatite standards (Ap004, Ap005, Ap018, Ap020 see McCubbin et al. 2012), along with a nominally anhydrous San Carlos olivine, were used to correct for instrumental mass fractionation of H isotopes and to calculate both apatite water contents and the total background water contribution.

Background water in the instrument can have a large effect on the D/H ratio measured in apatite, especially when apatite has a very low H2O content. The raw data for measured water contents in apatite...
were first corrected for the background contribution, which ranged from the equivalent of 14–31 ppm H₂O depending on the analytical session. The background was determined using the ¹H/¹⁸O ratios measured on the nominally anhydrous San Carlos olivine and the calibration slope for the corresponding analytical session. The background water content measured on San Carlos olivine represents the total background comprising detector dark noise (measured to be 0.0016 cps across all detectors), hydrogen desorbed by the electron beam, and the contribution from other sources (e.g., epoxy degassing). The raw D/H ratios were corrected based on the percentage contribution of the instrument background to the measured H₂O content, and the δD value of the instrument background (132 ± 150‰, based on 44 repeated measurements on the nominally anhydrous San Carlos olivine), following the relationship:

$$ D/H_{\text{measured}} = (f \times D/H_{\text{apatite}}) + ((1 - f) \times D/H_{\text{background}}) $$

where $f$ is the proportion of H emitted from the apatite and $1 - f$ the proportion of H attributed to the instrument background. The raw data along with background corrected data are listed in Table 2.

**Spallation Correction**

Spallation is a process caused by the interaction of cosmic rays with a rock residing within a few meters of the surface of a planetary body, which causes an increase in δD values through the spallogenic production of D. Effects of this process on δD values can be corrected by using the cosmic ray exposure (CRE) ages of the studied samples and the production rates of spallogenic H and D (e.g., Saal et al. 2008; Barnes et al. 2014). The cosmic ray flux for the asteroid 4-Vesta is not known; however, it is expected to be lower than that for the Moon, since 4-Vesta is at a greater heliocentric distance. Therefore, using the lunar production rates ($2 \times 10^{-10}$ mol H₂ g⁻¹ Ma⁻¹ for H and $0.5 \times 10^{-12}$ mol D₂ g⁻¹ Ma⁻¹ for D; see, Merlivat et al. [1976]; Saal et al. [2013]; Barnes et al. [2014], and references therein) is likely to result in maximum corrections for cosmic ray exposure. Since no CRE age currently exists for DaG 844 and DaG 945, these samples were corrected for the effects of spallation using the oldest grouping of CRE ages for HED meteorites (38 Ma) to give a maximum corrected value. For the studied samples, correction for spallation effects did not change δD values significantly (Table 2) since their CRE ages are relatively young.

**RESULTS**

**H₂O Content and δD Signatures in Apatite**

In total, 32 measurements were carried out on 23 apatite grains from six samples, and the results are listed in Table 2 and plotted in Fig. 2. The measured apatite H₂O contents span more than three orders of magnitude, from ~30 ppm in Moore County to 3500 ppm in DaG 844. Apatite in Stannern displays the largest variation in water content, with a bimodal distribution clustering at ~40 ppm and 1600 ppm, the lower values coming from a single grain out of the three grains measured (Fig. 2e). In DaG 945, on the other hand, apatite grains display relatively restricted variations in H₂O content, ranging from 54 ± 2 to 229 ± 7 ppm (Fig. 2b). Apatite in this sample, however, is characterized by the largest variation in H-isotopic composition, with δD values ranging from +697 ± 403‰ to −441 ± 379‰ (Fig. 2b). The large uncertainties associated with the δD values for all samples (DaG 945 in particular) are related to the poor counting statistics associated with the low water contents of some apatite grains, and hence very low total counts of D. The cumulate eucrite Moore County contains apatite grains with the lowest water contents of 26 ± 1 to 124 ± 3 ppm (Fig. 2f). The δD values of the wettest apatites (>800 ppm H₂O) studied in DaG 844, Millbillillie and Stannern are similar and range from −174 ± 185‰ to +84 ± 122‰ (Figs. 2a, 2c, 2e, and 3). In some cases, it was possible to obtain multiple measurements within the same apatite grain (Fig. 2). With the exception of a single grain in Millbillillie it was found for most cases that there is little intragrain variability in H₂O content.

**DISCUSSION**

**Potential Influence of Terrestrial Alteration**

Of the six eucrites analyzed, four are falls, which are likely to have suffered minimal terrestrial alteration (Table 1). The remaining two eucrites, DaG 844 and DaG 945, are hot desert finds with weathering grades of W3 and W1, respectively. In these finds it is important to consider the potential terrestrial alteration history when assessing the indigenous D/H signatures of the water within analyzed apatite grains. The H-isotopic composition of central Saharan meteoric water and groundwater has been shown to vary between −70‰ and +20‰ (Saighi et al. 2001), which overlaps with the D/H ratios that were measured in these two samples. Apatite in DaG 945 contains water displaying a range in δD from −441 ± 379‰ (2σ) to
It is unlikely that terrestrial water would have altered the $\delta/D$ systematics of some apatite grains and not others located only a few millimeters away; this applies to areas where cracks are pervasive as well as where they are less frequent. Water can diffuse in and out of apatite, and the diffusivity of $H$ in apatite (at $P = 0.1$ MPa) was experimentally determined by Brenan (1993). In that study it was shown that the diffusion of water at temperatures $<200$ °C is far too slow for exchange between terrestrial waters and apatite. As the maximum temperatures experienced by the two meteorites found in the Sahara are likely to have been significantly below 200 °C, there should have been negligible exchange with terrestrial waters. Besides, we routinely monitor terrestrial contamination during NanoSIMS analysis using real time imaging (see Tartese et al. [2013] for further details) that allows us to screen any spurious data. Furthermore, there does not appear to be any systematic difference between the $H$ isotopic compositions of meteorite finds and falls, analyzed in this study. Therefore, we are confident that the apatite grains we have analyzed in the meteorite finds have retained their original isotopic $H$ compositions.

| Sample ID | $\delta D$ value raw ($\%$) | $\delta D$ value bkg corr ($\%$) | $\delta D$ value final ($\%$) | $2\sigma$ ($\%$) | $H_2O$ content raw (ppm) | $H_2O$ content bkg (ppm) | $H_2O$ content bkg corr (ppm) | $2\sigma$ (ppm) |
|------------|-----------------------------|---------------------------------|-----------------------------|----------------|--------------------------|---------------------------|-----------------------------|----------------|
| DaG 945    |                             |                                 |                             |                |                          |                           |                             |                |
| Ap1a       | 218                         | 243                             | 211                         | 402            | 78                       | 14                        | 64                          | 2              |
| Ap1b       | 586                         | 717                             | 679                         | 403            | 68                       | 14                        | 54                          | 2              |
| Ap1c       | 74                          | 64                              | 40                          | 428            | 86                       | 100                       | 86                          | 3              |
| Ap2a       | −25                         | −53                             | −84                         | 449            | 83                       | 81                       | 67                          | 2              |
| Ap3a       | −25                         | −46                             | −55                         | 261            | 94                       | 243                       | 229                         | 7              |
| Ap3b       | −17                         | −44                             | −79                         | 487            | 81                       | 74                       | 60                          | 2              |
| Ap4        | 103                         | 98                              | 75                          | 367            | 87                       | 106                       | 92                          | 3              |
| Ap5        | 110                         | 107                             | 82                          | 367            | 86                       | 94                       | 80                          | 4              |
| Ap6        | −366                        | −425                            | −441                        | 379            | 90                       | 145                       | 131                         | 7              |
| Ap7b       | −79                         | −106                            | −119                        | 299            | 92                       | 172                       | 158                         | 8              |
| DaG 844    |                             |                                 |                             |                |                          |                           |                             |                |
| Ap1        | −87                         | −107                            | −109                        | 157            | 99                       | 1159                      | 1145                        | 57             |
| Ap2        | −154                        | −173                            | −174                        | 185            | 99                       | 3666                      | 3652                        | 181            |
| Ap3        | −71                         | −89                             | −90                         | 92             | 99                       | 2444                      | 2430                        | 121            |
| Millbillillie |                       |                                 |                             |                |                          |                           |                             |                |
| Ap1a       | −49                         | −76                             | −80                         | 220            | 94                       | 275                       | 258                         | 9              |
| Ap1b       | −101                        | −126                            | −127                        | 131            | 98                       | 860                       | 843                         | 31             |
| Ap1c       | 334                         | 329                             | 326                         | 447            | 95                       | 330                       | 313                         | 12             |
| Ap2        | 106                         | 85                              | 84                          | 122            | 98                       | 1080                      | 1063                        | 39             |
| Ap3a       | 239                         | 242                             | 234                         | 299            | 89                       | 163                       | 146                         | 5              |
| Ap3b       | 95                          | 89                              | 74                          | 373            | 81                       | 91                        | 74                          | 3              |
| Ap4        | 135                         | 127                             | 118                         | 278            | 88                       | 147                       | 130                         | 5              |
| Stannern   |                             |                                 |                             |                |                          |                           |                             |                |
| Section 1 Ap1 | 23                  | 0                                 | −1                          | 89             | 99                       | 1860                      | 1843                        | 68             |
| Section 2 Ap4a | −8                  | −39                                | −40                         | 111            | 99                       | 1579                      | 1556                        | 33             |
| Section 2 Ap4b | 17                  | −13                                | −14                         | 93             | 99                       | 1772                      | 1749                        | 38             |
| Section 2 Ap2b | 47                  | 28                                 | −24                         | 327            | 62                       | 59                        | 36                          | 1              |
| Section 2 Ap2d | −197                | −349                               | −396                        | 416            | 65                       | 64                        | 41                          | 1              |
| Sioux County |                             |                                 |                             |                |                          |                           |                             |                |
| Ap6a       | −64                         | −105                            | −110                        | 363            | 90                       | 217                       | 194                         | 5              |
| Ap7b       | −235                        | −340                            | −354                        | 365            | 78                       | 102                       | 79                          | 2              |
| Moore County |                             |                                 |                             |                |                          |                           |                             |                |
| Ap1a       | 80                          | 94                              | 79                          | 361            | 57                       | 45                        | 25                          | 1              |
| Ap1b       | −47                         | −106                            | −115                        | 503            | 69                       | 62                        | 42                          | 1              |
| Ap4a       | 74                          | 83                              | 68                          | 332            | 58                       | 47                        | 27                          | 1              |
| Ap7a       | −214                        | −288                            | −289                        | 271            | 84                       | 147                       | 124                         | 3              |
| Ap11a      | 130                         | 129                             | 124                         | 283            | 78                       | 102                       | 79                          | 2              |

$Bkg\ cor$ = background corrected.

$+679 \pm 403\%\{\sigma\}$ (2σ). It is unlikely that terrestrial water would have altered the $D/H$ systematics of some apatite grains and not others located only a few millimeters away; this applies to areas where cracks are pervasive as well as where they are less frequent. Water can diffuse in and out of apatite, and the diffusivity of $H$ in apatite (at $P = 0.1$ MPa) was experimentally determined by Brenan (1993). In that study it was shown that the diffusion of water at temperatures $<200$ °C is far too slow for exchange between terrestrial waters and apatite. As the maximum temperatures experienced by the two meteorites found in the Sahara are likely to have been significantly below 200 °C, there should have been negligible exchange with terrestrial waters. Besides, we routinely monitor terrestrial contamination during NanoSIMS analysis using real time imaging (see Tartese et al. [2013] for further details) that allows us to screen any spurious data. Furthermore, there does not appear to be any systematic difference between the $H$ isotopic compositions of meteorite finds and falls, analyzed in this study. Therefore, we are confident that the apatite grains we have analyzed in the meteorite finds have retained their original isotopic $H$ compositions.
Fig. 2. Plot showing the variations between, and within, apatite grains for the different samples studied.
Magmatic Degassing

In the case of lunar picritic glasses and mare basalts, it has been argued that magmatic degassing of volatile species such as H$_2$ could have caused a strong increase in the $D/H$ ratio of residual water dissolved in the parent melts (Saal et al. 2013; Tartèse and Anand 2013; Tartèse et al. 2013; Füri et al. 2014). This process would have efficiently fractionated the isotopes of hydrogen through the preferential loss of H$_2$ gas, which enriches the water in the remaining melt in $D$. Since apatite crystallizes late in the crystallization history of basaltic melts (>90% crystallization, e.g., Sha 2000), it is likely to record elevated $D/H$ signatures and not the undegassed (primitive) magmatic signature, if degassing occurred. To test if magmatic degassing of volatiles such as H$_2$ could have been an important process during petrogenesis of the studied eucrites, the evolution of the $D/H$ ratio of the water dissolved in the melt during the concomitant degassing of a H$_2$ gas phase was modeled (Fig. 3). The model obeys the Rayleigh fractionation relationship $R = R_o \times f^{(\alpha-1)}$, where $R_o$ and $R$ are the initial and final $D/H$ ratios of water in the melt, respectively, $\alpha$ is the fractionation factor, and $f$ is the fraction of water remaining in the melt. The most H$_2$O-rich apatite analysis in this study (DaG 844 Ap2) is considered as the starting point for both H$_2$O abundance and $\delta D$. Figure 3 shows that the $\delta D$/H$_2$O systematics of apatite in the studied eucrites do not follow the calculated degassing trend, except for one analysis in DaG 945 (DaG 945 Ap1b), which is characterized by an elevated $\delta D$ value of $+679 \pm 403%$. This analysis is from an apatite grain where multiple analyses were undertaken that yielded lower $\delta D$ values ($+211 \pm 402%$ and $+40 \pm 428%$). This particular measurement, while plotting close to the degassing trend, is still within error of the majority of apatite measurements. Excluding this point, all the remaining measured $\delta D$ values are identical within analytical uncertainty over a range of H$_2$O contents that vary by more than two orders of magnitude. This suggests that the $H$ isotope signature of eucritic melts was not fractionated by magmatic degassing of H$_2$. On this basis, the majority of the apatite grains appear to record the magmatic signature of their parental melts. In the case of the lunar basalts, which likely crystallized as lava flows, volatile degassing is believed to have occurred at, or near, the surface of the Moon (Ustunisik et al. 2015). Since the H$_2$O/$\delta D$ characteristics of apatite grains from eucrites do not hint at any significant degassing effects this could suggest that these eucrites crystallized at depth, which inhibited any significant magmatic degassing.
Petrological, Geochemical, and Metamorphic Trends

No resolvable difference between the $\text{H}_2\text{O}$ content and $\delta D$ value of apatite from the Stannern and Main Group/Nuevo Laredo trends is observed within the data presented here. Our results, obtained on DaG 844, yielded apatite $\delta D$ values and $\text{H}_2\text{O}$ abundance overlapping with those published by Sarafian et al. (2014) for Stannern (Fig. 3). The apatite $\delta D$ values of other Main Group eucrites typically show more variation but remain within error of the Stannern trend apatite $\delta D$ values (Fig. 3). The apatite water content of Main Group eucrites from this study, however, displays a significantly larger range than most of the Stannern apatite values (Fig. 3). This is different from the abundances for other Main Group eucrites reported by Sarafian et al. (2014), which have higher and more restricted water contents (~650–2600 ppm H$_2$O).

However, apatite in Stannern does show a large variability in $\text{H}_2\text{O}$ between one grain (see the Criteria for Sample Selection and Petrology of the Studied Samples section) and the other two measured in this study (Fig. 2e). The petrologic context of the two high-$\text{H}_2\text{O}$ apatite grains is also distinct from that of the low-$\text{H}_2\text{O}$ grain (See Fig. 1 for high-$\text{H}_2\text{O}$ apatite grain and Fig. 4 for the low-$\text{H}_2\text{O}$ apatite). The high-$\text{H}_2\text{O}$ grains are located in more mesostasis-rich areas, suggestive of late-stage crystallization. The apatite grain containing less $\text{H}_2\text{O}$ (37 ± 1 and 42 ± 1 ppm H$_2$O, as opposed to >1500 ppm), on the other hand, appears to have cocrystallized with the silicates surrounding it and, therefore, may have crystallized earlier than the other apatite grains (Fig. 4). This observation is consistent with the evolution of apatite chemistry during fractional crystallization, where earlier crystallized apatite is F-rich and OH-poor and late-crystallizing apatite is more OH-rich (Boyce et al. 2014; McCubbin et al. 2015).

Also, these results do not show any sign of correlation between the $\text{H}_2\text{O}/\delta D$ characteristics of apatite and the metamorphic grade of the eucrites since apatite from types 4 and 6 eucrites are observed across the entire range of $\text{H}_2\text{O}$ abundances (Fig. 3). Three of the eucrites in which apatites were analyzed are believed to be polymict eucrites, DaG 844, Millbillillie, and Sioux County (Yamaguchi et al. 1994, 1997). One drawback of studying polymict breccias is that they represent a mixture of different lithologies that may have undergone different thermal and chemical histories. These variations may be reflected in the isotope systematics of minerals belonging to different clasts, which may make interpretation more complex. It has been suggested that many eucrites are monomict, based on the compositional homogeneity of pyroxene. However, Yamaguchi et al. (1994, 1997) have suggested that detailed examination of multiple thin sections of a single monomict breccia sample can reveal small amounts of other lithologies. In the polymict eucrite breccias studied here, apatite grains were selected in areas that display mineralogical relationships (i.e., late-stage mesostasis regions), similar to those in the other basaltic eucrites analyzed in order to minimize the possibility of apatite having an exogenous origin. These apatite grains contain water with a $D/H$ ratio identical to those in the monomict eucrites.

Comparison with Previously Published Data

With the exception of Stannern, the eucrites analyzed here have not been investigated previously for their water content. The results obtained on two of the three Stannern grains (~1500–1800 ppm H$_2$O and $\delta D$ around $-20 \pm 10^\circ$o, section 1 Ap1 and section 2 Ap4) analyzed in this study are in close agreement with those reported by Sarafian et al. (2014) (~1500–2600 ppm H$_2$O and $\delta D$ around $-75 \pm 36^\circ$o). Apatite in the other eucrites analyzed here, however, show a larger variability in H$_2$O contents and $\delta D$ values, with most H$_2$O contents being a factor of 10 lower than previously published values (Sarafian et al. 2014). Similar to measurements of apatite in lunar plutonic and volcanic rocks, some apatite grains show large intragrain variability in H$_2$O contents (Tartèse et al. 2013; Barnes et al. 2014). For example, a single apatite grain in Millbillillie (Ap1) showed a range from 257 ± 9 to
842 ± 31 ppm H$_2$O. Such variations probably reflect crystallization processes, and an increase in the H$_2$O content from core to rim could reflect increasing $H/F$ and $H/Cl$ ratio in the melt as apatite crystallized (Boyce et al. 2014); however, this was not directly observed as neither $F$ nor Cl was measured in this study.

The weighted average $\delta D$ value of all apatite grains from this study ($-34 \pm 67\%$, $n = 32$, 95% confidence) is within error of the upper limit of the weighted average for water in bulk Vesta ($-162 \pm 127\%$) proposed by Sarafian et al. (2014). Combining the data obtained in this study with previously published results gives a weighted average $\delta D$ value of $-151 \pm 23\%$ (95% confidence level, $n = 43$).

**Possible Origin(s) for H in the Inner Solar System**

Since eucrites represent some of the oldest achondrite samples (Misawa et al. 2005; Zhou et al. 2013), determining the origin(s) of water in the HED parent body also provides temporal constraints regarding water delivery in inner solar system bodies, assuming that these bodies accreted largely dry (Boss 1998; Lucey et al. 2006; Albarède 2009). In this case, the ancient age of eucrites (typically 4547 to 4559 Ma) argues in favor of delivery of water very early in the inner solar system from homogeneous sources (Sarafian et al. 2014), but against the gradual increase in $D/H$ ratio with increasing distance from the Sun that has been proposed based on radial temperature gradients and equilibrium factors (Drouart et al. 1999; Mousis et al. 2000).

Early accretion of water to the inner solar system seems at odds with one of the current theories for the Moon’s volatile inventory, namely the late delivery of volatiles to the magma ocean (Bottke et al. 2010; Tartèse and Anand 2013; Füri et al. 2014, 2015; Hauri et al. 2015). One possible way to reconcile this apparent conflict is to imagine that the small planetesimals, such as Vesta, acquired their volatiles relatively early from a homogenus reservoir, consistent with the water $D/H$ ratios observed in these different planetary bodies.

Early in the history of the solar system, accreting bodies such as Vesta would have been hot and may have passed through a stage of global melting to produce partial or complete magma oceans (e.g., Snyder et al. 1992; Greenwood et al. 2005; Mandler and Elkins-Tanton 2013). It is plausible during the planetesimals’ magma ocean stage that degassing of volatile species could have led to elevated bulk $DH$ ratio (Sharp et al. 2013). However, this would require all inner solar system bodies to degas to a homogenous final $D/H$ ratio, an unlikely scenario given the difference in size between some of these bodies and that degassing was likely to have been more efficient in smaller bodies.

While addition of volatiles to planetesimals after their formation is a possibility, it can also be argued that water is indigenous in inner solar system objects, and that no late addition is necessary. Muralidharan et al. (2008) and King et al. (2010) demonstrated that water can be chemisorbed to fractal forsterite grains even at temperatures previously believed to be too hot for hydrous phases to be thermodynamically stable (Boss 1998). Unless water was fractionated during adsorption on forsterite grains, the $D/H$ ratio of the adsorbed water was likely to be similar to the protosolar $\delta D$ value of $-865\%$ (Lellouch et al. 2001). If inner solar system objects accreted water initially characterized by similarly low $D/H$ ratios then a mechanism capable of increasing $D/H$ ratios to the levels observed in inner solar system bodies, about an order of magnitude higher, is required.

Incorporation of materials to explain the increase in $D/H$ ratios from protosolar values is also a valid alternative. Objects formed at greater heliocentric distances, such as comets, seem to be characterized by a much larger range in $D/H$ ratios, ranging from terrestrial-like (e.g., 103P/Hartley 2; Hartogh et al. 2011) to those about three times higher than terrestrial values (e.g., 67P/Churyumov-Gerasimenko; Altwegg et al. 2015). However, these $D/H$ measurements were not made directly on water ice in the comet nucleus, but on the gas emitted during sublimation, which could have different water $D/H$ characteristics (Drake 2005; Drake and Campins 2005). Comets also contain a large amount of organic material, which is typically characterized by elevated $D/H$ ratios (Robert 2006), and therefore, the bulk composition of comets is likely to be more D-rich than cometary water. The addition of a minimum of $-25\%$ cometary material would be required (based on the most elevated $D/H$ ratio measured in 67/P) to elevate solar values to those observed in this study, with much more required if comets with lower $D/H$ ratios were added. Given the uniformity of the bulk $D/H$ ratio of Vesta (inferred from this study) versus the variably elevated $D/H$ ratio of water in most comets, it is unlikely that cometary impacts represent the sole method by which water was delivered to the inner solar system (e.g., Dauphas et al. 2000).
Alternatively, Alexander et al. (2012) demonstrated that the CI chondrites plot on a line connecting solar nebula values for both hydrogen and nitrogen isotopes and bulk Earth, and proposed that a ~10% contribution of solar isotopic composition to compositions similar to those of CI chondrites could explain the $D/H$ ratio of the Earth.

The $D/H$ signatures of water in apatite in eucrites measured in this study (weighted average $\delta D$ value of $-34 \pm 6\%_w$) and by Sarafian et al. (2014) (weighted average $\delta D$ value of $-162 \pm 127\%_w$) are consistent with $D/H$ values measured in CI, CV, CM, and CO carbonaceous chondrites (Robert 2006; Alexander et al. 2012), terrestrial materials (Lécuyer et al. 1998), and in some lithologies from the Moon (Saal et al. 2013; Tartèse et al. 2013, 2014a; Anand et al. 2014; Barnes et al. 2014) (Fig. 2). The lunar highland samples studied by Barnes et al. (2014) are lunar crustal material and, therefore, potentially provide an indication of the primordial lunar H-isotopic signature, especially because these plutonic samples crystallized deep in the lunar crust around 4.35 Ga ago, likely preventing any significant volatile degassing. Apatite in these rocks have a H$_2$O content range (~90–1800 ppm H$_2$O) and $\delta D$ values similar to those measured in apatite in the eucrites (Fig. 2). Taken together, the striking homogeneity displayed by inner solar system bodies would seem to indicate a common source for water in the inner solar system.

**CONCLUSIONS**

1. Apatite from eucrites records the indigenous H-isotopic composition of the HED parent body.
2. There is no resolvable difference between the H$_2$O content and $\delta D$ values of apatite in the Stannern versus the Main Group–Nuevo Laredo trends.
3. Metamorphism on the HED parent body appears to have had little effect on the H$_2$O content and $\delta D$ values of apatite in eucrites.
4. The $\delta D$ results presented suggest that most eucrites were not affected by volatile degassing.
5. The results from this study provide a fourfold increase in the number of $\delta D$/H$_2$O analyses available for apatite in eucrites.
6. The results are consistent with previous study and indicate that water in the HED parent body was characterized by a homogenous reservoir with $D/H$ signatures similar to those of most types of carbonaceous chondrites, the Earth’s mantle, and the Moon.

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