The History of Water and Other Associated Volatiles in Howardite-Eucrite-Diogenite Meteorites

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The History of Water and Other Associated Volatiles in Howardite-Eucrite-Diogenite Meteorites

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Abstract

Recent *in situ* measurements of volatiles (H\textsubscript{2}O, Cl and F), particularly in lunar and martian samples, have changed our understanding of the volatile inventory of the inner Solar System. Whilst this has provided a wealth of data for these planetary bodies, currently little is known about the history of volatiles in other bodies in the inner Solar System. The howardite, eucrite, diogenite (HED) meteorites form the largest suite of rocks representing a differentiated basaltic asteroid (4 Vesta) and are some of the oldest igneous rocks in the Solar System. Understanding their volatile histories, therefore, can help us to constrain some of the processes that operated on Vesta early in Solar System history.

Using the NanoSIMS 50L, six eucrites were analysed for their apatite H\textsubscript{2}O abundance and hydrogen isotopes, whilst seven eucrites (five of which were also investigated for H) were analysed for their apatite Cl content and isotopic composition. Apatite H\textsubscript{2}O abundances range from ~30 to ~3500 ppm and are associated with a weighted average δD value of -34 ± 67 ‰. No systematic variations or correlations are observed in H\textsubscript{2}O abundance or δD value with eucrite geochemical trend or metamorphic grade. These results are comparable to published literature and confirm the striking homogeneity in the H-isotopic composition of water in eucrites, and are consistent with a common source of water in the inner Solar System. Chlorine abundance in apatite ranges from ~25 to 4900 ppm and the δ\textsuperscript{37}Cl values range from -3.98 to +35.6 ‰. Samples with lower H\textsubscript{2}O content typically were enriched in δ\textsuperscript{37}Cl, however, no obvious correlation between δ\textsuperscript{37}Cl and δD values is seen. Cl isotope fractionation is likely to have occurred for some samples via magmatic degassing of ZnCl\textsubscript{2}. The observed variation in Cl isotopes, particularly the residual eucrites, however, remains enigmatic.
Patience is a virtue, and I’m learning patience. It’s a tough lesson.

Elon Musk
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Studying for a PhD is oftentimes described as a long, difficult slog of late hours and technical failures, but this is also a time of academic freedom and learning unmatched in many academic careers. First and foremost I would like to thank my supervisors; Dr Mahesh Anand, Dr Ian Franchi, Prof. Monica Grady, Dr Richard Greenwood and Dr Bruce Charlier, who throughout the course of my PhD, have provided invaluable feedback, support and advice whenever needed. I would also like to thank Jessica Barnes and Romain Tartèse who helped provide training on the ever-capricious NanoSIMS, advice, and insight during the writing and review stage of my published work.

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Chapter One: Introduction

1.1. Overview

Meteorites provide a window into the history of the Solar System and are key to understanding its formation and evolution. The majority of these samples come from a variety of small parent bodies (asteroids) whilst a small fraction originate from larger bodies such as the Moon or Mars. The variety of meteorites, both in terms of composition and age, enables us to study different parts of the Solar System as well as different points in its evolution.

Meteorites can be broadly separated into differentiated achondrites and undifferentiated chondrites, the latter typically contain chondrules, coalesced spherical dust aggregates that were subsequently rapidly melted and cooled (e.g. Grady and Wright, 2006; Connelly et al., 2012; Grady et al., 2014). Following their formation, chondrites remain unmelted and have compositions close to that of the solar photosphere in all but the most volatile of elements (Hutchison, 2004). Further sub-division of chondrites is based on mineralogy, mineral composition and textural characteristics (Weisberg et al., 2006), as well as oxygen isotope composition (Clayton et al., 1976; Clayton and Mayeda, 1996).

Achondrites are igneous rocks (melts, partial melts, melt residues) or breccias of igneous rock fragments, from differentiated asteroids and planetary bodies (Mars, Moon). These meteorites provide us with an analogue for early planetary differentiation and evolution, one that can be split into several steps based on the size of the body concerned. Meteorites from asteroids, such as 4 Vesta and the Angrite parent body, provide insight into processes operating in relatively small planetary bodies. In contrast, meteorites from large planets such
as Mars, which displays no current sign of plate tectonics or geological activity (e.g. Sleep, 1994; Lenardic et al., 2004), provide insights into processes and their products in bodies that are comparable to Earth-like analogues. Crucial to the formation and evolution of differentiated bodies is the presence of, delivery to and behaviour of volatiles on the parent body. An overview of the current state of meteorite classification is shown in Figure 1.1 highlighting the groups of interest for this thesis.

For the work described in this thesis, the volatiles of importance are hydrogen, chlorine and, to a lesser extent, fluorine. Hydrogen isotopic composition, reported using the standard delta (δ) notation in per mil (‰) (see Chapter 2 section 2.4.1.3 for details on the derivation of the delta notation), is used to investigate the source region(s) of parent body water, owing to the large range of values seen in the Solar System (Drouart et al., 1999; Mousis et al., 2000; Robert, 2006; Ceccarelli et al., 2014; Altwegg et al., 2015). It has been hypothesised that Cl isotopes, owing to the strong hydrophilic nature of Cl (Eggenkamp et al., 1994; Sharp et al., 2010a; 2016; Barnes et al., 2016), can be a useful proxy to investigate the histories of H (i.e. water) in the melt such that, in the presence of water, relatively small fractionation in Cl isotopes would occur than would otherwise be the case (Sharp et al., 2007). This property of Cl isotopes has been exploited to study meteorites and lunar samples, contributing towards the ‘wet’ vs. ‘dry’ Moon hypothesis (Sharp et al., 2010b; Boyce et al., 2015; Barnes et al., 2016). Thus, a comprehensive study of indigenous volatiles of a particular group of meteorites could provide insights into the evolution of the parent body from which the meteorites came and the role different processes may have played in their evolution.

One group of achondrites stands out as a good candidate for evaluating and assessing the history of volatiles in the inner Solar System, defined as the terrestrial planets and the asteroid belt: the Howardite-Eucrite-Diogenite (HED) meteorites. The HED group of
meteorites comprise the largest suite of crustal and sub-crustal igneous rocks available from a differentiated basaltic asteroid, and have a strong link to a parent body, namely 4 Vesta (see section 1.2 for more details). These meteorites also contain the mineral apatite, which contains fluorine, chlorine, and water (as OH⁻) as part of its crystal structure. As apatite in diogenites is very rare and, owing to the incorporation of exogenous material into howardites, the provenance of apatite in howardites can be uncertain; therefore, this work focuses on investigating the content and isotopic composition of volatiles in apatite in eucrites.

To date, relatively little work has been conducted on determining the volatile content and isotopic composition of HEDs. Sarafian et al. (2013) reported on the mineral composition and volatile content of eucritic apatite using electron microprobe analysis of three cumulate eucrites and 10 basaltic eucrites. They followed up their initial work to include in-situ isotopic measurements, by SIMS, of H in apatite from some of the same samples (Sarafian et al., 2014). Sarafian et al. (2014) concluded that, due to the similarity of H isotopic composition between eucrites and the Earth, and given the ancient ages of eucrites, volatiles could have been added early to the Earth rather than gained during a late accretion event (details of this work are discussed further in Chapter 4). Although pioneering, the work of Sarafian et al. (2013; 2014) was restricted to a small sample set for H isotope analyses and lacked variety in terms of eucrite geochemical and metamorphic grades. With additional investigation, of a larger and more representative sample set of available eucrites, the volatile content and isotopic composition of eucrites could be used to constrain the source(s) of volatiles to the HED parent body and the processes involved in eucrite formation. In addition to answering specific questions about the HED parent body, the timing of volatile accretion and/or delivery to the inner solar system can be assessed, owing to the ancient crystallisation
ages of eucrites (from 4547 Ma to 4559 Ma, Misawa et al., 2005; Zhou et al., 2013; Touboul et al., 2015), and a comparison to other planetary bodies, such as the Moon can then be made.

1.2. The HED Parent Body

1.2.1. The Vesta-HED link

One shortcoming of the analysis of meteorites is their lack of provenance which provides important parent body context to a sample (Cloutis et al., 2014). Other than the samples returned from asteroid 25143 Itokawa by the Hayabusa mission, and several postulated parent bodies based on spectroscopy (e.g. ordinary chondrites linked to S-type asteroids; Burbine et al., 2002), only the HED meteorites have a strong connection to a specific parent body.

The HED meteorites were first linked to asteroid 4 Vesta (from here on, Vesta) by McCord et al. (1970), based on the similarity in spectral reflectance in the 0.3 to 1.1 μm wavelength region between Vesta and the eucrite Nuevo-Laredo (Figure 1.2). A subsequent study demonstrated a series of diagnostic features in the reflectance spectrum of meteorites that could be related to analogous spectra from asteroids (Gaffey, 1976). Oxygen isotopes have also been used as a tool for distinguishing the genetic relationships among meteorites. The O isotopic signatures for the eucrites and diogenites are $\Delta^{17}\text{O} = -0.241 \pm 0.016 \%$ (2σ) and $\Delta^{17}\text{O} = -0.246 \pm 0.014 \%$ (2σ), respectively (a full discussion of oxygen isotope measurements protocol and associated notation for reporting the data are described in Chapter 3). These data are consistent with derivation of eucrites and diogenites from a single parent body (Clayton and Mayeda, 1983, 1996; Wiechert et al., 2004; Greenwood et al., 2014), but they do not identify the specific body.
Figure 1.1: Meteorite classification from Weisberg et al. (2006). The groups of interest are highlighted in red. EUC – Eucrites; DIO – Diogenites; HOW – Howardites.
Despite the spectral similarity between the eucrites and Vesta, there remained a dynamical problem in ejecting material into an Earth-crossing orbit. This problem was solved by modelling conducted by Farinella et al. (1993), demonstrating that asteroidal fragments could be injected into Earth-crossing orbits by orbital resonances, specifically the 3:1 mean motion resonance with Jupiter (a.k.a the Kirkwood Gap) at 2.5 AU and the ν6 secular resonance at 2.1 AU. Coincident with the work of Farinella et al. (1993), Binzel and Xu (1993) observed several small asteroids (dubbed ‘vestoids’; diameters ≤ 10 km), with similar spectra to Vesta and the HEDs, which occupied the region between Vesta and the 3:1 (Kirkwood Gap) and ν6 resonances. This provided a trail of evidence supporting the transport of Vestan fragments to Earth. This dynamic link was supported by later work.
demonstrating that impacts onto the surface of Vesta could eject material towards the orbital resonances required for transport towards Earth.

There is, however, still discussion over the Vesta-HED link. Wasson (2013) suggested that more than half (52%) of the V-type asteroids (i.e. basaltic asteroids with similar reflectance spectra to Vesta) do not actually belong to the Vesta dynamic family and, therefore, the HEDs probably do not come from Vesta. This assertion was based on the fact that the spectra of basaltic V-type asteroids were not sufficiently unique to link all V-type asteroids to Vesta, implying that another differentiated asteroid was disrupted and contributed to the total number of V-type asteroids. The favoured theory of Wasson (2013) is that the HEDs are part of the same parent body as the IIIAB iron meteorites and main group pallasites, as there is a similarity in the bulk $\Delta^{17}$O and $\varepsilon^{54}$Cr isotope composition of these groups. There are two strong lines of evidence that do not support the hypothesis proposed by Wasson (2013). Firstly, the oxygen isotopic composition of the main group pallasites is resolvably different from the HEDs (Greenwood et al., 2013; Greenwood et al., 2014), so pallasites and HED cannot be derived from the same body. Secondly, results from the Dawn mission significantly reinforce the Vesta-HED connection: for example, measurement of Fe/Si and Fe/O weight ratios of Vesta recorded by the Gamma Ray and Neutron Detector (GRaND) are comparable with those of the HEDs (De Sanctis et al., 2012b; McSween et al., 2012; Prettyman et al., 2012; Russell et al., 2012).

1.2.2. The Asteroid 4 Vesta

Discovered by Heinrich Olbers in 1807, and orbited for over a year in 2011-2012 by NASA’s Dawn mission, 4 Vesta is the brightest asteroid visible from Earth and comprises approximately 9% of the mass of the asteroid belt (Pitjeva, 2005; Russell et al., 2012).
With a semi-major axis of 2.36178 AU, Vesta is located inside the inner portion of the main asteroid belt (AstDyS-2 Dataset accessed 04.01.18). Vesta has an average diameter of 510 km and a mean density of 3456 kg/m$^3$ (Russell et al., 2012) and whilst the asteroid is large enough to have assumed a spherical shape under self-gravity, Vesta has a huge impact basin near the south pole which drastically distorts its shape (Schenk et al., 2012). This impact basin is believed to be comprised of at least two separate impact events, the Rheasilvian and older and smaller Veneneian (Schenk et al., 2012; McSween et al., 2014). The Rheasilvia impact has been suggested as the origin of the HED suite of meteorites (Thomas et al., 1997) as well as many of the ‘Vestoids’ (Binzel and Xu, 1993; Nesvorný et al., 2008).

Vesta itself is of particular interest as it is one of the few planetesimals that has undergone differentiation and has survived intact since its formation early in Solar System history (Mayne et al., 2009 and references therein). Degewij et al. (1979) observed a convincing variation in albedo with rotation and linked this with an associated difference in composition and/or surface texture. These results were later supported by the work of Gaffey (1983, 1997). Binzel et al. (1997) constructed one of the first false colour geological maps of Vesta using images from the Hubble Space Telescope. In the map, changes in colour signify changes in absorption band depth representing changes in albedo and therefore diversity of geological units, showing a contrast between eastern and western hemispheres (Figure 1.3). This compositional asymmetry suggests differences in main rock type between the two hemispheres. The eastern hemisphere is interpreted to be impact excavated plutonic material composed of Mg-rich and Ca-poor pyroxene, analogous to diogenites, whilst the western hemisphere is consistent with the basaltic signature of eucrites (Binzel et al., 1997; De Sanctis et al., 2012b).
Figure 1.3: A) False colour geological map of Vesta constructed from HST observations using the RGB colour scheme where red is indicative of deep, narrow 1 µm absorption bands and green indicates shallower, broader bands. B) Same map as A) but with labels corresponding to a selection of regions representative of the diversity of observed units. The alphabetical order of the labels indicates increasing 1-µm band depth. C) Four point spectra for several of the labelled regions in B). This map was constructed by first creating composite albedo maps which were then normalised so the average data number integrated over each map corresponding to the reflectance value observed in Vesta’s average groundbased spectrum at the same effective wavelength used as the filter used in the imaging sequence before adding an appropriate false colour scheme. Figure modified from Binzel et al. (1997).
The Dawn space mission was launched by NASA on September 27, 2007 with the aim of unravelling the conditions and processes in the early Solar System through investigation of two of the largest asteroids remaining intact since their formation, Ceres and Vesta. One of the reasons Vesta was chosen as a target for the Dawn mission was to assess the link between the asteroid and the HED meteorites. The spacecraft entered Vestan orbit on July 16, 2011 and spent one year in orbit making observations and measurements before departing to Ceres on September 5, 2012. A preliminary global geological map of Vesta using Dawn mission data was published by Yingst et al. (2014), significantly improving on the level of detail of previous maps and providing a contextual framework for the surface of Vesta (Figure 1.4). This latest geological map is based on an iterative process using data from the Framing Camera (FC) aboard the Dawn spacecraft at ever increasing resolutions. The first map obtained had a resolution of 3–9 km/pixel; the second, taken during the Survey orbit, was based on FC data at ~ 200 m resolution and a Digital Terrain Model (DTM) derived from orbit image data (Jaumann et al., 2012; Preusker et al., 2012) and the final iteration used data from the High-Altitude Mapping Orbit (HAMO) with a spatial resolution of ~ 61 m/pixel. These maps were constructed using well-established methods (Shoemaker and Hackman, 1962; Wilhelms, 1972; Greeley and Batson, 1990; Tanaka et al., 2010), units were defined using a variety of characteristics including morphological features, surface texture, colour (based on the colour scheme used in Clementine multispectral images) and albedo (Yingst et al., 2014). If the HED meteorites are indeed all from the Rheasilvia impact (Thomas et al., 1997) then the incredible geologic diversity observed in Figure 1.4 would suggest that some rock types observed on Vesta may not currently be represented within the meteorite collection.
Figure 1.4: Global geologic map of Vesta. Map and map legend are from http://dawn.jpl.nasa.gov/multimedia/GeologicalMap_Vesta.asp
A chronostratigraphic scheme for Vesta has also been produced by Williams et al. (2014) using two independent approaches based on cratering statistics. The absolute cratering retention ages derived for the surface of Vesta were then compared to the commonly accepted timescales for other bodies in the Solar System (Figure 1.5). The first approach used by Williams et al. (2014) is an extrapolation of the lunar-derived crater production scheme (Neukum and Ivanov, 1994; Schmedemann et al., 2014) whilst the second applies a production rate derived from models of asteroid dynamics (Marchi et al., 2012; 2013; 2014; O’Brien et al., 2014b; Williams et al., 2014). The lunar-derived and asteroid flux-derived chronologies do not produce similar absolute model ages for two main reasons. Firstly the crater production and chronology functions (i.e. the size-frequency distribution for craters with diameters between 10 m and 1000 km and the correlation between crater frequency and age data; Neukum and Ivanov, 1994) differ in both methods (O’Brien et al., 2014b; Schmedemann et al., 2014) meaning that even where both functions are applied to the same crater distribution dataset, they would produce different results. Secondly, the two chronology systems have assessed different geologic terrains to derive ages for certain stratigraphic units. Both schemes derived by Williams et al. (2014) divided the history of Vesta into four broad geological time periods: The Pre-Veneneian, Veneneian, Rheasilvian and Marcian, each terminated by a large impact. As stated earlier, the large Rheasilvia impact crater located near the south pole of Vesta is cited as the possible source-region for the majority of the HEDs within our collection (Binzel and Xu, 1993; Thomas et al., 1997; Bogard and Garrison, 2003; Nesvorný et al., 2008; McSween et al., 2013). Coupled with the ancient crystallisation ages (> 4.4 Ga, Misawa et al., 2005; Zhou et al., 2013) of many HED meteorites and \(^{40}\text{Ar}/^{39}\text{Ar}\) ages ranging from 4.5 to ~ 3.5 Ga generally being interpreted to correspond to impact events (Bogard, 1995; Bogard and Garrison, 2003; Kennedy et al., 2013), the HED meteorites would appear to be part of the ‘Pre-Veneneian’ period.
1.2.3. Orbital detection of volatiles on the surface of 4 Vesta

With the arrival of the Dawn mission into orbit around 4 Vesta in 2011, detailed observations of the surface of the asteroid became possible. Dawn’s Gamma Ray and Neutron Detector (GRaND) recorded significant hydrogen concentrations coincident with older, low-albedo regions near the equator (Prettyman et al., 2012). These observations were attributed to the gradual accumulation of hydrogen by the infall of carbonaceous chondrites, which is also consistent with younger regions displaying the lowest H concentrations. This is at odds with the older, ground-based observations conducted by Hasegawa et al. (2003),
who reported the presence of the 2.8 µm OH absorption band on the high albedo southern hemisphere of Vesta, indicative of hydrated and/or hydroxylated minerals. This is somewhat similar to the detected OH on the lunar surface, which is correlated with high albedo areas (Pieters et al., 2009). Using the Visible and Infrared (VIR) imaging spectrometer aboard the Dawn spacecraft, De Sanctis et al. (2012a) also observed the 2.8 µm OH absorption band. Their study noted that the hydrated mineral phases were unevenly distributed, showing no significant correlations of the 2.8 µm band depth with illumination or temperature (Figure 1.6), agreeing with Prettyman et al. (2012) that there appeared to be a link to low-albedo regions.

![Figure 1.6: H map (A) superimposed on shaded relief compared with an albedo map (B) of Vesta. The dashed white circle outlines a depression containing the Oppia crater. Approximate contours of smoothed crater density are given in dashed yellow on the H map, on the albedo map the yellow contours represent H (in µg/g). Figure taken from Prettyman et al. (2012).](image-url)
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Improvements to the VIR calibration were conducted by Combe et al. (2015), enabling more accurate analysis, especially in the 1.4 μm and the 2.8 μm hydroxyl absorption band depth (Figure 1.7).

As well as global coverage, specific regions of Vesta have been investigated. Tosi et al. (2015) studied the equatorial Oppia region, named after the Oppia crater (black rectangle in Figure 1.7). Their analysis found that the strongest OH signature in the region is found west of Oppia crater (cyan arrow on Fig. 1.7), previously mapped as ‘light mantle material’ and showing moderate reflectance rather than the typical low-albedo of the dark material more commonly associated with OH. In moving away from Oppia crater in the north and east directions, the strength of OH-bearing phases in ‘light mantle material’ decreases to background levels showing that this feature is localised. The authors suggest that one possible cause for these observations is the impact that created the Oppia region could have affected an area originally rich in hydrated material locally, and the impact penetrated the crust sufficiently deeply to excavate and mix less processed and brighter coloured material with the dark material that had covered the area prior to impact. The Marcia quadrangle, another equatorial region, has been studied by De Sanctis et al. (2015) and has a similar proposed history to that of the Oppia region, whereby a more recent impact has interlaced and mixed uncontaminated bright material (characterised by strong pyroxene absorption bands) and darker material (with strong OH absorption bands).
Figure 1.7: Colour composite of spectral slope vs. 2.8 µm band depth using the colour scheme outlined in Combe et al. (2015) overlain on an equi-rectangular projection of the entire surface of Vesta. Blue colours represent dark hydrated regions and orange represents non-hydrated materials. The black rectangle represents the Oppia region. The hydrated region south of Oppia crater is indicated by the white arrow whilst the cyan arrow marks the western ejecta blanket of Oppia. Figure modified after Combe et al. (2015).
Some of the topographical features on Vesta have also been linked to the presence of volatiles (Denevi et al., 2012; Scully et al., 2015). Denevi et al. (2012) used images obtained during Dawn’s Low-Altitude Mapping Orbit (LAMO) to identify distinct terrains with pitted morphologies, the most widespread of which is associated with the Marcia crater located on the equator. These authors compared the pitted terrains on Vesta to similar features on Mars (e.g. McEwen et al., 2007; Tornabene et al., 2012) and suggested that the pitted terrains on Vesta could have formed through degassing of volatile-bearing material heated by impacts. Their work also suggested that water-rich carbonaceous chondrite material may be the source of the volatiles. Scully et al. (2015) studied the various types of gully seen on the surface of Vesta. Linear systems contain straight, non-intersecting gullies that are parallel to one another and are analogous to lunar gullies in morphology and the presence of talus deposits (Scully et al., 2015). Curvilinear systems consist of interconnected, non-linear gullies, which are particularly well developed in Cornelia and Marcia crater (Scully et al., 2015). These curvilinear gully systems share many indicative features with curvilinear and lobate deposits on Earth and Mars, specifically a set of young martian gullies called surficial gullies (Schon and Head, 2011, 2012). Scully et al. (2015) hypothesised several different methods of formation for the gullies and suggested that whilst linear gullies can be formed by dry granular flows, for curvilinear gullies, the transient flow of water in a debris-flow-like process is required. The source of the water that produced these gullies is also discussed; they note that unlike the pitted terrains, which can be linked to dark material areas, possibly rich in carbonaceous chondrite debris (Denevi et al., 2012), there is no systematic correlation between occurrences of dark material and the number or type of gullies seen. Scully et al. (2015) attribute the source of water to localised ice-bearing sub-surface deposits which are evaporated instantaneously during impact, forming transient water which facilitates gully formation (Figure 1.8).
Figure 1.8: Diagram showing possible locations of ice sources (a – c) and the stages proposed to form curvilinear gully systems (d – f). (a) Source possibility 1: ice-bearing subsurface deposits are only present at shallower levels. (b) Source possibility 2: ice-bearing subsurface deposits are only present at deeper levels. (c) Source possibility 3: ice-bearing subsurface deposits are present at both shallow and deep levels. (d) Stage 1: an impactor provides the energy necessary to melt some of the shallow and deep ice-bearing subsurface deposits. (e) Stage 2: water is released onto the crater walls and flows transiently in a debris-flow-like process to the crater floor, forming the curvilinear gullies as it flows. (f) Stage 3: evaporation of water that remains after flow may contribute to the formation of the pitted terrain on lobate deposits. Sublimation of deep ice-bearing subsurface deposits may contribute to the formation of pitted terrain on the crater floor. Figure and caption from Scully et al. (2015).

1.3. Introduction to HEDs

The HED meteorites comprise the largest suite of crustal and sub-crustal rocks available for study from any Solar System body, barring the Earth and the Moon. The HEDs account for between 2-3% of all meteorites collected globally (Janots et al., 2012), about 5% of all falls, and about 60% of all achondrites. As of December 2017, there were over 1931 named HED achondrites with 117 new HED meteorites announced during this year (Meteoritical
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Bulletin; https://www.lpi.usra.edu/meteor/). As discussed in section 1.2.2, Williams et al. (2014) proposed a time-stratigraphic system for Vesta which suggests that the HED meteorites are part of the ‘Pre-Veneneian’ period which lasted from 4.6 Ga to 3.8 Ga (lunar-derived chronology, Figure 1.5).

The HED parent body is generally considered to have formed from a mix of various chondritic precursor materials (Boesenberg and Delaney, 1997; Righter and Drake, 1997; Ruzicka et al., 1997a; Toplis et al., 2013). For example, using mass-balance and thermodynamic constraints, Toplis et al. (2013) suggested that the HED parent body could be a mix of 75% Na-depleted H chondrite and 25% CM chondrite. The size of Vesta’s core has been modelled based on siderophile element depletions (Newsom and Drake, 1982, 1983; Righter and Drake, 1996, 1997), the best estimates of which are between ~ 4 % and ~ 6 % of the mass of Vesta (Ruzicka et al., 1996, 1997a) with a maximum value of ~ 10 % depletion (Righter and Drake, 1996).

Because the eucrites are the most numerous of the HED suite, and they are the focus of this thesis, their characteristics will be described first; this also makes it easier to describe howardites, as they are mainly a mixture of eucrite and diogenite fragments.

1.3.1. Eucrites

Eucrites are plagioclase, pigeonite-bearing basaltic achondrites (Duke and Silver, 1967) and make up the largest portion of the HEDs. The eucrites have magmatic textures and chemical compositions indicating formation as basaltic lavas or intrusions, and hence, are regarded as samples from the outer crustal layers of their parent body (Barrat et al., 2007; De Sanctis et al., 2012b; 2013). Many eucrites have undergone extensive brecciation with ~ 85 % of breccias being polymict (composed of clasts from different rocks) or monomict
(composed of clasts from a single rock), although some are unbrecciated (Delaney et al., 1984a; Warren and Jerde, 1987; Mayne et al., 2009).

Based on their petrographic and chemical characteristics, monomict and unbrecciated eucrites are subdivided into basaltic and cumulate groups (See Fig. 1.9; Stolper, 1977; B.V.S.P., 1981; Mayne et al., 2009) with cumulate eucrites potentially forming at greater depths where elevated temperatures kept isotopic systems open for a significant time after eucrite formation (Bogard and Garrison, 2003). Kitts and Lodders (1998) conducted a survey and evaluation of the bulk compositions of 101 eucrites. Their analysis found an excellent agreement between the calculated norm and the actual petrographic modal analysis for the basaltic eucrites. This agreement, however, does not hold for the cumulate eucrites which they attribute to centimetre-scale heterogeneities, possibly owing to the typically coarser-grained nature of cumulate eucrites.

Figure 1.9: Schematic of the HEDs and the subsets of the basaltic eucrites.
Takeda and Graham (1991) divided eucrites into six types (1-6) based on the mineralogical characteristics of pyroxene and reflecting increasing degrees of metamorphism (Table 1.1). Type 1 eucrites represent the lowest levels of thermal metamorphism with pyroxene grains that are extensively zoned; conversely, type 6 pyroxenes are homogenous with easily resolvable exsolution lamellae and some pigeonite grains inverting to orthopyroxene. An additional type seven was proposed by Yamaguchi et al. (1996) who suggested that metamorphism by burial led to global metamorphism and could explain the different metamorphic types by their position within the crust during metamorphism. The degree of metamorphism, therefore, may give some clue as to the relative timing of eucrite formation (Barrat et al., 2007).

1.3.1.1. Basaltic eucrites

The basaltic eucrites, are the most numerous of all eucrites, accounting for some 90% of the 1138 total. They are fine to medium-grained igneous rocks predominantly composed of pigeonite and calcic plagioclase (ranging from bytownite to anorthite; Mittlefehldt, 2015). Although most basaltic eucrites are brecciated, a few are unbrecciated (e.g. Mayne et al., 2009). Minor phases and accessory phases in these eucrites include apatite, chromite, ilmenite, silica polymorphs tridymite and quartz, troilite, metal, ferroan olivine, zircon and baddeleyite (Delaney et al., 1984b; Mayne et al., 2009; Haba et al., 2014; Hopkins et al., 2015; Mittlefehldt, 2015). The basaltic eucrites can be further subdivided based on their magnesium number (Mg#) or FeO_{total}/MgO weight ratio, and their Ti and incompatible trace element abundances (Stolper, 1977; Hsu and Crozaz, 1996; Hutchison, 2004; Barrat et al., 2007) into the Main Group-Nuevo Laredo and Stannern trends (Figure 1.10). Stolper (1977); Warren and Jerde (1987) suggested that most of the main group eucrites could belong to the Nuevo Laredo trend. The Main Group-Nuevo Laredo trend comprises the majority of the
eucrites and is widely accepted as a fractional crystallisation trend (Stolper, 1977; Warren and Jerde, 1987; Mittlefehldt and Lindstrom, 2003) showing a linked increase in incompatible element abundance with decreasing Mg#.

The Stannern trend eucrites have very similar major element abundances to main group eucrites. They have the highest abundances of Ti and incompatible elements, enrichments that are not linked to Mg# (Barrat et al., 2000; Hutchison, 2004; Barrat et al., 2007). Stolper (1977) first suggested that Stannern trend eucrites formed from a combination of partial melting of a relatively uniform source followed by fractional crystallisation; REE contents could be modelled successfully using such a model (Consolmagno and Drake, 1977; Mittlefehldt, 1979). In contrast, Shimizu and Masuda (1986) proposed that the Stannern trend eucrites were produced as residual liquids in a fractional crystallisation process from the main group eucrites such as Juvinas and Pasamonte. This theory was later disproved by Ruzicka et al. (1997a), who showed that fractional crystallisation models were incapable of reproducing the relationship between the Stannern and Nuevo Laredo trends. Barrat et al. (2007) suggested that the contamination of Main Group-Nuevo Laredo trend eucrites by crustal melts could explain both the elevated incompatible element concentrations and the distinctive Eu, Sr, Be anomalies shown by Stannern trend eucrites. A partial melt would leave behind a residual eucrite with LREE depletion, which Yamaguchi et al. (2009) observed in several eucrites and believed to be a third geochemical trend.
### Table 1.1: Classification of eucrites based on diagnostic pyroxene features

Table modified after Takeda and Graham (1991) with the additional type 7 eucrite pyroxene from Yamaguchi et al. (1996). Samples studied here are indicated in bold.

<table>
<thead>
<tr>
<th>Type</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical zoning</strong></td>
<td>Extensive</td>
<td>Metastable</td>
<td>Fe-Ca trend from</td>
<td>Homogenous</td>
<td>Homogenous</td>
<td>Homogenous</td>
<td>Homogenous</td>
</tr>
<tr>
<td>zoning is</td>
<td>zoning is</td>
<td>Fe-rich pyroxenes</td>
<td>core to rim</td>
<td>host and remnant of</td>
<td>host of exsolved</td>
<td>host of exsolved</td>
<td>host and remnant of</td>
</tr>
<tr>
<td>fully preserved</td>
<td>fully</td>
<td>are absent</td>
<td>zoning</td>
<td>pigeonite</td>
<td>pigeonite</td>
<td>pigeonite</td>
<td>zoning</td>
</tr>
<tr>
<td>Inversion to orthopyroxene</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>Stacking fault</td>
<td>Partly inverted</td>
<td>Partly inverted</td>
</tr>
<tr>
<td>Clouding of pyroxene</td>
<td>None</td>
<td>None</td>
<td>Trace</td>
<td>Present</td>
<td>Present</td>
<td>Present</td>
<td>Present</td>
</tr>
<tr>
<td>Mesostasis glass</td>
<td>Preserved</td>
<td>Not clear</td>
<td>Not clear</td>
<td>Recrystallised</td>
<td>Recrystallised</td>
<td>Recrystallised</td>
<td></td>
</tr>
<tr>
<td>Exsolution of augite</td>
<td>TEM scale</td>
<td>TEM scale</td>
<td>TEM scale</td>
<td>or absent resolvable by EPMA</td>
<td>or absent resolvable by EPMA</td>
<td>or absent resolvable by EPMA</td>
<td></td>
</tr>
<tr>
<td>Examples</td>
<td>Y75011, Clasts in Y75015, Y74450</td>
<td>Pasamonte</td>
<td>Stannern, Nuevo Laredo</td>
<td>Juvinas, Haraiya, Emmaville, Sioux County</td>
<td>Millbillillie, Y791186, Y792510</td>
<td>Jonzac, Palo Blanco Creek</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.10: La vs FeO$_{\text{total}}$/MgO and La vs. Sc plots for basaltic eucrites. Modified from Barrat et al. (2007).
1.3.1.2. Cumulate eucrites

Cumulate eucrites are less common than basaltic eucrites, accounting for ~ 3.7% of the total number of eucrites. They are medium to coarse-grained rocks (typical grain sizes ~ 0.5 – 5 mm in the longest direction; Mittlefehldt, 2015 and references therein), and are thought to have formed in shallow magma chambers, complementing the erupted melt that gave rise to the basaltic eucrites. Cumulate eucrites are mostly unbrecciated and with distinct chemical features (Bogard and Garrison, 1995; Takeda, 1997; Scott et al., 2009). They are mainly composed of low-Ca pyroxene and calcic plagioclase with minor chromite and accessory silica, phosphate, ilmenite, metal, troilite and zircon (Mittlefehldt, 2015). Compared with other eucrites, they display higher Mg-numbers, lower abundances of incompatible trace elements, and their REE patterns exhibit pronounced positive Eu anomalies that can be explained by plagioclase accumulation (Hsu and Crozaz, 1997; Barrat, 2004).

Pyroxenes in cumulate eucrites show characteristic inversion to orthopyroxene, and exsolution lamellae of high-Ca augite, visible under optical microscopy (Consolmagno and Drake, 1977; Takeda, 1997). The pyroxene compositional range in cumulate eucrites merges with that of diogenites (Mittlefehldt and Lindstrom, 1993; Mittlefehldt et al., 2013a). The composition of plagioclase in cumulate eucrites is generally more calcic (An$_{91-95}$) than those of basaltic eucrites (An$_{75-94}$, Mittlefehldt, 2015 and references therein).

Since trapped magma can be an important repository of incompatible trace elements and may significantly affect the composition of the cumulate (Treiman, 1997; Barrat, 2004), cumulate eucrites that have abundances of these elements (e.g. Hf) that are too high for pure cumulates, they can be modelled as mixtures of cumulus phases and trapped melt (Treiman, 1997; Mittlefehldt and Lindstrom, 2003; McSween et al., 2012). This would allow for
normal, basaltic eucrites to be plausible parental melts of cumulate eucrites (Treiman, 1997; Barrat et al., 2000; Saiki et al., 2001; Barrat, 2004).

1.3.1.3. Anomalous eucrites

Not all eucrites can be easily categorised and some are considered to be anomalous texturally, compositionally and/or based on their oxygen isotopic composition (Figure 1.11). Some samples such as the cumulate eucrite Pomozdino (Warren et al., 1990) and EET 90020 (Yamaguchi et al., 2001), show textural and/or compositional differences from typical eucrites but are, on the basis of O isotopes, otherwise believed to be from the same parent body. For NWA 011 ($\delta^{18}O = + 2.54$, $\delta^{17}O = −0.48$) and Ibitira ($\delta^{18}O = + 3.72$, $\delta^{17}O = −1.90$), however, significant differences in oxygen isotopic composition from other eucrites, as well as other distinct textural and mineralogical features (e.g. the presence of vesicles and anomalous Fe/Mn ratios) means that a separate parent body for each is favoured (Yamaguchi et al., 2002; Wiechert et al., 2004; Floss et al., 2005; Mittlefehldt, 2005). Others show smaller oxygen isotopic variations but are otherwise petrologically and compositionally indistinguishable from basaltic eucrites (e.g., Pasamonte; Wiechert et al., 2004; Greenwood et al., 2005; Scott et al., 2009).

The three possible explanations that have been proposed to explain the origin of anomalous eucrites:

1) Normal and anomalous samples come from a single heterogeneous parent body
   (Wiechert et al., 2004)

2) Anomalous samples are from non-HED parent bodies (Scott et al., 2009)

3) Isotopic heterogeneity may be the result of impact mixing on a single parent body
   (Greenwood et al., 2005; Janots et al., 2012).
Figure 1.11: Oxygen isotope composition of anomalous achondrites shown in relation to HEDs, Angrites and Main-group pallasites. Taken from Barrett et al. (2017). Note NWA 011 has a $\Delta^{17}$O too low ($\Delta^{17}$O - 1.80 ‰; Yamaguchi et al., 2002) to fit on the scale of this figure. For eucrites that are, texturally and/or compositionally anomalous but with similar oxygen isotope values, it is unlikely to be the first of these options, as the tight grouping of most HED meteorites (excluding anomalous samples) suggests that O isotopes were homogenized within the parent body (Wiechert et al., 2004; Greenwood et al., 2005; 2014; 2017). Anomalous eucrites, with special reference to the Emmaville meteorite, are investigated in more detail in chapter three of this thesis.

1.3.2. Diogenites

Most diogenites are coarse-grained ultramafic orthopyroxenites with 85-100 vol. % orthopyroxene (Beck and McSween, 2010; Mittlefehldt, 2015 and references therein). Minor phases include olivine and chromite with silica, plagioclase, troilite, metal and phosphates as trace minerals (Mason, 1962; Mittlefehldt, 1994 and references therein). A small
portion of the diogenite population is more harzburgitic in composition, with only ~ 64 vol. % orthopyroxene, the remainder being mainly olivine (Beck and McSween, 2010; Wittke et al., 2011; Mittlefehldt, 2015).

Major element compositions of orthopyroxene in diogenites are homogeneous and geothermometry calculations show that the main mineral phases of diogenites maintained equilibrium down to low temperatures (650-880 °C; Mittlefehldt, 1994). Exsolution features of these orthopyroxenes are closely related to their CaO content (Takeda et al., 1976). Pyroxenes with a content higher than 1.3 wt. % CaO show exsolution lamellae of augite.

Whilst major element compositions may be homogeneous, minor and trace element contents show considerable variation (e.g. Fowler et al., 1995; Barrat et al., 2006; Shearer et al., 2010). Trace element data from dimict diogenites (rocks composed of clasts from two distinct lithologies) revealed two distinct populations of pyroxene, relating to the harzburgite and orthopyroxenite clasts within the diogenite (Beck et al., 2013). This supports the hypothesis that the lithologies are related through fractional crystallisation whereby harzburgitic olivine and pyroxene crystallised first followed by the orthopyroxenite pyroxene (Beck et al., 2013).

One view is that diogenites formed from partial melts that were more primitive than eucrites during the crystallisation of a magma ocean (Barrat et al., 2008; Mandler and Elkins-Tanton, 2013). The petrogenesis of these meteorites, however, remains a matter of debate. Shearer et al. (2010) favoured the formation of diogenites as cumulates in multi-layered intrusions within the crust, a hypothesis also supported by Mittlefehldt et al. (2012). Barrat and Yamaguchi (2014) dispute the magma ocean model of Mandler and Elkins-Tanton (2013)
and suggest that the model is incapable of explaining some of the incompatible trace element characteristics of the diogenite suite.

The diogenites are thought to have crystallised at deeper structural levels in their parent body compared to the basaltic eucrites, and as a result, are less likely to have been modified by impact mixing processes (Greenwood et al., 2014) although they still show some impact-related features (Shearer et al., 2010). To date, only the highly shocked diogenite Dhofar 778 (shock stage S4) has an anomalous oxygen isotope composition ($\Delta^{17}O - 0.160 \pm 0.027 \%_o$ 1$\sigma$; Greenwood et al., 2017). The lack of anomalous diogenites relative to the number of anomalous eucrites and eucrite-like achondrites, would seem to favour the possibility that the majority of isotopically anomalous eucrites were produced by impact mixing at or near the surface of the HED parent body or that they are from a distinct parent body (Greenwood et al., 2014).

1.3.3. Howardites

Howardites are polymict breccias, the lithified remnants of the debris layer from Vesta, and are mostly composed of diogenitic and eucritic debris (Duke and Silver, 1967; Mazor and Anders, 1967). Wahl (1952) first recognised the difference between eucrites and howardites and proposed that the eucrites were unbrecciated, or monomict breccias, whereas the howardites were polymict breccias. The howardites, unlike most other specific meteorite types, show a wide range in concentration for most elements (Urey and Craig, 1953; Duke and Silver, 1967; Mason, 1967). Moore (1962) observed an almost continuous composition between the diogenites and the eucrites with the howardites occupying the middle ground; this was attributed, at the time, to igneous differentiation. A similar model was proposed by Mason (1962) who suggested that the original parent material may have had a similar bulk
composition to chondrites. McCarthy et al. (1972) suggested that howardites were mechanical mixtures of diogenites and eucrites and represented an intermediate member of an essentially continuous sequence of polymict breccias (Takeda et al., 1976; Delaney et al., 1983; Mittlefehldt et al., 1998). The transition between the howardites and polymict eucrites is defined by the volume of orthopyroxene, the dividing line for which is (arbitrarily) set at 10 vol. % orthopyroxene (Figure 1.12) (Takeda et al., 1980; Delaney et al., 1983; Mittlefehldt, 2015).

Chondritic material is also present in howardites; Zolensky et al. (1996) and Gounelle et al. (2003) found that most chondritic clasts in HEDs are CM2 materials (~ 81 vol %), with less abundant clasts of CR2 (~ 19 vol %). More recent studies of exogeneous materials in HEDs have shown that ordinary chondrites, mesosiderites and potentially pallasite clasts, are also present (Lorenz et al., 2007; Beck et al., 2012; Prettyman et al., 2012).

Figure 1.12: Classification of HED breccia types taken from Mittlefehldt (2015).
Some howardites have been categorised as regolithic, based on features including impact-melt clasts, fragmental breccia clasts, and carbonaceous chondrite fragments (Cartwright et al., 2011; Beck et al., 2012). True regolithic nature, however, is characterised by elevated noble gas contents owing to Solar Wind (SW) implantation of species into the upper-most layer of solar system bodies (Cartwright et al., 2013; Mittlefehldt et al., 2013b; Cartwright et al., 2014). The maximum penetration depth of implanted solar wind ions is \( \sim 500 \text{ nm} \) and the mean implantation depth is around \( 40 \text{ nm} \) (Lunning et al., 2015). Whilst work by Warren et al. (2009) suggested that high siderophile element contents (e.g. Ni of 300 – 1200 \( \mu \text{g/g} \)) were regolithic indicators, Cartwright et al. (2013) found no obvious correlation between solar wind implantation and high siderophile element content. Howardites, classified as regolithic based on solar wind concentrations, are composed of surficial material and are believed to be analogous to the uppermost portions of Vesta’s 1-2 km thick regolith (Jaumann et al., 2012; Lunning et al., 2015). It has also been noted that, relative to eucrite pyroxene, plagioclase is depleted in howardites. This could be caused by plagioclase being preferentially comminuted in the vestan regolith and the extent of plagioclase depletion could, therefore, be an indicator of regolith maturity (Lunning et al., 2015).

### 1.3.4. HED meteorite petrogenesis

Despite extensive research, the petrogenesis of the eucrites has remained controversial. The central issue in all the models is whether main-group eucrites are primary partial melts or residual liquids, with two distinct schools of thought (fractional crystallisation vs. partial melting) regarding the origin of the HEDs which are discussed below.

The earliest model for asteroidal differentiation was that of Mason (1962) who noted the HED suite may be explained by a fractional crystallisation trend in which the cumulate
fraction is represented by the diogenites, and the eucrites are the residual melts (Delaney et al., 1984a; Ikeda and Takeda, 1985; Warren, 1985; Longhi and Pan, 1988; Bartels and Grove, 1991). None of the variations on the fractional crystallisation model, however, have been able to account for all the compositional variations seen in either the liquids or the cumulates without appealing to several different melting or fractionation events, polybaric fractionation (Longhi and Pan, 1988) or localized heating within the mantle of the parent body (e.g., Grove and Bartels, 1992).

An alternative model was proposed by Stolper (1975, 1977) based on melting experiments of basaltic eucrites. In this model, the basaltic eucrites represent primary partial melts of their parent body. The Main Group and Stannern trend eucrites are believed to be the result of different degrees of equilibrium partial melting of chondritic material (Consolmagno and Drake, 1977; Stolper, 1977) and have been a focus of many studies (Jurewicz et al., 1991; 1995; Jones et al., 1996). Work on the non-cumulate eucrites by Hsu and Crozaz (1996) generally showed support for the Stolper (1977) model. Although this second hypothesis is consistent with the clustering of the eucrites around the olivine-pyroxene peritectic point on an olivine-pyroxene-plagioclase phase diagram, and calls on later fractional crystallisation of Main Group eucritic liquid to produce the Nuevo Laredo trend, it fails to account for the diogenites in a simple petrogenetic model (Shearer et al., 1993; Mittlefehldt, 1994) and for the low Na contents of the eucritic plagioclase and HED parent body (Gast, 1960; Mason, 1967). The model of Stolper (1977) has continued to lose favour based on arguments including mass balance considerations for major elements (Warren, 1985, 1997), the difficulty of explaining the very low siderophile element contents of eucrites (McSween et al., 2012), and the homogeneity in O isotopic compositions of HEDs (Greenwood et al., 2005).
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Warren and Jerde (1987) presented a hybrid model of the Mason and Stolper models, in which the Stannern-trend eucrites are partial melts of the HED parental asteroid whilst the Nuevo Laredo-trend and main-group eucrites are the residual liquids left over from the crystallisation of the diogenite cumulates. Ikeda and Takeda (1985) developed the first magma ocean model for the petrogenesis of the HED suite which included a simple model with a layered structure. Since then the magma ocean model has undergone several revisions (e.g. Ruzicka et al., 1996; Righter and Drake, 1997; Ruzicka et al., 1997b; Mandler and Elkins-Tanton, 2013). The magma ocean model is supported by the abundances of moderately siderophile elements in the mantle of Vesta and is consistent with a core comprising ~ 10 % of the mass of Vesta (Righter and Drake, 1996, 1997, 2000).

Despite the magma ocean model of Righter and Drake (1997) taking into account many compositional features in the eucrites, it fails to reconcile the low Na and K abundances of eucrites, an issue highlighted by several previous investigators (Gast, 1960; Mason, 1967; Jurewicz et al., 1995). The cooling of a magma ocean does, however, appear to provide a more comprehensive explanation for the diverse lithologies represented by the HED suite of meteorites than the partial melting model (Righter and Drake, 1997; Ruzicka et al., 1997a). The magma ocean model has also been questioned on the basis of trace element data, which indicate that the parental magmas of some diogenites were contaminated by partial melts derived from the fusion of pre-existing eucritic crust (Barrat et al., 2010). This suggests that at least some diogenites formed later than some eucrites. It can also be shown that not all eucrites formed in the same way. Cumulate eucrites clearly formed as cumulates and do not represent liquid compositions and not all noncumulate eucrites appear to have formed as residual liquids in a magma ocean (Ruzicka et al., 1997a).
An upgraded two-step magma ocean model for HED petrogenesis was recently presented by Mandler and Elkins-Tanton (2013) (Figure 1.13). Their model used a combination of 60-70% equilibrium crystallisation of a magma ocean followed by extraction of the residual melt into shallow magma chambers, where fractional crystallisation took place. To produce all of the eucritic and diogenitic lithologies, the shallow magma chambers underwent either periodic or continuous magmatic recharge. In a comment on the Mandler and Elkins-Tanton (2013) work, Barrat and Yamaguchi (2014) suggest that the model still fails to explain the trace element diversity of the diogenites, in particular, the diversity of the heavy REE (HREE) enrichment. More recent work by Weisfeiler et al. (2017) models the heat transport of early Vesta and supports a global magma ocean, which would cool rapidly through the foundering of a solid outer crust in a similar fashion to that envisaged by Mandler and Elkins-Tanton (2013). In their work they demonstrate melting would commence very early on (~130,000 yr) and solidification would occur at around 10 Myr. These results are in good agreement with $^{53}\text{Mn}-^{53}\text{Cr}$ ages of HEDs given by Lugmair and Shukolyukov (1998) who suggest igneous activity began ~ 3 Myr after CAIs and continued until ~ 10 Myr.

On balance, the evidence seems to favour relatively late emplacement of diogenite plutons into pre-existing eucritic crust, and is supported by olivine-rich lithologies in crater walls on Vesta, suggesting the high-level emplacement of cumulate materials (Ammannito et al., 2013). The paradox, where diogenites show isotopic evidence of global melting, but also geochemical features indicative of late interaction with eucritic crust, may reflect a rapid transition from global to serial magmatism on their parent body (Greenwood et al., 2014).

The calculations of Wilson and Keil (2012; 2013) challenge the magma ocean model for small differentiated asteroids. They argue that the fast melt production and easy melt migration in differentiated asteroids, up to sizes including Vesta, imply the formation of
multiple isolated magma chambers or even a globally-extensive sill. Thus magma oceans, in the sense of largely molten mantles, should not have existed.

Figure 1.13: The four-stage model of the formation of Vesta by Mandler and Elkins-Tanton (2013).

1.4. Apatite

To quote Hughes and Rakovan (2015), “apatite, in the strictest sense, is not a single mineral,” owing to the fact that the mineral structure of apatite can incorporate more than
half of the elements in the periodic table. The calcium phosphate commonly known amongst geologists as apatite \([\text{Ca}_5(\text{PO}_4)_3(\text{F, Cl, OH})]\) (for the rest of this work we refer to this formula when discussing apatite unless otherwise specified), is a widely occurring accessory phase in planetary materials, and has been used as a recorder of volatile abundances in magmas and magmatic source regions (e.g. Patiño Douce and Roden, 2006; McCubbin et al., 2011; 2014; Patiño Douce et al., 2011; Barnes et al., 2013; Sarafian et al., 2013; Tartèse et al., 2013; 2014b) as well as a plethora of different measures such as age dating (Koike et al., 2016; Snape et al., 2016) and trace-element distributions (Workman et al., 2006; Webster and Piccoli, 2015; Mao et al., 2016). Apatite is also highly susceptible to metasomatic processes which allows the mineral to be used as a perfect tracker of metasomatic fluids (Jones et al., 2014; Harlov, 2015; Webster and Piccoli, 2015; Lewis and Jones, 2016). In this study, we have focused on apatite as the most common volatile-bearing mineral phase in eucrites (Delaney et al., 1984b; Sarafian et al., 2013).

1.4.1. Water and other volatiles in apatite

Apatite contains hydrogen in the form of structurally bound hydroxyl (OH); we convert the measured OH abundance to its equivalent H\(_2\)O for the purposes of comparing our data with those in the literature. In contrast, merrillite \([(\text{Mg,Fe})_2\text{REE}_2\text{Ca}_{16}\text{P}_{14}\text{O}_{56}]\), is a volatile-free phosphate, but is a major reservoir of REEs in eucrites (20,000-30,000 times chondritic, compared to apatite at 500-1,000 times chondritic for LREEs) (Delaney et al., 1984b). The occurrence of merrillite has been used as an indicator for a volatile-depleted system (e.g. Patiño Douce and Roden, 2006; Patiño Douce et al., 2011; Sarafian et al., 2013), although recent work by McCubbin et al. (2014) suggests that this may not necessarily be the case. McCubbin et al. (2014) observed merrillite, with no discernible whitlockite \([\text{Ca}_9(\text{MgFe})(\text{PO}_4)_6\text{PO}_3\text{OH}]\) component, coexisting with OH-rich apatite in the martian

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meteorite Shergotty. They concluded that the presence of merrillite in the magmatic system has more to do with the ratio of P to F + Cl, as this controls the stability of apatite relative to merrillite, and the presence of merrillite would either indicate that the system is depleted in halogens or enriched in phosphorus (Patiño Douce and Roden, 2006; McCubbin et al., 2014). Since merrillite in HEDs are not known to contain significant abundances of volatiles, this study focusses on apatite as the major host of water.

Apatite standards typically have their hydrogen isotopic composition and water content assessed either by the step-heating of mineral separates (e.g. Nadeau et al., 1999) or continuous flow mass spectrometry (e.g. McCubbin et al., 2012). The apatite standards used at the Open University were characterised by McCubbin et al. (2012) using continuous flow mass spectrometry. The precision on hydrogen isotopic measurements given in their work is ± 4 ‰ (2σ) for hydrous minerals that have at least 0.1 µl H₂O (equivalent to 5000 ppm H₂O in apatite standards analysed in their study). Uncertainties on H₂O content range from 100 to 500 ppm representative of the varying water content of the apatite standards.

It was previously assumed that the partition coefficient for OHapatite could be used to calculate the abundance of H in silicate melts and in magmatic source regions (e.g. Boyce et al., 2010; McCubbin et al., 2010a; Tartèse et al., 2013; 2014b; Barnes et al., 2014). Recent experimental studies, however, have shown that apatite preferentially incorporates F over Cl, and Cl over OH (Boyce et al., 2014; McCubbin et al., 2015b; Webster and Piccoli, 2015). They suggest that the self-inflicted loss of F from the melt during apatite crystallisation increases the OH content of subsequent apatite grains; therefore, a greater range of OH abundances can be achieved with the same amount of parental OH just by varying the amount of fluorine in the melt. These results also imply that relatively OH-poor apatite grains can form from relatively OH-rich parent magmas and that calculating melt OH abundance
from apatite data should be treated with caution. As a result of these works, five requirements, or assumptions, are now needed in order to use apatite as a hygrometer (McCubbin and Jones, 2015):

1) Apatite must be a primary crystallisation product from a rock that, as closely as possible, represents a melt composition
2) Apatite must have formed through equilibrium crystallisation rather than fractional crystallisation
3) From melting to apatite crystallisation the system should have been closed with respect to F, Cl, and H\(_2\)O (i.e. no late additional fluids prior to crystallisation)
4) Apatite must be the only mineral phase for which F, Cl, and OH are essential structural constituents
5) The bulk-rock abundance of F must be known, along with an approximate temperature of apatite crystallisation.

Once these assumptions are satisfied it is possible to use the F-OH apatite-melt exchange coefficient (\(~ 75\), Boyce et al., 2014; McCubbin et al., 2015b) to determine the F-OH ratio of the bulk rock. Assuming the bulk rock is representative of a primary melt, the F-OH can then be used to determine the H\(_2\)O content of the parent liquid.

1.4.1.1. Hydrogen isotopic composition of water in apatite

Hydrogen is the lightest element in the periodic table and the most abundant chemical substance in the universe. It has three naturally occurring isotopes, two of which hydrogen, (\(^1\)H) and deuterium (\(^2\)H or D), are stable. Isotope species can be fractionated, either by kinetic processes (associated with incomplete and unidirectional processes such as evaporation and diffusion), or by isotope exchange (equilibrium fractionation, where the isotope distribution
changes between different chemical species but there is no net change in the isotopic composition of the system) (Hoefs, 1987). Owing to the large difference in mass between H and D it is possible for significant fractionation to occur during geological processes such as degassing (Hoefs, 1987; Kendall and Caldwell, 1998; Kendall and Doctor, 2003). It is because of this potentially significant fractionation that the hydrogen isotope ratio (D/H ratio) of a sample can be used as a ‘fingerprint’ for the source(s) of water and any process that may have affected the sample with D/H ratios ranging from the protosolar nebula (−865 ‰, Levison et al., 2010; Altwegg et al., 2015) to the martian atmosphere (+4950 ± 1080 ‰, Webster et al., 2013).

Hydrogen can be found in many phases in planetary materials such as water ice, phyllosilicates, organic compounds, glasses and melt inclusions and minerals such as amphibole and apatite (Mousis et al., 2000; Robert, 2006; Saal et al., 2008; 2013; McCubbin et al., 2010b; Sarafian et al., 2014). Small quantities of H can also be found in nominally anhydrous minerals such as olivine and pyroxene (Aubaud et al., 2004; Peslier, 2010; Mosenfelder et al., 2011; Stephant et al., 2016) with their high pressure polymorphs potentially able to accommodate much more (up to 2.5 wt.% Pearson et al., 2014; Németh et al., 2017). The most significant mineral for this project is the phosphate apatite, where the OH ion occupies the X site, and the mineral can contain up to 1.81 wt.% OH (Deer et al., 2013).

1.4.1.2. Abundances and isotopic composition of chlorine in apatite

Apatite accommodates chlorine as well as water. Chlorine is the second lightest of the halogens, extremely reactive and strongly oxidising. Chlorine has 24 isotopes with mass numbers ranging from $^{28}\text{Cl}$ to $^{37}\text{Cl}$, however, there are only two stable isotopes, $^{35}\text{Cl}$ and $^{37}\text{Cl}$.
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$^{37}\text{Cl}$. Owing to its strongly hydrophilic nature and incompatibility in nearly all silicates, the Cl isotope composition ($^{37}\text{Cl}/^{35}\text{Cl}$) of meteorites can be used as a tracer for volatile reservoirs, specifically water, in the early Solar System and processes that may have affected them. Natural variations in chlorine isotope ratios are expected owing to the large relative mass difference between the two isotopes as well as variations in coordination and bonding of chlorine between vapour, aqueous, and solid phases (Magenheim et al., 1994; Schauble et al., 2003). Chlorine does not typically fractionate under magmatic temperatures (Schauble et al., 2003; Bonifacie et al., 2008), however, larger variations have been observed on Earth at low temperature such as during hydrothermal alteration (Kaufmann et al., 1984; Magenheim et al., 1995; Schauble et al., 2003; Bonifacie et al., 2008). The incompatibility of Cl in most silicates limits the phases within which Cl can be found mainly to salts (e.g. NaCl, KCl), perchlorate, and mineral apatite (Eggenkamp et al., 1994; 1995; Chevrier and Rivera-Valentin, 2012; Barnes et al., 2016; Mitchell and Christensen, 2016; Sarafian et al., 2017a). In apatite, Cl, like the OH ion, also occupies the X site; pure chlorapatite can contain up to 6.81 wt. % Cl.

1.4.2. Apatite in lunar rocks

The Moon shares several similarities to Vesta, both are airless bodies believed to be volatile depleted and have undergone differentiation, possibly through a magma ocean stage. Apatite is also a common volatile-bearing mineral in samples from both bodies. Understanding the volatile composition of apatite on the Moon, and any secondary processes it may have undergone, can provide useful insight into the origin and history of volatiles on Vesta as well as allowing us to draw comparisons between the two airless planetary bodies.
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After the detection of magmatic water in lunar volcanic glasses (Saal et al., 2008), apatite was one of the next phases to be studied for its water content (Boyce et al., 2010; McCubbin et al., 2010a; 2010b; Greenwood et al., 2011; Barnes et al., 2013; 2014; Tartèse and Anand, 2013; Tartèse et al., 2013; 2014b). Much of the investigation of lunar apatite has focused on lunar basalts and breccias, which have H$_2$O abundances of ~ 380 up to ~ 14500 ppm (Boyce et al., 2010; McCubbin et al., 2010b; Barnes et al., 2013; Tartèse et al., 2013; 2014a). Work has also been conducted on lunar highland samples (Barnes et al., 2014) as well as evolved and KREEP-rich lunar rocks (KREEP being the acronym for rocks elevated in potassium (K), rare earth elements (REE) and phosphorus (P)) (Tartèse et al., 2014b; Robinson et al., 2016b). Highlands samples are typically H$_2$O-poor and have a lower range of contents from ~ 130 to ~ 2100 ppm (Barnes et al., 2014). KREEP-rich rocks display a comparable range of H$_2$O abundances to that of the highland samples, with values ranging from ~ 94 to ~ 2850 ppm H$_2$O (Tartèse et al., 2014b), whereas the more evolved rocks are typically dryer with a more restricted range (< 267 ppm, Robinson et al., 2016b). These values, particularly the basaltic samples, display H$_2$O abundances at levels similar to terrestrial apatite (Figure 1.14).

The hydrogen isotopic compositions of lunar apatite grains have also been examined. Mare basalts show a wide range of hydrogen isotope values (with δD values ranging from ~ -277 ‰ to ~ +1200 ‰, Barnes et al., 2013; Anand et al., 2014) but are generally enriched in deuterium with respect to Earth (Figure 1.14a). The origin of this enrichment is under debate and has been attributed to the addition of D-rich material, possibly of cometary origin, early in the Moon’s history (Greenwood et al., 2011) or to the preferential loss of H over D during magmatic degassing (e.g. Tartèse and Anand, 2013; Tartèse et al., 2013; Tartèse et al., 2014b). Work by Treiman et al. (2016) suggested that in some cases δD is correlated with Fe-Mg chemical zoning of pyroxenes in the sample, which is one measure of the basalts’
thermal history. They suggest that some samples with lower δD values could have experienced extensive thermal processing and suggest that the light H component is derived from solar wind implanted into the lunar regolith; this could enter basalts either by assimilation of regolith or by vapour transport from regolith heated by the lava flow.

Figure 1.14: (a) Hydrogen isotope data (in ‰) vs. apatite H₂O content in low-Ti and high-Ti Apollo mare basalts and basaltic meteorites. (b) Histograms of H₂O content in terrestrial apatite grains and apatite grains in lunar mare basalts. Taken from Anand et al. (2014).

Results from the lunar highland samples have δD values similar to terrestrial values and some carbonaceous chondrites, which suggests a common origin for water in the Earth-Moon system (Barnes et al., 2014). As these results are from some of the earliest-formed rocks, the data advocate either the survival of primordial terrestrial water in the aftermath of the giant impact, or that water was added to the Earth-Moon system shortly after the accretion of the Moon (Barnes et al., 2014). The more evolved rocks studied by Robinson et al. (2016b) display moderately elevated δD values as well as values similar to the terrestrial upper mantle. The Apollo 15 quartz monzodiorites, however, display the lowest δD values
measured from the Moon so far (as low as – 749 ‰) and suggest that the lunar interior could be heterogeneous with respect to H isotopes (Fig. 1.15; Robinson et al., 2016b).

Figure 1.15: δD values versus H₂O content of apatite in evolved lunar rocks (coloured points) compared with literature data (greyscale points). QMD = Quartz Monzodiorite. Taken from Robinson et al. (2016b).

Apatite in lunar rocks has also been studied for chlorine isotopes. It has recently been demonstrated that lunar samples display a significant range in Cl isotopic composition, especially lunar apatite, which shows δ^{37}Cl values ranging from ~ − 4 ± 2 ‰, lower than typical terrestrial values (0 ± 2 ‰), to extremely enriched values of ~ + 36 ± 2 ‰ (Figure 1.16) (Sharp et al., 2010b; Tartèse et al., 2014a; Treiman et al., 2014; Boyce et al., 2015; Barnes et al., 2016; Robinson et al., 2016a). Currently, there are two main models proposed for the fractionation of Cl isotopes: the degassing of Cl in the absence of H as metal chlorides
(Sharp et al., 2010b; Ustunisik et al., 2015) and the inheritance of heavy $\delta^{37}$Cl values from a residual magma ocean reservoir in the Moon (urKREEP) which had undergone Cl isotope fractionation early in the Moon’s history (Boyce et al., 2015; Barnes et al., 2016).

Figure 1.16: Chlorine isotope data (in ‰) vs. Cl content. Uncertainties represent 2σ errors. Data for basaltic fields (Sharp et al., 2010b; Boyce et al., 2015), KREEP basalt 72275 (Sharp et al., 2010b), and the Earth range (Sharp et al., 2013b). Figure taken from Barnes et al. (2016).

1.5. Aims and objectives of the research

The main aim of this research is to: determine the volatile content (F, Cl, OH) and associated isotopic compositions of apatite in a range of eucrite samples. The volatile inventories (F, Cl, H) of volatile-depleted bodies such as the Moon or Vesta have been poorly constrained until recently because of the limitations in in situ analytical techniques.
Advances in secondary ion mass spectrometry (SIMS), however, have permitted the successful *in situ* measurement of H in volcanic glasses and minerals such as apatite from a variety of lunar samples (Saal et al., 2008; Greenwood et al., 2011; Hauri et al., 2011; Barnes et al., 2013; Tartèse et al., 2013). Recently, nominally anhydrous minerals (NAMs) such as pyroxene have been suggested to contain up to ~100 ppm H₂O and, therefore, could constitute another important reservoir of water in eucrites (Stephant et al., 2016). In this study, however, mineral apatite is the focus of investigation as in eucrites and in many planetary samples apatite has been shown to be the major carrier of volatiles e.g. OH, Cl, F (McCubbin et al., 2014; 2015a).

The HED meteorites are a natural extension of these pioneering studies as the early crystallisation ages of eucrites (Misawa et al., 2005; Zhou et al., 2013) can help to further constrain the source(s) of volatile elements in the early inner Solar System. Currently, the volatile inventory and isotopic composition of apatite in eucrites is poorly understood, partly owing to a limited number of studies (Sarafian et al., 2013; 2014). This makes this work part of an emerging area of research which could contribute significantly to the assessment of the volatile inventory of the inner Solar System.

Utilising the information gathered during the course of this PhD research, coupled with literature data, the potential processes which have affected the abundances and isotopic compositions of H and Cl in eucrites will be determined. It is anticipated that results from the study will provide insight into some of the currently unanswered questions, specifically:

1) What is the volatile inventory of eucrites, as determined through measurement of volatile abundances in apatite grains?
2) Can we distinguish and account for secondary processes that may have altered the indigenous volatile signature in eucrites?

3) Are there differences in the amount and isotopic composition of volatiles in apatite grains from different eucrite petrologic, metamorphic and geochemical trends?

4) From where did water in Vesta originate? Is the inner Solar System homogenous in volatile content and isotopic composition?

To answer the questions above, the following objectives will be pursued:

1) Using scanning electron microscopy (SEM), create high-resolution backscatter electron (BSE) and elemental X-ray montage maps of each polished thin-section of a given sample selected for this study in order to determine the presence or absence of phosphate minerals in each sample.

2) Where phosphates have been observed, use energy dispersive spectroscopy (EDS) to identify mineral apatite from merrillite. Where apatite has been identified, use BSE and secondary electron (SE) imaging to establish whether the apatite grains are of suitable quality for SIMS analysis with regards to their size (ideally an area of ~ 10 × 10 µm per analysis), shape, and extent and abundance of cracks, fractures, and inclusions.

3) Measure the abundance and isotopic composition of hydrogen in suitable apatite grains using the Cameca NanoSIMS 50L at The Open University.

4) Measure the abundance of volatiles (F, Cl, OH) and chlorine isotopic composition of apatite using the Cameca NanoSIMS 50L at The Open University. Where possible, measurements should be conducted upon the same mineral grains that were previously analysed for H isotopes.
A suite of eucrites was selected for analysis to address the above questions. The suite also included the anomalous eucrite Emmaville. Although Emmaville has the petrology of a basaltic eucrite, it has an unusual oxygen isotopic composition that implies that Emmaville is not from Vesta (Greenwood et al., 2013). In order to determine how Emmaville fits into the overall scheme of volatiles in the early Solar System, a specific study was undertaken on the meteorite, which had the following objectives:

1) Characterise the petrology and mineral composition of the Emmaville eucrite using SEM, electron probe microanalysis (EPMA) and Raman spectroscopy

2) Obtain bulk major, minor, and trace element data for Emmaville and a suite of eucrites for comparison using the ICP-MS and ICP-OES instruments at The Open University

3) Determine the O isotopic composition of differing fractions of Emmaville to assess whether impactor material may be the cause of the anomalous O isotopic signature observed

4) Obtain H and Cl isotope data on apatite grains from Emmaville.

Unfortunately, only one apatite grain was found during the course of the PhD in sections of Emmaville and this grain was too small to analyse. We were also unable to procure a new section of Emmaville during the period of my PhD research.

In chapter two of this thesis, I will outline the methods used during the course of this work. Chapter three characterises the mineralogy, petrology and oxygen isotopic composition of the anomalous eucrite Emmaville. Chapter four gives details on the abundance and isotopic composition of water in apatite from eucrites and provides a comprehensive data set for a suite of eucrites, representative of the principal geochemical trends and metamorphic trends.
Chapter five investigates the variation in chlorine isotopic composition of many of the same eucrites analysed in chapter four. The final chapter, chapter six, provides a synthesis of the work undertaken for this thesis within the context of understanding the history of volatiles in the early Solar System, with a specific focus on Vesta (the HED parent body).

1.5.1. Declaration of published work and personal contribution

The majority of the contents of chapters three and four have been published in the journal Meteoritics and Planetary Sciences (Barrett et al., 2016; Barrett et al., 2017). The contents of chapter five are currently being used to prepare a submission to Geochimica et Cosmochimica Acta; below I outline my own specific contribution in each case.

Contribution to Chapter Three

I requested and acquired the Emmaville polished thin sections; the bulk chips used in the oxygen isotope measurements were already at the Open University. I performed SEM and EPMA analyses and collected all the data. D. W. Mittlefehldt and D. K. Ross provided guidance and helped with troubleshooting EPMA issues. Similarly, S. J. Hammond and P. Rafferty provided assistance in data collection using ICP-MS and ICP-OES. Sample preparation and loading for ICP-MS and ICP-OES were conducted by myself under the supervision of B. L. A. Charlier. The actual ICP-MS and ICP-OES analyses were conducted by S. J. Hammond and P. Rafferty, respectively. Data correction for ICP-MS and ICP-OES was performed by myself with their guidance, the interpretation of the results were my own. F. A. J. Abernethy helped with Raman work. I compiled, reduced and performed initial
interpretation of all the data and wrote the first draft of the manuscript. I addressed the comments from review of the manuscript and edited the manuscript accordingly. All co-authors participated in discussion and provided input at various stages of the publication process.

Contribution to Chapter Four

I collected all SEM and NanoSIMS data with some assistance from other experienced users (R. Tartèse and J. J. Barnes) and performed data reduction, interpretation and writing of the first draft of the manuscript. I addressed the comments from review of the manuscript and edited the manuscript accordingly. All co-authors participated in discussions and provided input at various stages of the publication process.

Contribution to Chapter Five

I collected all SEM and NanoSIMS data with some assistance from other experienced users (J. J. Barnes and I. A. Franchi) and performed data, reduction, interpretation and writing of the first draft of the manuscript. I addressed the comments from review of the manuscript and edited the manuscript accordingly. All co-authors participated in discussions and provided input at various stages of the publication process. Zinc isotope analyses were conducted by F. Moynier at IPGP, Paris.
Chapter Two: Methods and Samples

This chapter details the methods used to identify, characterise, and analyse mineral grains from HEDs in polished thin sections. The analytical protocol for the measurement of the hydroxyl (OH) content and other volatiles (F, Cl) as well as the hydrogen (H) and chlorine (Cl) isotopic compositions of the apatite grains by Nano Secondary Ion Mass Spectrometry (NanoSIMS) is also presented in this chapter.

2.1. Optical microscopy

For a general overview of the petrological context of a thin section, optical microscopy was conducted under plane and crossed polarised light using a Nikon Eclipse LV 100 microscope (maximum magnification x500) fitted with a Nikon Ds-Fi 1 camera, and NIS Elements D version 3.00 software package. This provides textural information and some information regarding the analytical history of the section, some of which have previously undergone SIMS analysis at other institutes.

Phosphates in these sections are typically too small to be observed and identified with any degree of certainty under optical microscopy; the majority of the characterisation was, therefore, conducted using Secondary Electron Microscopy (SEM) which provides greater magnification. Energy Dispersive (ED) spectroscopy, was used to enable easier identification of phosphate minerals.
2.2. **Electron microscopy**

2.2.1. **Sample preparation**

Silicate material is a poor conductor of charge and as such bombardment of a sample by an electron beam causes a build-up of negative charge on a sample. This charge results in imaging artefacts and poor X-ray totals during quantitative analysis (see section 2.2.3). To avoid these effects, a layer of 15 – 30 nm of carbon was sputtered onto the polished sample surface using an EMITECH K950X Turbo carbon sputter coater. After SEM analysis, the carbon coat was removed using isopropanol and laser-sealed wipes in preparation for ion-probe work. Samples were gold coated for NanoSIMS analyses (see section 2.4.2).

2.2.2. **Scanning Electron Microscopy (SEM)**

Scanning electron microscopy is primarily designed for imaging of extremely small objects. In geology and planetary sciences SEM is routinely used to study the surface topography of a sample, the petrography of a polished thin section (usually using Back Scatter Electron (BSE) imaging) in detail and perform quick, usually qualitative, mineral identification using energy dispersive X-ray spectroscopy (EDS) (Reed, 2005)(Figure 2.1).

Secondary Electron (SE) images provide information about the topography of a thin section. These images are useful references for navigation and identification of apatite during ion probe analysis as the NanoSIMS imaging system uses a reflected light microscope which bears some similarities to a SE image. BSE images were also used to provide textural context and along with EDS analysis, for distinguishing mineral phases in the polished section.
2.2.2.1. Electron imaging and X-ray elemental mapping protocol

The image and X-ray elemental mapping of samples were conducted on a Quanta 3D Focused Ion Beam Scanning Electron Microscope (FIB-SEM) fitted with an Oxford Instrument INCA energy dispersive X-ray detector at The Open University. The INCA software AutoMate SmartMap feature was used to create high-quality BSE and elemental maps crucial for the search of apatite. The mapping of sections in this fashion is required as apatite grains are typically small (< 50 µm), can be difficult to distinguish optically and occur as an accessory phase in the polished sample.

Typical mapping conditions included an acceleration voltage of 20 kV and a beam current of 0.6 nA. The major constraints on mapping were the duration of the analysis and the final file size. Image resolution for both BSE images and elemental maps was typically 1204 × 896 pixels, at magnifications ranging from × 312 to × 498 (smaller sections ranged up to × 719). The dwell time used for the EDS during elemental mapping ranged from 100 – 150 µs.
with between 1 and 2 frames on average. For particularly large sections the image resolution was reduced to 512 × 448 pixels along with decreasing magnification and dwell time to fit within file size constraints. Where possible the working distance from the end of the electron column to the point where the electron beam is focused was kept to 15 mm for both mapping and imaging to produce the highest quality images possible. A typical map took between 8 – 12 hours to complete.

Once the SmartMap was completed the BSE images were stitched together using the INCA montage software (Figure 2.2a) before overlaying the phosphorous elemental map over the BSE montage map (Figure 2.2b). Site(s) of interest (SoI) were then identified by areas of elevated P for further point analysis. Once located, high-resolution BSE and SE images of the phosphates were collected using the same beam conditions used for the mapping of the section. Rapid EDS spot analyses (~ 30 s exposure) were then acquired to distinguish apatite from anhydrous merrillite and characterise the surrounding mineral assemblage (Figure 2.3) (the short exposure times were chosen based on previous studies which confirmed that low beam currents do not affect the water contents or δD values of apatite; Barnes et al., 2013; see section 2.2.3.1 for further discussion). Apatite grains suitable for NanoSIMS analysis were then selected based on their dimensions (ideally greater than 10 µm × 10 µm, however, the smallest area that could be analysed were of the order of 3 × 3 µm) and for being relatively fracture and inclusion-free.
Figure 2.2: a) BSE montage map of Moore County. Px = pyroxene, Pl = plagioclase and Cr = Chromite; b) The same BSE map overlain with the P X-ray map (in false-red colour) to highlight phosphate grains. Ap = Apatite. The scale bar in each image is 3 mm.
Figure 2.3: BSE image of apatite and merrillite in Camel Donga. The EDS spectra for both minerals clearly highlights the compositional differences between the two with merrillite containing REEs and a higher P/Ca ratio.

2.2.3. Electron Probe Microanalysis (EPMA) using Wavelength Dispersive Spectrometry (WDS)

In a WD spectrometer X-rays are filtered by wavelength rather than by energy and operate sequentially as opposed to the simultaneous collection used in EDS. A WD detector has the advantage over the ED in terms of quantitative analysis by providing higher wavelength resolution and lower detection limits. Abundance of elements with an atomic number greater than five (Boron) can be measured to within ± 1 % (Reed, 2005). A series of diffraction crystals is employed for analysis of different elements. Common crystals include lithium fluoride (LIF), pentaerythritol (PET), thallium acid phthalate (TAP) and PCO synthetic multi-layer W-Si crystal.


2.2.3.1. Electron beam exposure and volatile mobility

In the literature, there has been some discussion regarding the effects of exposing an apatite grain to an electron beam with beam currents typical of routine analysis by SEM or EPMA and whether this may mobilise the volatiles within and/or out of the apatite’s crystal structure (e.g. Stormer et al., 1993; McCubbin et al., 2010b; Goldoff et al., 2012; Barnes et al., 2013; Stock et al., 2015). Stormer et al. (1993) demonstrated that both F and Cl X-ray intensities increase during analysis and that this effect was strongly anisotropic. It was also noted that there appeared to be no relaxation or decay of the effect when re-analysed up to several weeks later. The intensity variation and its anisotropy were explained by the diffusion of F, and to a lesser extent Cl, to the surface of the crystal driven by the electrical field produced by the implantation of electrons from the primary beam (Stormer et al., 1993). Further work by McCubbin et al. (2010b) confirmed the mobilisation of F (the Cl count-rates during their analyses were constant) and used a time-dependent intensity (TDI) correction to project F X-ray count rates back to time-zero, provided the variation was positive-sloped and linear. These works suggest that F and Cl anions are not lost from the apatite crystal structure, rather, they are mobilised to the surface (Stormer et al., 1993). This mobilisation could increase count rates leading to apparently non-stoichiometric apatite.

Regarding the effects on hydrogen, Wagner et al. (2008) analysed amphibole using EPMA under a variety of beam currents (from 10 to 240 nA) and a 30 µm spot size, before subsequent SIMS analysis, and found that H is driven out of the crystal structure at beam currents > 50 nA. If this is also the case for apatite, then the utilisation of high beam currents during SEM and EPMA to locate suitable apatite grains for analysis may compromise the results of subsequent ion microprobe OH measurements due to the potential loss of H. Neither the SEM of EPMA work reported used such a high beam current.
To minimise the effects of electron beam damage on apatite, Goldoff et al. (2012) determined the optimal EPMA operating conditions for anhydrous apatite to be 10 kV accelerating voltage and 4 nA beam current. These conditions were later tested for their effects on OH by Barnes et al. (2013) compared to more typical beam conditions. In their experiments, Barnes et al. (2013) exposed apatite grains to a variety of beam currents to reflect different levels of exposure to electron beams during SEM and EMPA analysis. It was found that ‘light’ analytical conditions (0.60 nA and 20 kV) used during SEM analyses, did not affect the OH content or δD values in apatite within the measurement uncertainties. There was, however, a slight increase in the measured OH content (~ 500 ppm OH) for areas exposed to relatively stronger beam currents of 4 nA and 20 nA. They also noted no obvious effect on δD values at these higher beam currents (Barnes et al., 2013).

To avoid any potential mobilisation of volatiles in the apatite grain prior to NanoSIMS analysis, the samples analysed during this works did not undergo EPMA work until after they had been measured on the NanoSIMS. When identifying apatite grains using SEM, the ‘light’ analytical conditions outlined by Barnes et al. (2013) above were used. It should be noted that, as several of these polished thin sections were obtained from various world-wide collections, it could not be guaranteed that the sections were not exposed to high electron beam conditions during investigations conducted by previous researchers.

2.2.3.2. Analytical method

*Analysis of major mineral phases in eucrites*

Major minerals in Emmaville were analysed using the new JEOL8530F field emission EPMA at the NASA Johnson Space Center. Beam conditions included an accelerating voltage of 20 kV, and beam current of 40 nA for pyroxene, with a spot size set to ~0.01 μm.
(giving an excitation volume of ~1 μm$^3$). These beam conditions and the counting times used are similar to those of Mittlefehldt (2005) that result in greater precision on Fe/Mn ratios, used as a discriminator for parent bodies, than commonly used EPMA protocols. Plagioclase was analysed with a 15 kV, 20 nA beam, and 3 μm spot size to minimise beam damage.

Other meteorite samples were analysed using a Cameca SX100 both at the NASA Johnson Space Center and at The Open University. Beam conditions used for minerals in these meteorites were a 20 kV accelerating voltage, 20 nA beam current, and a 10 μm spot size. The calibration standards used for all the EPMA analyses were: for pyroxene, diopside (Ca, Mg, Si), kaersutite (Al), rutile (Ti), rhodonite (Mn) and fayalite (Fe); for plagioclase, anorthite glass (Si, Al, Ca, ), oligoclase (Na), kaersutite (Mg), orthoclase (K); for chromite, ilmenite and oxides, chromite (Al, Cr, Fe, Mg), diopside (Ca, Si), rutile (Ti), vanadium metal (V), rhodonite (Mn). Reproducibility was found to be better than 0.55 wt. % 2σ based on analyses of secondary standards.

Analytical protocol for mineral apatite

Apatite grains were analysed using the Cameca SX100 at The Open University. The beam conditions used were the same as those specified by Goldoff et al. (2012) (10 kV, 4 nA see section 2.2.3.1 for more details) with a spot size of 5 μm. To minimise the mobilisation of F (Stock et al., 2015; see also section 2.2.3.1 for more details), F was measured first in isolation on a PCO crystal. The crystal was then rotated out of position and the remaining elements were analysed together. Calibration standards used for these analyses include jadite (Na), strontium fluoride (F), bustamite (Mn, Ca), yttrium phosphate (Y, P), turgutite (Cl), cerium metal (Ce), barite (S), haematite (Fe), forsterite (Mg), feldspar (Si). Secondary apatite standards were analysed prior to analysing unknowns to ascertain
precision and reproducibility (accuracy better than 2.9 % for all elements other than F which
was better than 9.7 %; reproducibility better than 0.43 wt. % 2σ).

2.3. Raman spectroscopy

Raman spectroscopy is based on the scattering of light from a monochromatic incident
beam and is used to observe the vibrational and rotational, and other low-frequency modes
in a system (Graves et al., 1989). As Raman scattering is inelastic the energy of both the
molecule and the exciting photon are changed in order to conserve energy (Colthup, 2012).
If the resultant energy state of the molecule is higher than its initial ground state (i.e. the
molecule gains energy from the beam) the vibrational frequency of the molecule will
increase and that of the beam will decrease (Stokes Effect, Long, 1977; Félix-Rivera and
Hernández-Rivera, 2012). Should the scattered photon experience a gain of energy, it will
be shifted to a higher frequency at the cost of the molecule (Anti-Stokes effect, see Fig. 2.4,

The difference between the frequencies of the incident beam and that of the scattered light
is expressed in wavenumbers (cm⁻¹) where the wavenumber is the reciprocal of the
wavelength expressed in cm (Colthup, 2012).

In order to be Raman active, the vibration must be capable of changing the polarisability of
the molecule (Colthup, 2012). Polarisability can be imagined as the deformability of the
electron cloud of the molecule by the electric field. In modern Raman systems, lasers with
wavelengths in the visible to near infrared are typically used as they are capable of producing
high intensity, self-collimated, plane-polarised monochromatic beams that prove ideal for
analysis of scattering (Long, 1977). In the analyses produced for this work only the Stokes
bands are shown.
2.3.1. Analytical method

Areas suitable for analysis by Raman spectroscopy (i.e. containing the target mineral phase) were identified from BSE images made during the analysis of Emmaville. Raman
spectroscopy was conducted using a Horiba Jobin Yvon LabRam HR instrument at the Open University. A 514.53 nm laser with a laser power of 1.45 – 1.71 mW and spot size of ~ 2 µm was used for analysis and standardized with a Si chip. Hole and slit settings were 300 µm and 150 µm, respectively. Analyses consisted of two 10-second collections using a 50x objective lens and a 600 grooves per mm grating, giving a spectral range of ~ 0 – 1900 wavenumbers. Three maps were collected ranging in size from 29 µm x 44 µm to 91 µm x 135 µm with separations ranging from two to five microns.

Once obtained, maps were split into individual spectra using the program LabSpec 5 software. These individual spectra were then visually checked against reference spectra. A linear baseline was used for data correction.

2.4. Nano Secondary Ion Mass Spectrometry (NanoSIMS)

2.4.1. Principles of NanoSIMS

Secondary Ion Mass Spectrometry, more commonly known as SIMS can provide ppm or better detection limits for most elements covering almost all of the periodic table, imaging and depth profiles along with isotopic analysis of elements with sub-micrometre resolution on a variety of sample materials (Hoppe et al., 2013). When compared to other SIMS instruments, the NanoSIMS is designed for very high spatial resolution (down to 50 nm) isotope/element analyses, typically with lower primary beam currents. Larger SIMS devices (e.g. Cameca IMS 1270/1280) generally use higher primary beam currents coupled with high transmission of secondary ions allowing high-precision measurements to be more easily obtained. A unique feature of the NanoSIMS is the fact that the primary beam impinges perpendicular to the sample surface, giving a shorter distance between the probe-forming lenses and the sample surface compared to the oblique set-up of conventional SIMS. This
shortened distance (typically 400 µm) reduces the focal length and number of aberrations whilst allowing a much smaller beam spot for a given primary current (Hoppe et al., 2013). The NanoSIMS is also fitted with a magnetic sector mass analyser capable of multi-collection of up to seven secondary ion species simultaneously. A schematic of the whole instrument is shown in Figure 2.5.

Figure 2.5: Schematic of the NanoSIMS 50L ion optics. Modified after Hoppe et al. (2013). Note the arrangement of the primary column and egun are slightly different in the case of the Open University instrument.
To generate the secondary ions needed for SIMS analysis the sample surface is sputtered whereby primary ions impinging the surface, at a net 16 keV trigger a collisional cascade and eject atoms from the uppermost layers (typically down to 5-20 nm depth, Hoppe et al., 2013) (Figure 2.6).

Many of the ejected particles are neutral and therefore are not analysed, however, a small portion are ionised during ejection and it is these secondary ions that are collected, separated, and analysed in the mass spectrometer. The sputter yield is the ratio of the number of atoms sputtered to the number of impinging primary ions which typically ranges from 5 to 15 (Benninghoven et al., 1987). To obtain high precision isotope measurements, high counts are required which is facilitated by a high proportion of secondary ions being transmitted to the detectors coupled with the ability to accurately separate the ions of interest from other molecules of very similar mass (high mass resolving power). Transmission of ions is > 50 % using ES-3 for the setup used in Cl and H isotope analyses. High production of secondary ions is achieved by using large probe sizes and high beam currents, this, however, precludes a high spatial resolution (e.g. 10 nA on a Cameca 1280 is ~ ≥ 15 µm). At high spatial resolutions, smaller primary beam currents are required (e.g. for NanoSIMS imaging with ~ 100 nm spatial resolution the probe size is ≈ 1 pA) and therefore there are correspondingly fewer secondary ions being transmitted to the detector making high analytical precision more challenging to obtain (Hoppe et al., 2013).
For the purposes of this work, the only option on the NanoSIMS for the collection of negative secondary ions is a Cs$^+$ beam generated from a CsCO$_3$ source. A Cs$^+$ beam yields electronegative elements such as $^1$H$^-$ and $^2$H$^-$ (D) (Benninghoven et al., 1987; Hoppe et al., 2013). Bombardment of a sample by primary Cs$^+$ ions also has the added benefit of an increased yield of negative ions owing to the reduction of work functions (the minimum amount of energy to remove an electron from the surface of a solid) by the implantation of Cs into the sample surface (Benninghoven et al., 1987). As more secondary electrons are excited the increased availability of electrons leads to increased negative ion formation (Benninghoven et al., 1987).

Implantation of Cs$^+$ ions at the surface of the sample causes a build-up of positive charge. To compensate for charge build-up an electron flood gun can be used on the analysis area which directs a low energy (~ 10 eV) cloud of electrons toward the sputtered crater. As the electron gun must maintain a continuous flood of electrons at the point of charge build-up
(the sputter crater), difficulties arise involving 1) steering the electron beam to the correct spot and 2) preventing the electron beam from drifting off the spot during analysis and while driving the sample to a new analysis location. Even when the electron gun is correctly positioned, if it is operated at too high a current it can induce a higher level of background noise by ejecting loosely bound material.

Starting at the surface, as the primary ion dose implanted in the target increases, the primary ion species concentration will reach an equilibrium depending on the sputtering conditions and the nature of the target. This equilibrium corresponds to a sputtering steady state, and once it is achieved, reliable quantification is possible with reference standard samples (Benninghoven et al., 1987). Mass interferences occur whenever another ion has the same nominal mass as the analyte ion. To eliminate any isobaric interference the mass resolving power (MRP, Cameca definition in Equation 2.1) of the instrument must be greater than the mass resolution \( \frac{m}{\Delta m} \) where \( m \) is the mass and \( \Delta m \) is the difference in mass between the two atoms) of atoms/molecules in question.

\[
MRP_{\text{cameca}} = \frac{1}{4} \times \frac{r}{L} \tag{Equation 2.1}
\]

Where \( r \) is the turning radius of mass \( m \) in the magnet and \( L \) is the width of the portion of the mass peak between 10 % and 90 % of the maximum intensity, a measure of the steepness of the peak flanks. When \( MRP > \) Mass resolution the two different species of ions will appear as separate mass lines.

Secondary ions are focused by several slits and lenses that shape the secondary ion beam into a rectangular cross-section before entering the mass spectrometer through the entrance slit (ES). The main lenses and deflectors that are routinely adjusted for analysis are EOS,
Cy, and P$_2$P$_3$ (Figure 2.5). The aperture slit AS was also adjusted routinely for Cl isotope measurements.

2.4.2. Sample preparation

The Cameca holders for the NanoSIMS can accommodate three sample sizes: 1 inch, 10 mm and 15 mm round sections. These sections can either be typical polished thin sections or thick sections, mounted in a resin block or pressed into indium. For this work, most of samples were 1 inch round polished thin sections.

Before ion-probe analyses, samples were stored in a vacuum oven at ~ 55 °C. For charge dispersion purposes during ion-probe analysis, samples were coated with ~ 30 nm of gold using an EMITECH K575X peltier-cooled gold sputter coater. The time between the sample removal from the vacuum oven, gold coating and transfer to the NanoSIMS airlock was kept typically to < 1 hour. Once in the airlock, the sample was left to degas under vacuum at ~ 55 °C for at least 24 hours before transferring it to the vessel chamber. Subsequent to NanoSIMS analysis, 0.25 µm diamond paste and an ALPHACLOTH polishing cloth were used to remove the gold coat. Care was taken not to apply too much force as this can lead to plucking of grains or the rounding of the softer mineral grains in the sample. After the gold coat was removed samples were sonicated at ~ 60 % power in isopropanol for two 15 minute sessions to remove any residual diamond paste.
Chapter Two: Methods and Samples

2.4.3. Analytical methods

2.4.3.1. Protocol for measurement of OH content and H isotopes

Analyses were conducted using a Cameca NanoSIMS 50L at the Open University using an existing protocol developed on the same instrument (Barnes et al., 2013; 2014; Tartèse et al., 2013). The NanoSIMS was used in spot mode to benefit from the pre-existing protocol at the institute, maintain internal laboratory consistency, and also allow for comparison between external laboratories and previously published literature (e.g. McCubbin et al., 2010a; 2010b; Barnes et al., 2013; 2014; Tartèse et al., 2013; 2014b; Robinson et al., 2016b).

Imaging mode trades poorer sensitivity for improved lateral resolution (Benninghoven et al., 1987; Ireland, 1995). The background contribution during imaging mode is also typically higher and consequently a higher probe current is required to improve the signal to background ratio. As samples were predicted to be very low in H₂O content spot mode is also used for its higher sensitivity and lower background in comparison to imaging mode.

Once apatite was located using the reflected light camera on the NanoSIMS, the zero probe and real-time imaging (RTI) were used to hone in on a suitable crack-free area for analysis within the apatite grain. Prior to analysis, areas (typically 12 µm × 12 µm ) containing target apatite grains were pre-sputtered to remove surface contamination and achieve sputter equilibrium, using a high 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 multi-collection mode, measuring negative secondary ions of ¹H, D, ¹²C, ¹⁸O and, ⁴⁰Ca¹⁹F on electron multipliers with a mass resolving power of ~ 4300 (Cameca definition) sufficient to resolve ¹H₂⁻ from D⁻. 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 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 $^{1}\text{H}$ and $^{12}\text{C}$ were monitored in real time during pre-sputtering to ensure that the area to be analyzed was free of cracks or hotspots indicative of contamination. Monitoring the $^{1}\text{H}$ and $^{12}\text{C}$ 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 the analysis of pristine material were considered and isolated using the NanoSIMS DataEditor software (Frank Gyngard, Washington University).

Pulse height detection (PHD) adjustment was conducted at the start of each session for $^{1}\text{H}$, D and, $^{18}\text{O}$ and every few sessions for $^{12}\text{C}$ and $^{40}\text{Ca}^{19}\text{F}$ to account for detector aging. External coils were adjusted to eliminate mass discrimination at the entrance slit. A mass resolving power of > 3000 was achieved to ensure discrimination between $^{1}\text{H}_2$ and D. 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 $^{1}\text{H}/^{18}\text{O}$ ratio of standards analysed 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 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 H and D were $9.3 \times 10^3$ and 1.9, respectively, for samples with ~ 1000 ppm H$_2$O and $8.5 \times 10^2$ and $1.9 \times 10^1$, respectively, for ~ 100 ppm H$_2$O 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 (see section
2.4.4.1 for more details). The H isotope composition of the water in apatite measured in this study is reported using the standard δD (per mil, ‰) notation whereby:

\[
\delta D = \left\{ \frac{D_{\text{sample}}}{D_{\text{VSMOW}}} - 1 \right\} \times 1000
\]  

Equation 2.2.

The reference used is VSMOW with a D/H ratio of 155.76 \times 10^{-6} (Hagemann et al., 1970).

2.4.3.2. Chlorine isotope measurements

The Cl content and isotopic compositions were measured using the Cameca NanoSIMS 50L at The Open University in multi-collection mode using a refined protocol based on Tartèse et al. (2014a) and Barnes et al. (2016), acquiring negative secondary ions of \(^{16}\)O\(^{1}\)H, \(^{18}\)O, \(^{35}\)Cl, \(^{37}\)Cl, and \(^{40}\)Ca\(^{19}\)F, simultaneously on electron multipliers. Apatite grains were located in the same manner as outlined in section 2.2.2.1. 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 hours. 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. The primary current for three of the four analytical sessions was ~ 50 pA (in Cs\(^+\) mode). The January 2016 session, however, used the lower probe current of ~ 25 pA. Typically a 5 µm × 5 µm area was analysed, however for some smaller grains this area was decreased to as small as 3 µm × 3 µm. No electronic gating was used. Pulse height detection (PHD) adjustment was carried out at the start of each session for \(^{18}\)O, \(^{35}\)Cl and, \(^{37}\)Cl and every few sessions for \(^{16}\)O\(^{1}\)H and \(^{40}\)Ca\(^{19}\)F to account for detector aging. Counts per second for Cl were also kept to below 85,000 counts per second (cps) using AS and ES as experience has shown a significant increase in detector aging at, and above this value. External coils were adjusted to eliminate mass discrimination at the entrance slit. Terrestrial
apatite standards (Ap003, Ap004, Ap018, Ap020; see McCubbin et al., 2012) were used to correct for instrumental mass fractionation and calculate apatite chlorine contents. Figure 2.7 shows an example of the reproducibility of $\delta^{37}$Cl values measured on apatite standard Ap004 which has a $\delta^{37}$Cl value of $\sim +0.11 \‰$ (Barnes et al., 2016). A nominally anhydrous San Carlos olivine and measurements made on pyroxene grains near to analysed apatite were used to assess the total background Cl contribution. The total background Cl was found to be less than 2 ppm.

![Figure 2.7](image.png)

Figure 2.7: Plot of $\delta^{37}$Cl values for standard Ap004 and sample DaG 945 over the course of a single day (January 23, 2017). The red diamond is the average $\delta^{37}$Cl value for the session; error bars $2\sigma$ of the measured values.

All chlorine isotope data are reported in the standard delta notation (per mil, ‰) format where:

$$\delta^{37}Cl = \left\{ \left( \frac{R_{\text{sample}}}{R_{\text{SMOC}}} \right) - 1 \right\} \times 1000$$

Equation 2.3
R is $^{37}\text{Cl}/^{35}\text{Cl}$ ratio and the reference used is SMOC (standard mean ocean chloride) with a $^{37}\text{Cl}/^{35}\text{Cl}$ ratio of 0.31977.

2.4.4. Calibrations and assessment of background contribution

2.4.4.1. Background H$_2$O and data reduction in D/H-OH measurements

Background water in the instrument can have a large effect on both the H$_2$O content and the D/H ratio measured in apatite, especially when apatite has a very low H$_2$O content. The raw data for measured water contents in apatite were first corrected for the background contribution, which ranged from the equivalent of 14 to 31 ppm H$_2$O depending on the analytical session. The background was determined using the $^1\text{H}/^{18}\text{O}$ ratios measured on the nominally anhydrous San Carlos olivine and the calibration slope for the corresponding analytical session. The calibration slopes were calculated using $^1\text{H}/^{18}\text{O}$ ratio and true OH content of terrestrial samples regressed through the origin with the OriginPro software using the linear fit feature. This software incorporates the uncertainties and scatter on the standards when providing the slope and 95 % confidence intervals used in the calculation of the samples H$_2$O uncertainties. The gradient of the calibration lines varied from one analytical session to another (Figure 2.8), with differences in gradient probably occurring because of differences in tuning parameters and substantial machine maintenance, specifically of the coaxial lense, during this period. 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).
Figure 2.8: H$_2$O content versus $^1$H/$^{18}$O ratio plots showing representative calibration lines from three different analytical sessions. These calibrations were obtained using standard apatites Ap003, Ap004, Ap005, Ap018, Ap020 (McCubbin et al., 2012).

**Uncertainty calculation**

When conducting analyses on the NanoSIMS, raw data are presented in the form of measured counts which are then made into isotope ratios. To assess the precision and reproducibility of the analysis and the stability of the instrument as a whole, uncertainties need to be calculated. Typically, standards were analysed before and after unknowns and the standard Ap004 was usually analysed in both standard runs.

As discussed previously, the reference standards were used to create a calibration line of $^1$H/$^{18}$O ratio versus true H$_2$O content which is used to determine the background OH
contribution. These calibration lines were also used to calculate the OH content (in ppm) of the sample using Equation 2.4:

\[ a = H_2O \text{ content (ppm)} = (g \times b) - c \quad \text{Equation 2.4} \]

Where; \( g \) = gradient of the calibration slope, \( b \) = measured \(^1\text{H}/^{18}\text{O}\) ratio of sample, \( c \) = total instrumental background \( H_2O \).

Furthermore, each calibration curve was used to determine the uncertainties associated with the \( H_2O \) content. To calculate the uncertainties, the gradient of the calibration curve was subtracted from the 95% upper confidence limit (UCL) of the calibration line then made into a ratio with the gradient before being converted into a percentage (Equation 2.5). The variation in \(^1\text{H}/^{18}\text{O}\) between repeat measurements on the standards is incorporated into the calculation of the calibration slope and UCL. The total uncertainty on the sample was then determined by the square root of the sum of the squares rule (Equation 2.6), which includes the poisson error associated with the measured \(^1\text{H}/^{18}\text{O}\) ratio that is calculated directly by the NanoSIMS software and the slope error.

\[ d = H_2O \text{ uncertainty (\%)} = \left( \frac{\text{UCL} - g}{g} \right) \times 100 \quad \text{Equation 2.5} \]

Where; \( \text{UCL} = 95\% \) upper confidence limit of the calibration line, \( g \) = gradient of the calibration slope.

\[ H_2O \ 2\sigma \ (ppm) = \sqrt{\left( \frac{p}{100} \times 2 \right)^2 + \left( \frac{d}{100} \right)^2} \times a \quad \text{Equation 2.6} \]

Where; \( p \) = poisson error associated with the measured ratio, \( d \) = analytical uncertainty (2\( \sigma \)) as derived from Equation 2.5, \( a \) = calculated \( H_2O \) content of sample as derived from Equation 2.4.
2.4.4.2. Background δD and data reduction in D/H-OH measurements

The primary standard Ap004, which has δD value of −45 ± 5‰ and the highest H$_2$O content of the apatite standards (McCubbin et al., 2012), was used to standardise the δD value of the meteorite samples. The average D/H ratio and standard deviation for a short chain of analyses (typically five analyses) were determined at the start and end of each day as well as whenever any significant adjustments were made to the tuning parameters during the day. Once analysed, the D/H ratio of the sample is compared firstly to the average D/H ratio of the primary reference standard (Equation 2.7) and then to the known δD value for the standard (Equation 2.8). The uncertainty associated with the D/H measurements were calculated using Equation 2.9 following the square root of the sum of the squares rule.

\[
a = \left(\frac{b}{c} - 1\right) \times 1000 \quad \text{Equation 2.7}
\]

Where; b = measured D/H ratio of the sample; c = average D/H ratio of Ap004.

\[
\text{corrected } \delta D = (a - 45) + \left(\frac{a - 45}{1000}\right) \quad \text{Equation 2.8}
\]

Where; \(a\) = δD value produced in Equation 2.7.

\[
\delta D \ 2\sigma \ (\%) = \sqrt{b^2 + c^2} \times 10 \times 2 \quad \text{Equation 2.9}
\]

Where; \(b\) = relative standard deviation of standard Ap004 in percent; \(c\) = D/H poisson error as measured by the NanoSIMS.

Instrument background δD calculation

The raw D/H ratios were corrected based on the percentage contribution of the instrument background to the measured H$_2$O 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:

\[
\frac{D}{H}_{\text{measured}} = (f \times \frac{D}{H}_{\text{apatite}}) + ((1 - f) \times \frac{D}{H}_{\text{background}}) \quad \text{Equation 2.10}
\]

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 chapter 5.

To calculate the instrumental background \( \delta D \) value, the primary standard Ap004, which has a pre-determined \( \delta D \) value of -45 ± 5 ‰ (McCubbin et al., 2012), and the nominally anhydrous San Carlos olivine for all analytical sessions are utilized. The D/H ratio and D/H poisson error for Ap004 and San Carlos are used to calculate a weighted mean for each standard in the Microsoft Excel Add-in program Isoplot (Berkeley Geochronology Center). A \( \delta D \) value is then produced using a modified version of Equation 2.2, referencing the weighted mean D/H ratio of Ap004 instead of VSMOW (Equation 2.11), which is then used to calculate the instrumental background (Equation 2.12).

\[
\alpha = \left\{ \left( \frac{D}{H}_{\text{San Carlos}} \bigg/ \frac{D}{H}_{\text{Ap004}} \right) - 1 \right\} \times 1000 \quad \text{Equation 2.11}
\]

\[
\text{Instrument background} = (\alpha - 45) + \left( \frac{\alpha \times 45}{1000} \right) \quad \text{Equation 2.12}
\]

Where; \( \alpha = \delta D \) value produced in Equation 2.11

The associated 2\( \sigma \) error of background \( \delta D \) was calculated using the relative weighted average error in percent of San Carlos and Ap004 and the square root of the sum of squares rule (Equation 2.13).
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\[ IMF \ 2\sigma = \sqrt{d^2 + e^2} \times 10 \quad \text{Equation 2.13} \]

Where; \( d \) = relative weighted average error of San Carlos (%); \( e \) = relative weighted average error of Ap004 (%)

Once the instrumental background \( \delta D \) was calculated, a correction can be applied to the measured \( \delta D \) values (Equation 2.14) which provides a background corrected \( \delta D \) value. It should be noted the correction for background OH and its associated \( \delta D \) value are applied before any additional corrections, such as for spallation (as discussed in chapter 5).

\[ Background \ corrected \ \delta D = \frac{\delta D_{\text{measured}} - (\delta D_{\text{background}} \times \frac{b}{100})}{(100 - c_{100})} \quad \text{Equation 2.14} \]

Where; \( b \) = background H\textsubscript{2}O content; \( c \) = contribution of the background (%).

2.4.4.3. Background volatile (F, Cl, OH) content and data reduction of Cl isotope measurements

During chlorine isotope analysis, the abundance of chlorine and the other common volatile elements that are incorporated into the apatite X-site, F and OH, were measured.

The abundance of chlorine and H\textsubscript{2}O during Cl isotope analyses were determined in a similar manner to the H\textsubscript{2}O content during D/H-OH measurements. The measured volatile ratio (\(^{16}\text{O}^{1}\text{H}^{18}\text{O} \text{or} \ 35\text{Cl}^{18}\text{O}) was multiplied by the slope of the corresponding calibration line (determined using the same apatite standards as above), and the background value, as measured on the San Carlos Olivine, was then subtracted.
2.4.4.4. Reproducibility of $\delta^{37}\text{Cl}$ and Cl abundance at low Cl abundance levels

Apatite within several samples have very low (< 150 ppm) Cl abundances when compared to the standards used in this study (Ap003, Ap004, Ap018). A standard noted to contain below EPMA detection levels of Cl (Ap020, McCubbin et al., 2012) was analysed as an unknown to test the reproducibility of $\delta^{37}\text{Cl}$ and Cl abundance at low Cl abundance levels (Figure 2.9).

![Figure 2.9: Reproducibility of $\delta^{37}\text{Cl}$ in low Cl content standard Ap020 (January 23, 2017). The error bars represent 2σ uncertainties and are a combination of the reproducibility on the primary standard (Ap004) and analytical error associated with individual measurements. Red diamond is the average value of Ap020.](image)

From this figure it can be seen that there is no systematic isotopic effect at low Cl abundances other than higher uncertainties, owing to poorer counting statistics. The average abundance
(n = 8) measured was found to be 17.3 ± 3.5 ppm (2σ) Cl in agreement with 15 ± 3 ppm Cl measured by McCubbin (pers. comm. August 22, 2016).

2.4.4.5. Calculation of fluorine content from baseline measurements

Owing to the large abundance of fluorine in many apatite grains, an alternative method of measuring F was devised to minimise the effects of high counts per seconds (cps) aging the detector. During each morning set-up, the F peak centre was acquired to optimise the F count rate. Once the optimal F peak was located, the detector was deflected + 8 V away from the optimal peak centre line to where counts were minimal. This new ‘peak’ position was then used for most of the analysis cycle (collecting essentially 0 counts). At regular intervals, typically 8-12 times an analysis, a F baseline was conducted, measuring the cps at a voltage of – 8 V from the newly defined peak position. This baseline measurement corresponds to measuring on the optimal F peak centre for a limited amount of time to limit detector aging.

After the analysis, the NanoSIMS software provides a mean count rate and a standard deviation for F across all of the intervals of that analysis. If the analysis was conducted using no beam blanking, which was the case for all analyses conducted here, then the mean count rate can be used as the ‘F rate’ for that analysis. The ‘F rate’ is then used to plot calibration lines in the same manner as with the other volatile elements. The F content of the sample is then calculated by multiplying the ‘F rate’ of the sample with the gradient of the calibration slope. To calculate the poisson error in percent associated with the F content the following equation was used:

\[
poisson \% = \left( \frac{\sqrt{Fr \times t}}{Fr \times t} \right) \times 100
\]

Equation 2.15
Where \( t \) is the count time in seconds calculated by multiplying the total number of F measurements by the cycle time of 0.54. The value of \( t \) ranged from 43.2 to 108 s across the entire analytical campaign.

The fluorine uncertainty was then calculated using the same formula as previously (Equation 2.6).

2.5. Measurement of bulk major, minor and trace element compositions

2.5.1. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is a technique that allows for rapid high-precision multi-element determinations at the ppm to ppb level. A sample is digested in acid, and an appropriately diluted solutions analysed. The digestion protocol followed is detailed in section 2.5.1.1. ICP-MS was used to analyse the minor and trace element compositions of samples.

2.5.1.1. Sample preparation

Before analysis, previously powdered samples were weighed into clean 7 ml Savillex Teflon beakers. Sample weights ranged from 13.57 mg (Ibitira) to 113.30 mg (Tirhert). Sample digestion was achieved with the addition of 2 ml TD HF + trace concentrated HNO\(_3\) to the beaker, which was then sealed and placed on a hotplate (ca. 120 °C) overnight. Excess HF and volatile SiF\(_4\) were removed by subsequent evaporation of the sample solutions to incipient dryness. Following evaporation, the sample was taken up and dried down in 2ml 6 M HCl. Once dry, concentrated HNO\(_3\) was added to give a 2 % HNO\(_3\) concentration upon
final dilution. Finally, samples were made up to 1000-fold dilutions in MilliQ water (resistivity > 18 MΩ) for analysis.

2.5.1.2. Analytical method

Trace elements were analyzed using the Agilent 7000a ICP-MS (inductively coupled plasma-mass spectrometer) fitted with a quartz spray chamber and PFA nebulizer at The Open University. Oxides (measured as CeO/ Ce in the tune solution) were kept low, at < 0.4%, and doubly charged species (Ce^{++} / Ce^{+}) at < 1.0 %. Count rates were 4 x 10^6 cps/ppm for ^7 Li, 12 x 10^6 cps/ppm for ^89 Y and ^140 Ce, and 7 x 10^6 cps/ppm for ^205 Tl. During ICP-MS analysis, after every five analyses, a ‘monitor block’ consisting of one reference standard (BIR-1) one unknown (Tirhert) and a blank solution of 2% HNO₃ was measured. The average and relative standard deviation of these repeated analyses were used to assess precision (see section A.2.1).

2.5.2. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

ICP-OES is a technique for determining the elemental composition of a solution at the ppm to the ppb level. It is complementary to ICP-MS and utilizes the properties of electromagnetic emission from atoms ionized by the plasma. The plasma is used to generate photons of light by the excitation of electrons of a ground-state atom to a higher energy level. When the electrons relax back to the ground state, wavelength-specific photons are emitted that are characteristic of the element of interest. The concentration of a particular element is directly proportional to the photon intensity. ICP-OES was used to measure major elements only.

2.5.2.1. Sample preparation
For ICP-OES analysis, aliquots of the solution prepared for ICP-MS analysis (the preparation of which is detailed above in section 1.5.1.1) were used. These aliquots were then subjected to a further dilution of 10x and for particularly abundant elements (Mg, Al, Ca and Fe) dilution of 100x using MilliQ water.

2.5.2.2. Analytical method

Aliquots of the final dilution were analysed for bulk major element analysis in the Teledyne-Leemans Prodigy high dispersion ICP-OES at The Open University, operating in axial view. Standards for ICP-OES were prepared using a certified stock solution of 1000 ppm multi-element standard from Fisher Scientific. The instrument was aligned for individual elements using solutions prepared from individual certified stock solutions of 1000 ppm (Fisher Scientific). Mean values were taken from three replicate analysis carried out per sample. Instrument drift was assessed by using a mid-range standard after every 5th sample. Precision and reproducibility are provided in section A.2.1.

2.6. Additional isotopic analyses

2.6.1. Oxygen isotope analysis

Oxygen isotope analyses are one of the cornerstones for investigating the origin and evolution of extra-terrestrial material (Clayton et al., 1976; Miller et al., 1999; Franchi, 2008). High analytical precision is required to understand subtle variations in O isotope composition owing to a variety of factors such as initial heterogeneities and the mixing of distinct components. Owing to the difficulty in breaking the Si-O bonds a strong oxidizing agent is required to liberate oxygen from the minerals (Miller et al., 1999; Rai et al., 2015). During the 1990s, the arrival of infrared laser-assisted fluorination, pioneered at The Open
University by Miller et al. (1999), enabled rapid, high-precision three oxygen measurements in silicates and oxides. The advantage of this particular technique is the low blank, potential for analysis of small samples (< 1 mg) and the acquisition of data from refractory minerals such as garnet and magnesian olivine (Miller et al., 1999).

For analysis, between 0.5 – 2 mg of fine-grained or powdered samples are weighed and loaded together with references into the sample chamber. These samples are then heated by a laser in the presence of BrF$_5$ and the released oxygen gas is subsequently purified by passing through two cryogenic N traps and over a bed of heated KBr before analysis in the mass spectrometer.

### 2.6.1.1. Analytical method

Similar to many eucrites, Emmaville shows evidence of brecciation and presence of shock melt veins. In order to verify whether Emmaville is isotopically homogeneous, or if the different lithologies preserve distinct oxygen isotope compositions, an attempt was made to separate the various lithological fractions. An approximately 400 mg fusion-crusted chip (removed from the single fragment analyzed by Greenwood et al., 2013; 2017) was gently crushed in an agate mortar and various fractions were hand-picked with the aid of a binocular microscope. Three distinct fractions were separated from Emmaville for the current study: E1 a relatively homogeneous grey coloured lithology which was free of shock melt veins, E2 material containing a relatively high proportion of dark fine-grained shock melt veins, and E3 a fine-grained light coloured fraction.

Oxygen isotopic analysis was performed at the Open University using a modified version of the infrared laser-assisted fluorination system described by Miller et al. (1999), the details of which can be found in Greenwood et al. (2015).
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Oxygen isotopic analyses are reported in standard δ notation:

\[ \delta^{18}O = \left( \frac{^{18}O / ^{16}O}_{\text{sample}} / \frac{^{18}O / ^{16}O}_{\text{ref}} - 1 \right) \times 1000 \ (\text{‰}) \]  
Equation 2.16

\[ \delta^{17}O = \left( \frac{^{17}O / ^{16}O}_{\text{sample}} / \frac{^{17}O / ^{16}O}_{\text{ref}} - 1 \right) \times 1000 \ (\text{‰}) \]  
Equation 2.17

The reference being VSMOW: Vienna Standard Mean Ocean Water. \( \Delta^{17}O \), which represents the deviation from the terrestrial fractionation line (\( \Delta^{17}O = 0 \text{ ‰} \)), has been calculated using the linearized format of Miller (2002):

\[ \Delta^{17}O = 1000 \ln \left( 1 + \frac{\delta^{17}O}{1000} \right) - \lambda \times 1000 \ln \left( 1 + \frac{\delta^{18}O}{1000} \right) \]  
Equation 2.18

where \( \lambda = 0.5247 \) (Miller et al., 1999; Miller, 2002).

An estimate of the present level of precision of the Open University system is provided by 39 analyses of our internal obsidian standard analysed during six separate sessions, which gave the following combined results: ±0.052‰ for \( \delta^{17}O \); ±0.093‰ for \( \delta^{18}O \); ±0.017‰ for \( \Delta^{17}O \) (2σ). The precision (2σ) quoted for individual meteorite samples is based on replicate analyses (Greenwood et al., 2015).

2.6.2. Zinc isotope analysis

The zinc isotopic composition of sample Dar al Gani 945 was measured in collaboration with F. Moynier at IGP, Paris. Acquisition of this data were deemed important in order to
fully assess the Cl isotopic composition of apatite in this sample (Chapter 5). Below is a brief overview of the technique used by Moynier to obtain the data (see Chapter 5, section 5.2).

2.6.2.1. Analytical method

Approximately 100 mg of sample powder was dissolved in conc. HNO₃/HF (1:3) and heated at 130 °C in PTFE containers. Subsequently, the samples were dried down and 5 ml of 6N HCl was added to the residue before heating again to dissolve remaining fluoride complexes. The sample was then dried down again. The chemical purification of Zn was achieved by anion exchange chromatography following the procedure described by Moynier and Le Borgne (2015) whereby samples were redissolved in 1.5N HBr and then loaded onto AG-1 X8 (200-400 mesh) columns. Matrix elements were removed by further addition of 1.5N HBr and Zn was eluted using 0.5N HNO₃. This process was then repeated on smaller 0.1 mL columns to further purify Zn. The collected solution was then heated to dryness and subsequently taken up in 0.1N HNO₃ for mass spectrometry analysis.

Zinc isotope compositions of bulk DaG 945 were measured using a Thermo Scientific Neptune Plus Multi-Collector Inductively-Coupled-Plasma Mass-Spectrometer (MC-ICP-MS) at the Institut de Physique du Globe in Paris (IPGP) following a well-defined protocol (Chen et al., 2013; Moynier and Le Borgne, 2015; Pringle et al., 2017). Masses ⁶²Ni, ⁶³Cu, ⁶⁴Zn, ⁶⁵Cu, ⁶⁶Zn and ⁶⁸Zn were collected on Faraday cups. Isobaric interference from ⁶⁴Ni was controlled and corrected for by measuring the intensity of the ⁶²Ni peak. Assuming that the ⁶⁴Ni/⁶²Ni ration is natural (0.2548) the real ⁶⁴Zn value can be corrected by:

\[
\text{Zn}_{\text{Real}}^{64} = \text{Zn}_{\text{measured}}^{64} - \text{Ni}_{\text{measured}}^{64} \times \left( \frac{\text{Ni}_{\text{measured}}^{64}}{\text{Ni}_{\text{measured}}^{62}} \right)_{\text{Natural}}
\]
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Equation 2.19

External precision for these measurements is 0.04 ‰ for δ\(^{66}\)Zn (2\(\sigma\)) (Pringle et al., 2017). Results are reported as permil (‰) deviations from the JMC-Lyon (Moynier et al., 2017) Zn isotope standard using the following equation.

\[
\delta^{X}Zn = \left[ \frac{\left( \frac{xZn}{64Zn} \right)_{\text{Sample}}}{\left( \frac{xZn}{64Zn} \right)_{\text{JMC-Lyon}}} - 1 \right] \times 1000
\]

Equation 2.20

Where \(x = 66\) or 67.

2.7. Sample descriptions

Meteorite samples used in this thesis are described in detail below along with the criteria used for sample selection. For a broad overview of HED meteorites, see section 1.3.
Representative BSE images of apatite-bearing areas for each sample can be found in Figure 2.10.

Figure 2.10: Representative Back Scatter 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. Black line outlines apatite grains. Solid white squares are the approximate location of SIMS raster area for hydrogen isotopes measurements whilst solid red squares indicate chlorine isotope measurements.

2.7.1. Criteria for sample selection and petrology of the studied samples

The samples studied here are broadly representative of eucrites as a whole since they fulfil each of the five criteria listed below (see Table 2.1 for more details):
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1. Samples were selected to represent the different geochemical trends, the Main Group-Nuevo Laredo trend \( (n = 3) \), Stannern trend \( (n = 1) \), residual \( (n = 3) \) and cumulate eucrite \( (n = 1) \) (see Chapter 1 section 1.3.1).

2. 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 (see Chapter 1 section 1.3.1).

3. A range of breccia types was chosen in order to assess any lithological-volatile patterns.

4. Samples with a range of cosmic ray exposure (CRE) ages were selected to allow for more precise cosmic ray spallation corrections to hydrogen isotope data.

5. To ensure both a representative sampling and to enable comparisons with the existing dataset both falls and finds were studied. In order to reduce the potential influence of terrestrial contamination on measured values, however, eucrite falls were preferred where possible. For further discussion of the potential influence or terrestrial/museum weathering see section 4.4.1

Several additional meteorite samples which fit into the criteria above were also studied but were found to contain no apatite grains within the sections provided:

- Diogenites: Bilanga, Shalka, Johnstown (contained two apatite grains but both were too small to measure), and Tatahouine
- Eucrites: Jonzac
- Cumulate Eucrites: Talampaya, Serra de Mage
- Anomalous Eucrites: Ibitira
Table 2.1: Main characteristics of the meteorites studied. OU = Open University, NHM = Natural History Museum London, SI = Smithsonian Institution, WAM = Western Australian Museum, NHW = Naturhistorisches Museum Wien, UNM = University of New Mexico. WG = Weathering Grade, MG = Metamorphic Grade. Individual section numbers are provided within the brackets. Cosmic ray exposure (CRE) ages for eucrites Stannern and Millbillillie are taken from Miura et al. (1998); Sioux County and Moore County ages are from Eugster and Michel (1995).

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Find / Fall</th>
<th>Collection</th>
<th>Geochemical Trend</th>
<th>Brecciation</th>
<th>WG*</th>
<th>MG</th>
<th>CRE age (Ma)</th>
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<td>Polymict</td>
<td>W3</td>
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<td>Stannern Trend</td>
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<td>Stannern Trend</td>
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</table>

*Weathering grade W1 – Minor oxide rims around metal and troilite; minor oxide veins. W3 – Heavy oxidation of metal and troilite, 60-95 % being replaced. Weathering grade classification from Wlotzka (1993).

2.7.2. Basaltic eucrites
All basaltic eucrites studied here are part of the Main Group-Nuevo Laredo trend with the exception of Stannern which gives its name to the Stannern trend eucrites. For more details on basaltic eucrites see Chapter 1 section 1.3.1.1.

2.7.2.1. Dar al Gani 844

General description

Dar al Gani (DaG) 844 is a highly fractured, polymict breccia composed of large coarse-grained clasts supported in a fine-grained matrix (Figure 2.11). Currently there are very few data available for this sample. The thin-section contains a single large clast which appears to be from a diogenite as it is composed entirely of large coarse-grained orthopyroxene whilst another smaller clast has a symplectite texture. The lack of Ca zoning in pyroxene and inversion of pigeonite to orthopyroxene suggests that it is a type 6 eucrite (Takeda and Graham, 1991). Minor phases include phosphates (apatite and merrillite), troilite, ilmenite, chromite, zircon, and Fe-Ni metal. Pyroxene Fe/Mn ratios range from 23.4 to 34.1 with an average of 29.8 typical of basaltic eucrites. There are currently no crystallisation or cosmic ray exposure ages for this meteorite.

Phosphate details and textural context

Apatite occurs as subhedral to anhedral crystals within fine-grained mesostasis areas, typically ranging in length from 5 - 20 µm, and is associated with other late-stage minerals such as ilmenite, silica and chromite. Apatite and merrillite were found together only in one area of this sample (Figure 2.10).
Figure 2.11: BSE montage map of DaG 844 overlain with false colour X-ray map. Red indicates hotspots of P.
Chapter Two: Methods and Samples

Justification for sample selection

DaG 844 was selected owing to the sample being a eucrite find which allows for comparison to falls and it has a known weathering grade of W3 (Meteoritical Bulletin Database; Wlotzka, 1993) so variations between finds of different weathering grades can also be assessed. Polished thin sections of the sample were also readily available at The Open University.

2.7.2.2. Millbillillie

General description

Millbillillie is a polymict breccia comprising type 6 pyroxene which is an indicator of significant thermal metamorphism (Figure 2.12) (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). Modal mineralogy for Millbillillie as described by Delaney et al. (1984a) are orthopyroxene (26.7 %), pigeonite (11.6 %), high-Ca pyroxene (10.5 %) and plagioclase (45.5 %). Minor phases occur in both lithologies and include chromite (0.5 %), phosphates (apatite and merrillite; combined total 0.1 %), ilmenite (0.7 %), a silica polymorph (4.3 %), troilite (trace), and zircon (trace). The different lithologies observed within Millbillillie also have different $^{244}$Pu-Xe ages relative to the absolute crystallization age of 4.5578 Ga for Angra dos Reis (ADOR), with the fine-grained portion at $+8 \pm 24$ Ma and $-51 \pm 21$ Ma for the coarse grained portion (Miura et al., 1998). Assuming the age of ADOR, their relative ages would
correspond to 4.566 ± 0.024 (fine-grained) and 4.507 ± 0.021 Ga (coarse-grained). Miura et al. (1998) theorise that the difference in age is related to the cooling rate of the two lithologies: either the coarser-grained portion cooled more slowly, or the coarser-grained lithology underwent recrystallisation about 60 Ma after the start of Xe retention in the fine-grained portion. Later work by Hopkins et al. (2015) provides a $^{207}\text{Pb} - ^{206}\text{Pb}$ age of a zircon core at 4555 ± 17 Ma, in agreement with earlier works (Bukovanská et al., 1997; Miura et al., 1998).

Phosphate details and textural context

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 analysed in this study (Figure 2.10) owing to the size of the grains.

Justification for sample selection

Millbillillile was selected as it is a polymict eucrite fall with type 6 pyroxene grains. The meteorite has also been well studied and has CRE age data available which allows for more accurate spallation corrections.
Figure 2.12: BSE montage map of Millbillillie overlain with false colour X-ray map. Red indicates hotspots of P.
2.7.2.3. Sioux County

General description

Sioux County is a heavily fractured, coarse-grained breccia. Pyroxene crystals are mainly type 5 (Figure 2.13). According to the Meteoritical Bulletin Database, Sioux County is monomict, however, Yamaguchi et al. (1997) suggested that there were also minor amounts of type 4 and type 6 pyroxene within the sample, suggestive of a polymict breccia. Major phases include orthopyroxene (26.9 %), pigeonite (8.9 %), high Ca-pyroxene (12.5 %) and plagioclase (46.6 %) (Delaney et al., 1984a). Pyroxene composition ranges from Wo$_{1.7}$En$_{36.1}$Fs$_{62.2}$ – Wo$_{43.9}$En$_{29}$Fs$_{27.1}$ and average Fe/Mn ratios for high Ca-pyroxene and orthopyroxene are 30.58 and 31.57 respectively (Mittlefehldt, 2015), consistent with basaltic eucrites. 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 phosphates (apatite and merrillite; combined total 0.1%), chromite (0.3 %) troilite (0.4 %), zircon (trace), ilmenite (0.6 %), and a silica polymorph (3.6 %). A $^{87}$Rb-$^{87}$Sr age for Sioux County was found to be 4.19 ± 0.14 Ga (Birck and Allègre, 1978).

Phosphate details and textural context

Apatite grains in this thin-section are mainly subhedral, ranging in size from 10 – 60 µm, occurring interstitially between the larger silicate minerals (Figure 2.10). Owing to the heavily fractured nature of this sample, very few apatite grains were suitable for NanoSIMS analysis.
Figure 2.13: BSE montage map of Sioux County overlain with false colour X-ray map. Red indicates hotspots of P.
Justification for sample selection

This sample was selected as it is a eucrite fall with type 5 pyroxene, allowing for a comparison to be made with samples of differing metamorphic grades. CRE age data for this sample are also available.

2.7.2.4. Stannern

General description

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 (Figure 2.14). Modal mineralogy for major phases in Stannern is as follows: Orthopyroxene (15.6 %), pigeonite (12.1 %), high-Ca pyroxene (19.9 %) and plagioclase (42.8 %) (Delaney et al., 1984a). Pyroxene composition ranges from Wo$_2$En$_{36}$Fs$_{62}$–Wo$_{44}$En$_{29.6}$Fs$_{26.4}$ and average Fe/Mn ratios for high Ca-pyroxene, pigeonite, and orthopyroxene are 31.87, 32.01, and 32.12, respectively (Mittlefehldt, 2015), consistent with typical basaltic eucrites. Minor phases include phosphate (apatite and merrillite; combined total 0.4 %), chromite (0.1 %), ilmenite (1.0 %), troilite (0.4 %), a silica polymorph (7.7 %), and zircon (trace). There have been several age dating studies conducted on Stannern. Birck and Allègre (1978) obtained an $^{87}$Rb-$^{87}$Sr age of $3.1 \pm 0.5$ Ga though they believed the sample had not completely equilibrated but had initially formed at 4.55 Ga and been metamorphosed at 3.1 Ga. Tera et al. (1997) used Pb-Pb mineral isochrons to obtain an age of $4.128 \pm 0.016$ Ga, intermediate between the Sm-Nd age of $4.48 \pm 0.07$ Ga obtained by Lugmair and Scheinin (1975) and the younger Rb-Sr of Birck and Allègre (1978). The authors suggest that Stannern has a complex history of disturbances which did not affect the Sm-Nd age, but reset the other chronometers by varying degrees. An age date of $-124 \pm 13$
Ma relative to ADOR giving an age of 4.434 ± 0.013 Ga which the authors attribute to either Stannern having experienced a separate differentiation process from other basaltic eucrites, or a shock disturbance (Miura et al., 1998). Recently $^{182}\text{Hf} - ^{182}\text{W}$ gave an age date of ~ 4 Ma after CAI formation (Touboul et al., 2015).

**Phosphate details and textural context**

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. In one region of Stannern (discussed later), apatite appears to have co-crystallized with pyroxene, whilst apatite in other areas appears to have crystallized later, along with other late-stage phases such as ilmenite and troilite (Figure 2.10).

**Justification for sample selection**

Stannern was selected as this sample typifies the group of meteorites to which it lends its name. It has also been extremely well characterised, with apatite mineral compositions and hydrogen isotopic composition reported by Sarafian et al. (2013; 2014), which allows for comparisons with data obtained in these studies.
2.7.3. Residual eucrites

Residual eucrites are all basaltic eucrites that have undergone extreme metamorphism to the point that a small amount of partial melt has been extracted from these rocks, hence the name residual eucrite. For more details see Chapter 1 section 1.3.1.1.

Figure 2.14: BSE montage map of Stannern overlain with false colour X-ray map. Red indicates hotspots of P.
2.7.3.1. Agoult

General description

Agoult is a relatively fine-grained granulitic eucrite, when compared to other eucrites with granulitic textures, with granular pyroxene (∼ 100 µm in size) and elongated plagioclase (∼ 50 × 300 µm). Minor phases include apatite, ilmenite, Ti-chromite, a silica phase and rare Fe-FeS (Figure 2.15) (Yamaguchi et al., 2009). Yamaguchi et al. (2009) labelled Agoult a ‘Type B’ granulitic eucrite, based on its texture and mineralogy. ‘Type B’ granulitic eucrites are typically finer-grained with homogenous pyroxene and slightly more calcic plagioclase than ‘Type A’ (An91-88 as opposed to An89-85). The meteorite is a very fresh find and, although no official classification work for weathering has been conducted on Agoult, Barrat et al. (2003) noted no evidence of secondary minerals.

Phosphate details and textural context

Apatite in Agoult are typically small (< 10 µm to 50 µm) subhedral crystals occurring in mesostasis pockets spread evenly throughout the thin-section (Figure 2.10).

Justification for sample selection

This sample was selected once the anomalous Cl isotope signature of residual eucrite DaG 945 was discovered in order to ascertain if this was a unique signature of an individual sample or that of a eucrite type. Agoult is another of the most residual of eucrites studied by Yamaguchi et al. (2009) along with NWA 2362, both of which were available on short notice.
2.7.3.2. Dar al Gani 945

*General description*

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 (Figure 2.16). Pyroxene compositions are between Wo$_{4.1}$En$_{34.3}$ to Wo$_{40.3}$En$_{27.6}$, whilst plagioclase preserves igneous zoning with widely varying compositions from An$_{91.0}$Or$_{0.4}$ to An$_{83.3}$Or$_{0.9}$ (Yamaguchi et al., 2009). The sample shows well-defined 120 $^\circ$ 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.

**Phosphate details and textural context**

Apatite grains in this sample are abundant and subhedral, ranging in size from ~10 to 50 µm in the longest dimension (Figure 2.10). Apatite is commonly found in mesostasis regions, usually in contact with silica or another late-stage phase such as ilmenite.

**Justification for sample selection**

DaG 945 was selected as it is one of the most residual eucrites studied (Yamaguchi et al., 2009) which allows comparisons to be made between the three main geochemical trends observed in basaltic eucrites. It is also a eucrite find with a weathering grade of W1 (Meteoritical Bulletin Database). The sample was readily available at The Open University for analysis.
Figure 2.16: BSE montage map of DaG 945 overlain with false colour X-ray map. Red indicates hotspots of P.
2.7.3.3. North West Africa 2362

General description

North West Africa (NWA) 2362 is a slightly shocked, medium-grained, subophitic to gabbroic eucrite composed of anhedral type 5 pyroxene and elongated plagioclase (~0.3 to 0.6 mm in size Figure 2.17) (Yamaguchi et al., 2009). Pyroxene contains two type of lamellae which are differentiated by thickness, a thin set (< 1 – 2 µm thick) and a thick set (30 – 40 µm thick) and the composition varies from Wo$_{2.7}$En$_{37.3}$Fs$_{59.5}$ to Wo$_{44.3}$En$_{30.2}$Fs$_{25.6}$ (Yamaguchi et al., 2009). Plagioclase in this section preserves its original igneous zoning (An$_{91.8}$Or$_{0.2}$ – An$_{87.4}$Or$_{0.5}$) (Yamaguchi et al., 2009). Minor phases include apatite, chromite, ilmenite, troilite, tridymite and quartz (Yamaguchi et al., 2009). Relict mesostasis (0.1 – 0.4 mm in size) are present in large, irregular shaped areas and typically contain apatite grains.

Phosphate details and textural context

Apatite is sparse in this meteorite, though commonly associated with a silica phase, and can have a large range in size (< 10 to ~ 120 µm, Figure 2.10). Typical crystal shape for apatite in this thin-section are subhedral to anhedral.

Justification for sample selection

This sample was selected once the anomalous Cl isotope signature of residual eucrite DaG 945 was discovered in order to ascertain if this was a unique signature of an individual sample or that of a eucrite type. NWA 2362 is another of the most residual of eucrites studied by Yamaguchi et al. (2009) along with Agoult, both of which were available on short notice.
2.7.4. Cumulate eucrites

Cumulate eucrites are rocks that have typically formed at deeper levels on the eucrite parent body and have experienced slower cooling compared to basaltic eucrites. As such they have distinct features such as higher Mg-numbers and lower abundances of incompatible trace elements (Hsu and Crozaz, 1997). For more details see Chapter 1 section 1.3.1.2.
2.7.4.1. Moore County

*General description*

Moore County is a coarse grained, unbrecciated cumulate eucrite (Figure 2.18). The meteorite consists of large, mm-sized euhedral to subhedral pyroxene grains (Wo$_{5.64}$En$_{45.88}$Fs$_{48.49}$ – Wo$_{41.94}$En$_{35.42}$Fs$_{22.64}$; Pun and Papike, 1995; Mayne et al., 2009) with coarse augite exsolution features (~15 - 100 µm) and granular plagioclase (An$_{91.35}$Or$_{0.35}$; Mayne et al., 2009; Mittlefehldt, 2015). The modal mineralogy for Moore County is as follows: orthopyroxene (21.8 %) pigeonite (9.2 %) high-Ca pyroxene (5.7 %) and plagioclase (61.1 %). Minor phases include tridymite (1 %), ilmenite (0.2 %), chromite (0.4 %), troilite (0.6 %), Fe-Ni metal (trace), and apatite (trace) (Hess and Henderson, 1949; Mayne et al., 2009). Tera et al. (1997) reported a Pb-Pb age of 4.484 ± 0.019 Ga but believed that the sample may have suffered some terrestrial contamination as their leachates were contaminated so could not rule out the residues also being contaminated. Their Pb-Pb results are within error of their $^{147}$Sm-$^{144}$Nd age for Moore County which yielded a value of 4.456 ± 0.025 Ga. More recent $^{147}$Sm-$^{143}$Nd work by Boyet et al. (2010) yielded a slightly older age of 4542 ± 85 Ma but similar to the $^{244}$Pu-Xe age of ~ 4584 Ma of Shukolyukov and Begemann (1996).

*Phosphate details and textural context*

Apatite primarily occurs as subhedral or acicular grains typically enclosed in pyroxene grains (Sarafian et al., 2013) near other inclusions of late-stage phases such as chromite. Apatite grain sizes range from 10 – 50 µm in longest dimension (Figure 2.10). Hess and Henderson (1949) noted that acicular apatite (up to 100 µm long) can be in interstitial tridymite grains, however these were not observed in this thin section.
Chapter Two: Methods and Samples

Figure 2.18: BSE montage map of Moore County overlain with false colour X-ray map. Red indicates hotspots of P.

*Justification for sample selection*

The Moore County eucrite was selected for study as it is a cumulate eucrite and thus can be compared to basaltic eucrites. It is also an unbrecciated sample with the youngest CRE age of all the samples selected.
2.7.5. Anomalous eucrites

Anomalous eucrites are samples that display certain characteristics which set them apart from other known eucrite types. This includes anomalous bulk, mineral, and/or isotopic compositions. For more details regarding anomalous eucrites see Chapter 1 section 1.3.1.3.

2.7.5.1. Emmaville

*General description*

Emmaville is an anomalous eucrite with an unusually fine-grained, hornfelsic-textured metabasalt, pervasive impact melt veins and mineral compositions similar to those of typical basaltic eucrites. Three subsections of Emmaville were separated for O isotopic analysis; a dark grey fraction (E1), a shocked lithology (E2) and a lighter grey portion likely containing more feldspar (E3). The characterisation of this anomalous eucrite forms the basis for Chapter three of this thesis; the description is, therefore, given in more detail in that chapter.

*Justification for sample selection*

Despite there being several anomalous eucrites, Emmaville was selected for the following reasons. Firstly, it is an observed fall and therefore likely to have experienced minimal terrestrial alteration. Another reason for its selection was its limited characterisation in existing literature, which provided a unique opportunity to undertake a full characterisation study of this sample.
Chapter Three: The Mineralogy, Petrology, and Composition of the Isotopically Anomalous Eucrite Emmaville

3.1. Introduction

A small sub-group of basaltic achondrites has been identified that have anomalous oxygen isotope compositions, distinct from those of the well-populated HED group. Two of these, Ibitira and Northwest Africa 011 (NWA 011) are distinct both in terms of their isotopic compositions and petrologic characteristics, consistent with being derived from separate parent bodies to that of the HED group of meteorites (Yamaguchi et al., 2002; Wiechert et al., 2004; Floss et al., 2005; Greenwood et al., 2005; Mittlefehldt, 2005). In the case of other anomalous basaltic achondrites, differences with the HED group are less clear-cut. Some have oxygen isotopic compositions that are resolvable from the HEDs at the ± 3σ level ($\Delta^{17}$O), but are mineralogically and compositionally similar to ‘normal’ eucrites e.g. A-8811394, Bunburra Rockhole and Elephant Moraine (EET) 92023 (Bland et al., 2009; Scott et al., 2009; Greenwood et al., 2017). Yet another group is only marginally different isotopically from the HEDs at the ± 3σ level and indistinguishable from them in terms of their mineralogy and geochemistry. This group comprises Pasamonte, NWA 1240 and PCA 91007 (Wiechert et al., 2004; Greenwood et al., 2005; 2017; Scott et al., 2009).

Studying anomalous basaltic achondrites is important because it allows us to understand more completely the number of parent asteroids represented by eucrite-like basalts, as well as to constrain better the chemical and isotopic diversity present in the HED suite. Emmaville
is a eucrite that has a $\Delta^{17}$O value of $-0.137 \pm 0.024 \permil$ (1σ) (Greenwood et al., 2013) and so is significantly different from the eucrite mean of $-0.246 \pm 0.014 \permil$ (2σ) (Greenwood et al., 2014)(See section 1.3.1.3, Figure 1.11), but similar to that of A-881394 (Scott et al., 2009), Bunburra Rockhole (Bland et al., 2009) and EET 92023 (Greenwood et al., 2017). As one of only three currently identified anomalous eucrite falls, the other two being Ibitira and Bunburra Rockhole, Emmaville is clearly a critical sample in terms of constraining the origin of non-HED basaltic achondrites. As very little data existed for Emmaville in terms of petrology or geochemistry (Morgan and Lovering, 1973; Mason, 1974; Stolper, 1977; Yamaguchi et al., 1996), a detailed study of this important meteorite was warranted. It was also hoped that a sufficient number of large apatite grains could be located in Emmaville in order to be able to compare their volatile inventory to those located in main-group HED samples. Unfortunately, detailed petrographic investigation on two sections revealed only a single apatite grain which was too small for NanoSIMS analysis.

In this chapter the results of a comprehensive examination of the petrology, mineral chemistry, major and trace element geochemistry and O isotopic composition of Emmaville are presented. These results are then discussed in the light of three distinct possibilities: 1) the HED parent body is not as well homogenized as was previously considered, 2) Emmaville is from a separate parent body to the HEDs, that was also capable of generating eucrite-like basalts, and 3) that mixing of impactor material with a contrasting O isotopic composition to that of Emmaville disturbed the latter’s primary isotopic composition.

The results presented in this chapter have been published as an article in Meteoritics and Planetary Science (Barrett et al., 2017). My contribution to this work is outlined in detail in Chapter 1, section 1.5.1.
Chapter Three: The Mineralogy, Petrology, and Composition of Anomalous Eucrite

Emmaville

3.2. Results

3.2.1. Mineralogy

Emmaville is an unusually fine-grained, (typically < 60 μm compared to the 50 -100 μm grain size of other fine-grained basaltic eucrites; e.g. Mayne et al., 2009) hornfelsic-textured metabasalt (Figure 3.1). The mineralogy mainly comprises low-Ca pyroxene (23.3 % modal abundance), high-Ca pyroxene (21.1 %), plagioclase (38.1 %) and a silica phase (8.9 %), identified here as quartz by Raman spectroscopy (see Appendix b). Minor phases include ilmenite, chromite (combined oxide modal abundance 1.3 %), troilite (trace), and melt veins (7.3 %). During detailed petrographic analysis, two <10 μm zircon grains and two Ni-poor metal grains were also observed. Average mineral compositions are given in Table 3.1.

Pyroxene and plagioclase grains are typically 10 – 30 μm across, but some regions have noticeably coarser grain size of ~ 100 μm in the longest dimension. Emmaville also contains ~ 100 μm wide melt veins running through the length of both analysed sections. Despite the very fine-grained texture of Emmaville, suggestive of rapid cooling, the sample has undergone extensive thermal equilibration, with larger low-Ca pyroxene grains displaying coarse exsolution of augite and smaller grains completely re-crystallized to low-Ca pyroxene and augite grains (En_{35}Fs_{61}Wo_{4}; En_{30}Fs_{28}Wo_{42}) (Figure 3.2).
Chapter Three: The Mineralogy, Petrology, and Composition of Anomalous Eucrite

Emmaville

Figure 3.1: BSE image of Emmaville showing melt veins and fusion crust. Px = pyroxene, Aug = augite, Pl = plagioclase, Cr = chromite.

Inversion of pigeonite to orthopyroxene typifies type 6 eucrites rather than type 5 - the designation of Emmaville given by Takeda and Graham (1991). On the basis of pyroxene compositional data, it is possible that some of the low-Ca pyroxene has inverted to orthopyroxene (Table 3.1). It has, however, been shown that low-Ca pyroxene in some basaltic eucrites failed to invert to orthopyroxene and a low Ca abundance does not necessarily indicate an orthopyroxene crystal structure (see for example, Takeda, 1979). Thus, Emmaville may be either a type 5 or type 6 eucrite-like basalt.
## Chapter Three: The Mineralogy, Petrology, and Composition of Anomalous Eucrite

### Emmaville

Table 3.1: Average mineral compositions for Emmaville.

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* Notes: Wt. % = Weight %, SiO₂ = Silicon Dioxide, TiO₂ = Titanium Dioxide, Al₂O₃ = Aluminum Trioxide, Cr₂O₃ = Chromium Trioxide, FeO = Iron Oxide, MnO = Manganese Oxide, MgO = Magnesium Oxide, CaO = Calcium Oxide.

**Fe/Mn** = 31.7 31.5, **An %** = 88.5 49.1, **Fe/Mn** = 50.5 56.0

**Fe/Mg** = 1.75 0.94, **Ab %** = 11.1 47.5, **Fe/Mg** = 47.9 52.9

**Mg#** = 36.43 51.58, **Or %** = 0.4 2.1, **Mg#** = 81.1 84.1

**Wo %** = 3.99 41.92, **Cr#** = 31.1 31.5, **Si** = 2.095 0.983, **Cm %** = 71.9 58.77

**Fs %** = 61.04 28.1, **Al** = 1.915 0.001, **Mc %** = 1.8 1.97

**Si** = 1.968 1.968, **Mg** = 0.000 0.000, **Sp %** = 0.4 0.37

**Ti** = 0.003 0.005, **Ca** = 0.866 0.002, **Uv %** = 9.1 27.81

**Al** = 0.036 0.052, **Na** = 0.109 0.974, **Fe** = 0.014 0.004

**Cr** = 0.002 0.006, **K** = 0.004 0.000, **Mn** = 0.020 0.000, **Ti** = 0.088 0.272

**Fe** = 1.198 0.549, **Total** = 5.00, **Mg** = 0.021, **Si** = 0.002 0.003

**Mn** = 0.038 0.017, **Ca** = 0.006 0.006, **Cr** = 1.440 1.187

**Mg** = 0.687 0.584, **Total** = 2.01, **Al** = 0.337 0.224

**Ca** = 0.078 0.818, **Total** = 0.023 0.021

**Total** = 4.01 4.00, **Fe** = 1.069 1.251

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Emmaville

Figure 3.2: Truncated pyroxene ternary for Emmaville. Composition data for EET 87520, Sioux County and Stannern are from Mittlefehldt (2015).

The plagioclase composition in Emmaville (An$_{83-93}$) is also similar to that of typical basaltic eucrites (An$_{75-94}$, Mittlefehldt, 2015). The average ilmenite composition of Emmaville (Table 3.1), is consistent with basaltic eucrite values ($\text{TiO}_2 = \sim 52 \text{ wt.\% FeO} = \sim 44 \text{ wt. \%}$, Mayne et al., 2009; Mittlefehldt, 2015); although it can be noted that it is slightly enriched compared with other eucrites in FeO by $\sim 2$ wt. %.

3.2.2. Major, minor and trace elements

Major element compositions are given in Table 3.2. For all major elements analysed here, Emmaville plots within a similar range to most basaltic eucrites (Appendix b, SM2). Minor and trace element compositions are given in Table 3.3. The data presented here are broadly consistent with literature values for these meteorites (c.f. Table S7 of Mittlefehldt, 2015). Cobalt is slightly enriched and bears some similarities to values obtained for diogenites, polymict eucrites and howardites. In contrast, nickel is an order of magnitude higher than the other basaltic eucrites in this dataset (149 ppm as opposed to between 1.46
Chapter Three: The Mineralogy, Petrology, and Composition of Anomalous Eucrite

Emmaville

...ppm and 16.3 ppm). The overall REE element pattern for Emmaville is similar to other basaltic eucrites and clearly resolvable from the Stannern trend (Figure 3.3). Compared to the other eucrites studied here, Emmaville has high levels of enrichment of Pb (1041 ppb), slightly elevated abundances of U, Th and Rb, but with slight depletions in Zr and Hf.

Table 3.2: Bulk major element abundances as measured by ICP-OES. All measurements are in mg/g unless otherwise specified.

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<th>Ibitira</th>
<th>Juvinas</th>
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<th>Roda</th>
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<th>Tirhert</th>
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### Table 3.3: Bulk minor and trace element abundances. All measurements are in µg/g unless otherwise specified.

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<td>0.05847</td>
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### Chapter Three: The Mineralogy, Petrology, and Composition of Anomalous Eucrite Emmaville

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<td>0.190</td>
<td>0.134</td>
<td>-0.149</td>
<td>0.012</td>
<td>0.009</td>
</tr>
<tr>
<td>Emmaville E2</td>
<td>Shock vein-rich fraction</td>
<td>5</td>
<td>1.954</td>
<td>0.076</td>
<td>0.034</td>
<td>4.033</td>
<td>0.159</td>
<td>0.071</td>
<td>-0.160</td>
<td>0.020</td>
<td>0.009</td>
</tr>
<tr>
<td>Emmaville E3</td>
<td>&quot;light coloured&quot; lithology</td>
<td>1</td>
<td>2.430</td>
<td></td>
<td></td>
<td>4.873</td>
<td></td>
<td></td>
<td>-0.124</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emmaville E1+E2+E3</td>
<td>Overall average of 8 replicates</td>
<td>8</td>
<td>2.032</td>
<td>0.336</td>
<td>0.119</td>
<td>4.168</td>
<td>0.597</td>
<td>0.211</td>
<td>-0.153</td>
<td>0.030</td>
<td>0.011</td>
</tr>
<tr>
<td>Obsidian Standard*</td>
<td></td>
<td>39</td>
<td>3.808</td>
<td>0.052</td>
<td>0.008</td>
<td>7.267</td>
<td>0.093</td>
<td>0.015</td>
<td>0.001</td>
<td>0.017</td>
<td>0.003</td>
</tr>
</tbody>
</table>

* Obsidian standard values taken from Starkey et al. (2016).
Figure 3.3: REE pattern of Emmaville, anomalous eucrites Bunburra Rockhole and Ibitira along with representative eucrites. Published values for Bouvante and Stannern are from Barrat et al. (2007). Data for Bunburra Rockhole are taken from Spivak-Birndorf et al. (2015); FG, MG and CG correspond to the fine, medium and coarse grained domains within the meteorite (Spivak-Birndorf et al., 2015). The reference chondrite is from Lodders (2003).

3.2.3. Oxygen isotopic composition

Oxygen isotope results are given in Table 3.4 and plotted in Figure 3.4. Also shown in Figure 3.4 are the oxygen isotopic analyses for angrites (Greenwood et al., 2005), HEDs (2σ and 3σ from Greenwood et al., 2005; 2014; 2015), the anomalous howardite Jiddat al Harasis (JaH) 556 (Janots et al., 2012) and various anomalous basaltic achondrites (Greenwood et al., 2005; 2013; 2015; Bland et al., 2009; Scott et al., 2009). It is clear from Figure 3.4 that
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Emmaville is an isotopically anomalous eucrite on the basis that its $\Delta^{17}O$ composition lies at least 3σ outside the mean HED value for fall samples ($n = 26$) $\Delta^{17}O = -0.240 \pm 0.021$‰ (3σ) (Greenwood et al., 2017). This is in agreement with the definition for anomalous eucrites of Scott et al. (2009).

Figure 3.4: Oxygen isotopic composition of Emmaville compared to HEDs, angrites and anomalous basaltic achondrites. Light grey shading = ± 2σ variation of mean HED $\Delta^{17}O$ value, dark grey shading = ± 3σ variation of mean HED $\Delta^{17}O$ value (see text for further discussion. Abbreviations: TFL: Terrestrial Fractionation Line, AFL: Angrite Fractionation Line (Greenwood et al., 2005), BR-F, BR-M, BR-C: Fine, medium and coarse fractions from Bunburra Rockhole (Bland et al., 2009); E-B: Emmaville bulk (Greenwood et al., 2013; 2017); E-1, E-2, E-3: Emmaville fractions analysed in this study (see text for further details). Analyses of PCA 91007, Pasamonte and A-881394, NWA 1240 from Scott et al. (2009); Ibitira from Greenwood et al. (2017) and JaH 556 from Janots et al. (2012).
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The mean values of the grey (E1) and shock vein-rich (E2) lithologies plot close to the bulk sample (E-B) of Greenwood et al. (2013; 2015; 2016) and have $\Delta^{17}$O values of $-0.149 \pm 0.012 \%$ (2σ) and $-0.160 \pm 0.020 \%$ (2σ), respectively (Table 3.4). In contrast, the light-coloured lithology E3 has a somewhat heavier $\Delta^{17}$O value of $-0.124 \%$ and is also significantly heavier with respect to $\delta^{18}$O i.e. 4.873 \% compared to 4.151 \% for E1 and 4.033 \% for E2. The high $\delta^{18}$O value of E3 together with its light colour is consistent with a higher feldspar content compared to either E1 or E2 (Table 3.4).

The combined data for the three Emmaville fractions (E1+E2+E3) (n = 8) yields an average $\Delta^{17}$O value of $-0.153 \pm 0.030 \%$ (± 2σ). In comparison, data for 22 diogenites from Greenwood et al. (2014) gave a mean $\Delta^{17}$O value of $-0.246 \pm 0.014 \%$ (± 2σ). Oxygen isotopic composition of Emmaville is clearly more variable than the HED suite. Possible reasons for this higher level of heterogeneity are discussed in further detail below.

3.3. Discussion

3.3.1. Mineralogy and petrology

Primitive bodies in the solar system can have different Fe/Mn ratios in their silicate minerals as a consequence of volatility and oxidation state controls (Papike, 1998), and as such this ratio can be used to discriminate between different parent bodies. Figure 3.5 shows that the Fe/Mn ratio of Emmaville falls within the normal range of basaltic eucrites and also suggests a common oxidation state for its parental magma.
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Chromite grains plot in two discrete groupings within the basaltic eucrite trend (Figure 3.6), which represent chromite and a more titanian chromite. To achieve such distinct populations of chromite grains requires different early and late phases of crystallization. Elemental abundances of Cr and Ti in chromite have been linked to different degrees of oxidation, with Cr more abundant under reducing conditions and greater abundances of Ti under more oxidizing conditions (Bunch and Keil, 1971). It is therefore possible that the two populations of chromite grains are linked to a change in the oxidation state of the parental melt. High Ti chromite grains are also a typical feature of highly metamorphosed eucrites due to the decomposition of ulvöspinel (Yamaguchi et al., 2001; 2002; 2009). These Ti-rich chromite grains are typically found in close association with ilmenite, something not commonly observed in Emmaville.

Figure 3.5: Pyroxene Fe/Mn vs. Fe/Mg diagram. Basaltic eucrite, Cumulate eucrite, Diogenite and Ibitira data taken from Mittlefehldt (2015).
3.3.2. Major and trace elements

The major-element abundances for Emmaville are similar to those published in the literature for the sample (Mason, 1974; Stolper, 1977). The depletion of Hf and Zr could in principle be caused by an incomplete dissolution of zircons. As all of the samples presented here underwent the same acid digestion protocol, if partial digestion of zircon occurred, it is likely other samples would be similarly affected. Given the lack of evidence for partial zircon dissolution in the basaltic eucrite Camel Donga, which yields Zr and Hf abundances consistent with literature values (Cleverly et al., 1986; Palme et al., 1988; Barrat et al., 2000), it is unlikely that Emmaville would have been affected. Another possibility which fits with

Figure 3.6: Chromite ternary diagram. The light grey ellipse represents variations in basaltic eucrites, the darker grey box represents variations the diogenites. Data for ellipses are from Bunch and Keil (1971); Mittlefehldt (1994) and Mittlefehldt (2015).
the mineralogical data is that zircon grains are rare within the Emmaville eucrite and could potentially be under-represented within the powdered sample. If we assume that we analysed a representative bulk-rock for Emmaville then it is interesting to note that when compared to the Zr and Hf abundances of the anomalous achondrite Bunburra Rockhole (Spivak-Birndorf et al., 2015), Emmaville displays similar abundances for both elements, albeit at slightly lower concentrations (Zr = 41.1 ppm compared to Bunburra Rockhole’s ~ 45 ppm).

The eucrite Sioux County in Figure 3.3 is depleted in LREEs with an increase in abundance towards the heavier REEs. This could be due to the coarse-grained nature of the eucrite and reflect heterogeneity in the powdered sample used in this study with respect to REE-rich phases such as apatite. Tirhert is also a very coarse-grained eucrite, however in the case of this meteorite the REE pattern is flatter, with a small depletion towards the HREEs. While no preferential depletion of LREEs is observed, it may still be possible that the low abundances of REEs reflects a heterogeneous powder, which was under-represented in REE carrying phases, such as Ca-phosphate.

The achondrite Bunburra Rockhole shares several similarities with Emmaville in terms of its major element, REEs and oxygen isotope signature (Spivak-Birndorf et al., 2015). As a result of these similarities, in particular the similar oxygen isotope signature, it is possible that both of these two meteorites may be derived from the same parent body. The modal mineralogy of Bunburra Rockhole falls on the trend line defined by pyroxene versus plagioclase modal abundance for eucrites (Figure 3.7). In contrast, Emmaville lies off this trend, plotting below the pyroxene-plagioclase trend of basaltic eucrites on account of the large amount of quartz observed in the sample (8.9 % compared to ~ 3.9 % average for basaltic eucrites; Delaney et al., 1984a; Yamaguchi et al., 2001; Gardner-Vandy et al., 2011).
Despite this, both Emmaville and Bunburra Rockhole share similar mineralogies and Fe/Mn ratios of pyroxene with noncumulate eucrites. Trace-element data for these two meteorites are also comparable to typical eucrites. However, as noted before, the elevated Ni abundance of Emmaville (Table 3.3) is in stark contrast to Bunburra Rockhole, which is depleted in Ni relative to most eucrites (Spivak-Birndorf et al., 2015). This is particularly surprising as the most likely mineral to host Ni in Emmaville is pyroxene which has a lower modal abundance compared to typical basaltic eucrites and Bunburra rockhole, although Ni content has not been specifically analysed in pyroxene for either sample. It is also, however, possible that the main phase for Ni and Co are disseminated metal grains, too small to appear during modal abundance analyses. As mentioned in section 3.2.1, only two metal grains are observed and found to be Ni poor along with trace amounts of troilite. Taken at face value, this discrepancy could be attributed to a greater amount of Ni partitioning into the core of the anomalous eucrite parent body, or different initial abundances between eucrites and Bunburra Rockhole (Spivak-Birndorf et al., 2015). Cobalt in Emmaville is also enriched compared to basaltic eucrites and Bunburra Rockhole. The enrichment in Co and Ni abundance in Emmaville is difficult to reconcile with a similar Co abundance and depletion of Ni observed in Bunburra Rockhole if they are thought to originate from the same parent body. Recent work by Benedix et al. (2017) provides new major, minor, and trace element data for Bunburra Rockhole. Their work shows that the bulk major element composition of Bunburra Rockhole are slightly different to typical eucrites with Mg and Ca content lower than main-group basaltic eucrites and Ti slightly elevated. The trace elements, however, are indistinguishable from basaltic eucrites (Benedix et al., 2017). The fact that Bunburra Rockhole is anomalous with respect to its major elements, something not observed in
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Emmaville, combined with the Co and Ni discrepancies would suggest that it is unlikely these meteorites are from the same parent body.

Figure 3.7: A comparison of the relative modal abundances of plagioclase and pyroxene in eucrites after Mayne et al. (2009). Bunburra Rockhole data are taken from Spivak-Birndorf et al. (2015).

The Co abundance of Emmaville is similar to diogenites, polymict eucrites and howardites. This could imply that Emmaville has undergone some impact-mixing, however, based on the petrography and X-ray element maps of the sections and melt veins studied here no evidence for mixing with diogenitic or chondritic material is apparent. Another possible signature of impact-mixing is elevated siderophile elements such as Ni. To eliminate the possibility of an ordinary chondrite impactor, the percentage of impactor material needed to elevate a typical eucrite to the Ni abundance and O isotope values observed in this study can be calculated for H and L chondrites. These calculations are based on Ni contents of 16000
ppm and 12000 ppm for H and L chondrites respectively (Wasson and Kallemeyn, 1988), a Ni content of 2.3 ppm for pristine non-cumulate eucrites (Warren et al., 2009) and $\Delta^{17}$O values from Clayton et al. (1991) and Greenwood et al. (2017). An amount of ~ 1 % H or L chondrite material is required to elevate Ni to comparable levels, but such low values would significantly elevate the $\Delta^{17}$O of the target. To reconcile the O isotopes with impactor material ~ 10 % mixing is required, however, this results in approximately an order of magnitude more Ni than observed. This calculation serves to illustrate the fact that the oxygen isotope composition of Emmaville cannot be explained in terms of impact mixing between an HED target and ordinary chondrite impactor as seems to be the case for the anomalous howardite JaH 556 (Janots et al., 2012). Benedix et al. (2017) note the mixing lines established in Sanborn et al. (2016) demonstrate that mixing of ordinary chondrites and normal eucrites would not pass through Bunburra Rockhole in $\Delta^{17}$O-$\varepsilon^{54}$Cr space, effectively ruling out this scenario for this sample too.

An impact origin for an anomalous HED might be discounted if only a low percentage of impactor material was present, or the impactor was non-chondritic (i.e. had a low siderophile element content). In the case of Bunburra Rockhole, Benedix et al. (2017) observed that a Bunburra Rockhole-like oxygen isotope composition could be modelled by a 70:30 angrite:eucrite mix, however, this would produce a bulk chemistry closer to angrites than eucrites and so was ruled out. As Emmaville has bulk major- and trace-element abundances identical to typical basaltic eucrites, this type of mixing can also be ruled out for Emmaville. The possible role of impact mixing in the genesis of isotopically anomalous eucrites is discussed in further detail in Chapter 6.
3.3.3. Oxygen isotopes

The majority of diogenite, eucrite and cumulate eucrites samples have virtually identical $\Delta^{17}$O values (Figure 3.4) (Scott et al., 2009; Greenwood et al., 2014). This has been cited as evidence that all of the major HED lithologies are derived from a single, isotopically homogeneous, parent asteroid, widely believed to be Vesta (Greenwood et al., 2005; McSween et al., 2013). However, as pointed out by Scott et al. (2009), a relatively small group of basaltic achondrites (Figure 3.4) have $\Delta^{17}$O values that lie at least $3\sigma$ outside the mean value defined by the HED falls i.e. $-0.240\pm0.021\%$ ($3\sigma$) ($n = 26$) (Greenwood et al., 2017). With the exception of NWA 1240 (Scott et al., 2009) and NWA 011 (Yamaguchi et al., 2002) (not shown in Figure 3.4) all of the presently identified anomalous basaltic achondrites plot between the eucrite fractionation line (EFL) and the angrite fractionation line (AFL) as seen on Figure 3.4.

As pointed out by McSween et al. (2013), various scenarios have been envisaged to explain the origin of these isotopically anomalous basaltic achondrites. One such scenario proposed by Wiechert et al. (2004) is that both normal and anomalous samples come from a single heterogeneous HED parent body based on the variation of $^{16}$O observed in certain HEDs. In contrast, Scott et al. (2009) suggested that the isotopically anomalous samples may have come from distinct asteroidal sources. This latter explanation implies that the HED parent body itself had a very homogeneous $\Delta^{17}$O composition, consistent with magma ocean models for Vesta (Righter and Drake, 1997; Greenwood et al., 2005). As an explanation for the origin of at least some anomalous basaltic achondrites, Greenwood et al. (2005) and Janots et al. (2012) highlighted the possible role of impact processes as a mechanism for producing isotopic heterogeneity.
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For a few anomalous eucrites such as Ibitira (Wiechert et al., 2004; Mittlefehldt, 2005), A-881394 (Nyquist et al., 2003) and the anomalous achondrite NWA 011 (Yamaguchi et al., 2002) a range of evidence would suggest that they are not from the same parent body as most of HED samples (Scott et al., 2009). However, the situation is less clear cut for the other anomalous eucrites, with at least some showing significant degrees of brecciation (e.g. Pasamonte; Metzler et al., 1995). The tightly constrained O-isotope distribution of anomalous basaltic meteorites (with the notable exception of NWA 011), lying between the EFL and AFL (Figure 3.4) could be interpreted as supporting an origin by impact mixing between HED lithologies and material that lies above the AFL (i.e. with an isotopic composition that may be similar to that of the ordinary chondrites). A clear example of where this has actually taken place is provided by the anomalous howardite JaH 556 (Janots et al., 2012).

JaH 556 is an impact melt breccia, comprising highly-shocked clasts set in a finely recrystallized vesicular matrix containing abundant Fe-oxyhydroxides and near-complete lack of Fe metal (Janots et al., 2012). Unlike Emmaville, JaH 556 was a find and had experienced a high degree of terrestrial alteration. The bulk oxygen isotope composition of JaH 556 is anomalous, with a $\Delta^{17}$O value of -0.11‰ (Figure 3.4). One approach to removing weathering products, in particular Fe-bearing phases such as Fe-hydroxides and oxyhydroxides, is to leach the sample in EATG (ethanolamine thioglycolate; Martins et al., 2007; Greenwood et al., 2012; 2015; Janots et al., 2012; Alexander et al., 2018). EATG is preferred over conventional dilute HCl leaching as HCl can partially remove indigenous glass and feldspathic material (Greenwood et al., 2012), however, a recent study by Alexander et al. (2018) noted that EATG treatment can remove primary components in the
case of CO chondrite falls, probably Fe-rich phases in the matrix. In contrast to the anomalous results of the bulk, EATG-washed clasts in JaH 556 have normal HED $\Delta^{17}$O values (clasts 1-3, Figure 3.4). JaH 556 has a highly enriched siderophile element content and contains clasts that appear to be relict chondrules, with olivine compositions consistent with an H chondrite precursor. Both the siderophile element content and bulk oxygen isotope composition of JaH 556 point to admixing of a 10-15 % H chondrite component in this meteorite.

Unlike JaH 556, none of the various fractions separated from Emmaville (E1, E2, E3) plot close to the EFL (Figure 3.4). As Emmaville is a fall, it is unlikely to have undergone significant terrestrial alteration. As a differentiated achondrite with low metal content, it is also less prone to oxidation in the terrestrial environment than more Fe-rich meteorites. In the absence of metal it has been demonstrated that terrestrial weathering does not have a significant effect on O isotopes compared to noble gases (Schwenzer et al., 2013) and as EATG leaching on an Fe-poor fall is likely to remove primary phases (Alexander et al., 2018), Emmaville was not leached with EATG. Element maps for Emmaville showed no obvious evidence of exogenous material. Any incorporated material would also probably have affected the bulk major and trace element abundances, a feature not reflected in most of the data as discussed above (with the notable exception of Ni and Co). Another possibility is that the impact of an isotopically distinct body onto Vesta during the late stages of magma ocean crystallization could have resulted in isotopically distinct basalts. The petrologic model of Mandler and Elkins-Tanton (2013) invokes continuous or periodic recharge of shallow magma chambers by residual melts derived from deeper levels in the solidifying mantle as a means to produce the observed suite of HED lithologies. An impact at this stage
could produce a regional difference in O isotopic signature in the magma that was not homogenized throughout the body. Impact contaminated basalts, however, would be likely to have differing compositions from normal basaltic eucrites depending on the amount of exogenous material incorporated into their parental melt. For anomalous eucrites such as Ibitira or Pasamonte to be from Vesta, they would both require different, as yet unknown, types of impactor contamination (Wiechert et al., 2004; Scott et al., 2009). This evidence argues against the possibility that Emmaville represents a howardite-like impact breccia composed of projectile material with a Δ¹⁷O composition lying above the AFL that was mixed with isotopically normal HED material. Instead, Emmaville more closely resembles the case of Bunburra Rockhole (Bland et al., 2009; Benedix et al., 2014) in which there is evidence of some isotopic heterogeneity, but none of the various fractions have a HED Δ¹⁷O composition. Although the various fractions of Emmaville are slightly displaced to lighter Δ¹⁷O values than Bunburra Rockhole there would appear to be considerable overlap between the two meteorites, based on a comparison of O isotopes between Figure 3.4 of this study and Figure 2 of Benedix et al. (2017). Benedix et al. (2014) suggested that Bunburra Rockhole may be derived from the same parent body as A-881394. The more recent work of Benedix et al. (2017) discuss that whilst both samples are similar with regards to oxygen and chromium isotopes they are texturally quite distinct, with A-881394 being more akin to a cumulate eucrite, and the mineral chemistry, particularly plagioclase, is difficult to reconcile if the two samples are from the same asteroid. Given the differences between Bunburra Rockhole and Emmaville, where Emmaville more closely fits with basaltic eucrites in terms of major element composition and the anomalous Ni and Co content of the sample, it is possible each of these samples originated from a different parent body.
3.3.4. Possible parent bodies for the Emmaville eucrite

With mineral compositions and bulk-rock REEs indistinguishable from ordinary basaltic eucrites and an impactor component unlikely, there are two explanations to reconcile the difference in O isotopes with that of normal HEDs:

1) The HED parent body is not as well homogenized as was previously considered
   (Wiechert et al., 2004; Greenwood et al., 2005; Scott et al., 2009; Greenwood et al., 2014)

2) Emmaville is from a separate parent body which produced basalts of similar composition to the eucrites of the HED group (Scott et al., 2009).

The HED parent body, Vesta, is believed to have differentiated with a well-mixed magma ocean which should have homogenized the various isotopic systems (Righter and Drake, 1997; Greenwood et al., 2005; Mandler and Elkins-Tanton, 2013). If this magma ocean was not as well mixed as has been proposed, it is possible the isotopic composition may not have fully equilibrated. In this scenario basalts derived from different regions would still be similar in chemical composition, as they were derived from the same starting material, but their isotopic systematics would reflect the degree of local equilibration (Wiechert et al., 2004). Ghosh and McSween (1998) suggested that the outer layers of Vesta could have retained some isotopic heterogeneity and never reached the melting temperature to become equilibrated. Their model still predicts the perfect homogenization of the interior of Vesta but also allows some oxygen isotope heterogeneity. One problem with this idea, however, is
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that the outer layers are likely to have and been assimilated into the vestan mantle owing to differences in density (Mandler and Elkins-Tanton, 2013).

The argument for a heterogeneous Vesta encounters several problems, predominant amongst which is the striking homogeneity of the majority of HED meteorites. Impacts have excavated the HED parent body to significant depths and to date, only the highly-shocked diogenite Dhofar 778 (shock stage S4) has an anomalous oxygen isotope composition (Greenwood et al., 2017). It is possible, however, that most of the HEDs currently available could have been excavated from a single impact event (Bogard and Garrison, 2003), whereas the smaller group of eucrites with differing O isotopes might represent material excavated from a different area(s) of Vesta’s surface.

Bunburra Rockhole, A-881394, EET 92023 and Emmaville are all distinct in oxygen isotope composition despite being similar in petrology and mineral compositions to that of the HED parent body. Variations in $\varepsilon^{54}$Cr have also previously been used to identify meteorite groups or parent bodies (e.g. Trinquier et al., 2007; Qin et al., 2010). On a plot of $\Delta^{17}$O vs. $\varepsilon^{54}$Cr both A-881394 and Bunburra Rockhole form a distinct cluster that is fully resolvable from normal eucrites (Benedix et al., 2014). Acquiring the $\varepsilon^{54}$Cr composition of Emmaville and EET 92023 would help to test further impact mixing hypotheses (see section 3.3.2) as well as constrain their potential genetic relationship to other anomalous achondrites.

On the basis of their similar oxygen isotope compositions alone, it seems possible that all four samples (Bunburra Rockhole, A-881394, Emmaville and EET 92023) are derived from an isotopically distinct HED-like parent. As similarities in O isotopic composition do not necessarily imply a genetic relationship, however, it is possible for these meteorites not to
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be derived from a single parent body. Recent preliminary petrologic data by Mittlefehldt et al. (2016) suggests that A-881394 and EET 92023 may well be from separate asteroids in spite of their similar O isotopic composition. Based on subtle differences in bulk and mineral chemistry between Bunburra Rockhole, Emmaville, and A-881394 it would appear unlikely that these samples all originated from the same parent body. These petrological differences preclude these four meteorites forming a grouplet as defined by Weisberg et al. (2006).

3.4. Conclusions

Based on the results and discussion presented in this chapter, the following conclusions can be made:

- Mineral compositions of Emmaville are consistent with basaltic eucrites.

- Bulk major, minor and trace element abundances are also consistent with basaltic eucrites.

- The oxygen isotopic composition of bulk Emmaville plots in a similar region to Bunburra Rockhole, A-881394 and EET 92023.

- The oxygen isotopic compositions of separated lithologies of Emmaville are distinct: the dark grey and shocked lithologies plot near the bulk composition, whereas the light grey lithology is slightly enriched in $\delta^{17}$O and significantly enriched in $\delta^{18}$O.
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- Either Vesta is more heterogeneous than previously thought in terms of O isotopes or Emmaville originates from a separate parent body which had a similar composition and evolutionary history to Vesta.

These results provide a detailed account of the mineralogy as well as bulk chemistry of the Emmaville eucrite, and suggest that it is nearly indistinguishable from basaltic eucrites in terms of mineralogy and bulk composition, but its oxygen isotopes and fine-grained metamorphic texture stand out as anomalous. This study presents three hypotheses for the formation of this anomalous eucrite and though its origin is still uncertain, the differences in oxygen isotope composition coupled with evidence against a heterogeneous Vesta or obvious impactor contamination lead us to conclude that it is more plausible that Emmaville is from a separate parent body.
Chapter Four: The Abundance and Isotopic Composition of Water in Eucrites

4.1. Introduction

Asteroids formed early within the solar nebula (~ $10^5$ to $10^7$ years after Calcium-Aluminium-rich Inclusions (CAIs); Chambers and Wetherill, 2001; O’Brien et al., 2014a) 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 the development of habitable environments on the early Earth.

The volatile inventories of volatile-depleted bodies such as the Moon or Vesta have been poorly constrained until recently, mainly 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; See also Chapter 1 section 1.4.2). Similar to lunar and martian samples, eucrites contain two major phosphate minerals – apatite and merrillite. Apatite 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; Patiño Douce et al., 2011; Barnes et al., 2013; Sarafian
et al., 2013; 2014; Tartèse et al., 2013; 2014b; McCubbin et al., 2014). In contrast, the phosphate merrillite does not incorporate significant volatiles, but is a major reservoir of rare earth elements (REEs) (Delaney et al., 1984b). In this study, the focus is on apatite as it is the only known volatile-bearing mineral in eucrites (Delaney et al., 1984b; 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. For more information on apatite see Chapter 1, section 1.4.

Currently the water inventory and hydrogen isotopic composition of eucrites is poorly understood partly owing to a limited number of studies on apatite (Sarafian et al., 2013; 2014) and silicates (Stephant et al., 2016; Sarafian et al., 2017b). Here is presented a comprehensive dataset for the H$_2$O abundance and H isotopic composition of apatite in a suite of basaltic eucrites, representative of the principle geochemical trends and metamorphic grades, as well as for cumulate eucrites, which have not been analysed 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.

Most of this chapter has been published as Barrett et al. (2016) in the journal Meteoritics and Planetary Science. Details of specific contributions by the lead author and other co-authors can be found in Chapter 1, section 1.5.1.
4.2. Cosmic-ray spallation correction

Spallation is a process caused by the interaction of cosmic rays with a rock residing within a few metres of the surface of an airless planetary body, which causes an increase of δD values through the spallogenic production of D. Target elements for the production of D in rocks include O, Mg, Al, Si and Fe with O being the most important target for apatite (Merlivat et al., 1976; Reedy, 1981; Füri et al., 2017). 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, itself a function of chemical composition (i.e. the abundance of the target elements) and shielding depth (the depth of irradiation below the lunar surface) (e.g., Reedy, 1981; Saal et al., 2008; 2013; Barnes et al., 2014; Füri et al., 2017). The cosmic ray flux for the asteroid Vesta is not known, however, it is expected to be lower than that for the Moon, since Vesta is at a greater heliocentric distance. Therefore, using the lunar production rates (2 × 10^{-10} mol H₂ g⁻¹ Ma⁻¹ for H and 0.5 × 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. CRE ages for the eucrites analysed here can be found in Table 2.1. Since no CRE age is currently known 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 other studied samples, correction for spallation effects did not change δD values significantly (Table 4.1) since their CRE ages are relatively young.

Recently Füri et al. (2017) calculated a new production rate for D in MgO-FeO-rich silicates (e.g. olivine) for the Moon. Their production rate of (2.171 ± 0.111) × 10^{-12} mol(g rock)^{-1}
$^{13}$Ma$^1$ is more than twice that of the previous production rates and suggests that the production rates of Merlivat et al. (1976) significantly underestimated the production of cosmogenic D. In light of this new work, the new production rate was applied to samples DaG 945 and DaG 844 (Figure 4.1).

These two samples were selected to assess the affect of the different production rates because they contain the lowest (DaG 945) and highest (DaG 844) abundance of water and have been corrected using the oldest CRE age known for eucrites (38 Ma). As shown in Figure 4.1 the difference in correction at low water content (53 ppm) can be significant (maximum of 150 ‰ difference). For apatite grains in DaG 945 with greater than 100 ppm H$_2$O the difference between corrections is smaller (~ 50 ‰). In DaG 844, the sample with the highest H$_2$O abundance, the difference between pre-correction, Merlivat, and Füri corrections is

![Figure 4.1: Diagram displaying the variation between δD values and different spallation corrections.](image-url)

The pre-correction data are the δD values following correction for instrumental background. The pre-correction and Merlivat corrections for DaG 844 are behind the Füri correction.
insignificant. Füri et al. (2017) do state, however, that whilst this production rate can be used to correct the D/H ratio of water within MgO-FeO-rich silicates it is not appropriate for deriving the proportion of cosmogenic D in other minerals such as apatite or plagioclase as the differing chemical composition must be accounted for. It should be noted, however, that using either of the production rates for D does not affect conclusions of this work.

4.3. Results

4.3.1. H$_2$O content and δD signatures in apatite

In total, 32 measurements were made on 23 apatite grains from 6 samples, and the results are listed in Table 4.1 and plotted in Figure 4.2. The measured apatite H$_2$O contents span more than two 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 (Figure 4.2e). In DaG 945, on the other hand, apatite grains display relatively restricted variations in H$_2$O content, ranging from 54 ± 2 to 229 ± 7 ppm (Figure 4.2b). Apatite in this sample, however, is characterised by the largest variation in H-isotopic composition, with δD values ranging from + 697 ± 403 ‰ to − 441 ± 379 ‰ (Figure 4.2b). 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 to 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 (Figure 4.2f). The δD values of the wettest apatites (> 800 ppm H$_2$O) studied in DaG 844, Millibillillie and Stannern are similar and range from − 174 ± 185 ‰ to + 84 ± 122 ‰ (Figure 4.2a, c, e and Figure 4.3). In some cases, it was possible to obtain multiple
measurements within the same apatite grain (Figure 4.2). With the exception of a single grain in Millbillillie it was found for most cases that there is little intra-grain variability in H$_2$O content.

Figure 4.2: Plot showing the variation between, and within, apatite grains for the different samples studied. Note the x-axis scale varies between samples to better highlight the intra-sample variation in H$_2$O content.
Table 4.1: Background and spallation corrected D/H ratios, δD values, water contents, and the associated uncertainties for apatite in eucrites. Values for $f$ used in equation 2 are also provided. Bkg corr = background corrected.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>δD value raw (%)</th>
<th>δD value bkg corr (%)</th>
<th>δD value final (%)</th>
<th>2σ (%)</th>
<th>$f$ (%)</th>
<th>H$_2$O content raw (ppm)</th>
<th>H$_2$O content bkg (ppm)</th>
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Chapter Four: Abundance and Isotopic Composition of Water in Eucrites

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<th>-110</th>
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<th>90</th>
<th>217</th>
<th>23</th>
<th>194</th>
<th>5</th>
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</table>

| Moore County | Ap1a | 80  | 94  | 79  | 361 | 57 | 45  | 20 | 25  | 1 |
|              | Ap1b | -47 | -106 | -115 | 503 | 69 | 62  | 20 | 42  | 1 |
|              | Ap4a | 74  | 83  | 68  | 332 | 58 | 47  | 20 | 27  | 1 |
|              | Ap7a | -214 | -288 | -289 | 271 | 84 | 147 | 23 | 124 | 3 |
|              | Ap11a| 130 | 129 | 124 | 283 | 78 | 102 | 23 | 79  | 2 |

4.4. Discussion

4.4.1. Potential influence of terrestrial alteration

Out of the six eucrites analysed, four are falls (Millbillillie, Moore County, Sioux County, Stannern), which are likely to have suffered minimal terrestrial alteration (Table 4.1). 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 particularly important to consider the potential terrestrial alteration history when assessing the indigenous D/H signatures of the water within analysed 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 +679 ± 403 ‰ (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. It is also routine to monitor terrestrial contamination during NanoSIMS analysis using real time imaging (as described in Tartèse et al., 2013) to screen for any spurious data.

Figure 4.3: Plot showing δD values versus H₂O contents of apatite from the studied eucrite meteorites. The thick black line represents the evolution of the δD value of residual water in a magma undergoing H₂ degassing – see text for explanation. Uncertainties are reported at the 2σ level. Grey symbols are type 4 eucrites, crosses type 5 and open symbols type 6. The light-grey ellipse is the field for lunar highland samples (Barnes et al., 2014) and the dark grey ellipse highlights the range of previously published δD-H₂O data for apatite in eucrites (Sarafian et al., 2014). For comparison purposes, data from silicophosphates in angrites are also displayed (Sarafian et al., 2017d). The bulk carbonaceous chondrite δD range is derived from Alexander et al. (2012) and the terrestrial range (-60 ‰ ± 20 ‰) taken from Lécuyer et al. (1998). It should be noted that values as low as -218 ‰ have recently been reported for terrestrial lavas (Hallis et al., 2015) which would still plot within the band defined by carbonaceous chondrites.
Furthermore, there does not appear to be any systematic difference between the H isotopic compositions of meteorite finds and falls, analysed in this study. It is, therefore, possible to have confidence that the apatite grains analysed in the meteorite finds have retained their original H isotopic compositions.

*Museum weathering*

Much of the published literature on weathering focuses on the alteration of a sample by terrestrial processes prior to the recovery of the meteorite (see above). So called ‘museum weathering’ refers to weathering that can occur post-collection within museum and laboratory environments and has focused mainly on chondrites (Buchwald, 1990; Lee and Bland, 2004; Bland et al., 2006; Velbel, 2014; Steer, 2016). Post-collection weathering can be found in many forms and as it can affect all meteorite samples in a collection, meteorite falls, which are traditionally viewed as pristine samples, can also be affected (Velbel, 2014). Lee and Bland (2004) report the formation of Ni-, S- and Si-bearing alteration products of kamacite oxidation in the L6 chondrite fall New Concord and minor mobilisation of Mg, Ca and Si into the rusty products of kamacite from silicates. Jull et al. (1988) and Socki et al. (1991) note the formation of carbonate minerals post-recovery of the non-Antarctic OC fall Holbrook. These carbonates have incorporated terrestrial C and O which has affected the isotopic signature of these phases. A qualitative study by McSween (1979) and a quantitative study by Browning et al. (1996) of CM carbonaceous chondrites resulted in the creation of the mineralologic alteration index (MAI) (Browning et al., 1996). Bland et al. (2006) plotted MAI vs. year of fall for all the CM chondrites for which an MAI had been determined. Their graph shows a strong positive correlation between MAI and year of fall ($R^2 = 0.93$) where older falls show more weathering. There is, however, no systematic correlation between year
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of fall and matrix or bulk $\Delta^{17}$O, $\delta^{18}$O (Clayton and Mayeda, 1999), water content, or $\delta$D (Eiler and Kitchen, 2004).

As carbonaceous chondrites are believed to be particularly susceptible to terrestrial weathering (Bland et al., 2006), and many of the alteration products seen within these meteorites are associated with metal grains, achondrites such as eucrites with low metal contents are likely to be less susceptible to weathering, especially when none of the weathering products mentioned above have been reported in the literature or in the thin sections examined in this study. With no correlation observed between water content, $\delta$D, and year of fall in these easily weathered samples (Eiler and Kitchen, 2004), and experiments by Brenan (1993) demonstrating that H does not diffuse within an apatite grain under ambient terrestrial conditions, it would seem reasonable to suggest that eucrites falls preserve their original parent body H isotope signature.

4.4.2. Magmatic degassing

In the case of lunar picritic glasses and mare basalts, it has been argued that magmatic degassing of volatile species such as $\text{H}_2$ 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 $\text{H}_2$ gas, which enriches the water in the remaining melt in D. Since apatite crystallises late in the crystallisation history of basaltic melts (>90% crystallisation, e.g., Sha, 2000), it is likely to record elevated D/H signatures and not the un-degassed (primitive) magmatic signature, if degassing occurred. To test if magmatic degassing of volatiles such as $\text{H}_2$ could have been an important process during the 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 modelled (Figure 4.3). The model obeys the Rayleigh fractionation relationship $R = R_0 \times f^{(\alpha-1)}$, where $R_0$ 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 4.3 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 characterised 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, whilst plotting close to the degassing trend is still within error of most of the 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, most of the apatite grains appear to record the magmatic signature of their parental melts. In the case of the lunar basalts, which likely crystallised 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 crystallised at depth, which inhibited any significant magmatic degassing.
**4.4.3. 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 (Figure 4.3). 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 (Figure 4.3). The apatite water content of Main Group eucrites from this study, however, displays a significantly larger range than most of the Stannern apatite values (Figure 4.3). 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 \( \text{H}_2\text{O} \)).

Apatite in Stannern, however, does show significant variability in \( \text{H}_2\text{O} \) between one grain (section 2 Ap2) and the other two measured in this study (Figure 4.2e). 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 Chapter 2 Section 2.7, Figure 2.10 for high-\( \text{H}_2\text{O} \) apatite grain and Figure 4.4 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 crystallisation. The apatite grain containing less \( \text{H}_2\text{O} \) (37 ± 1 and 42 ± 1 ppm \( \text{H}_2\text{O} \), as opposed to > 1500 ppm), on the other hand, appears to have co-crystallised with the silicates surrounding it and, therefore, may have crystallised earlier than the other apatite grains (Figure 4.4). This observation is consistent with the evolution of apatite chemistry during fractional crystallisation, where earlier crystallised apatite is F-rich and OH-poor and late-crystallising apatite is more OH-rich (Boyce et al., 2014; McCubbin et al., 2015b).
Figure 4.4: BSE image of Stannern apatite grain (Section 2 Ap2). Pl = Plagioclase, Px = Pyroxene, Ap = Apatite, Mrl = Merrillite, ilm = Ilmenite, Tr = Troilite, Si = Silica phase. Solid white squares represent approximate location of SIMS raster area.

Also, these results do not show any sign of correlation between the H$_2$O/δD 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 H$_2$O abundances (Figure 4.3). Three of the eucrites in which apatite grains were analysed 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 analysed in order to minimise 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.

4.4.4. Comparison with previously published data

With the exception of Stannern, the eucrites analysed here have not been investigated previously for their water content. The results obtained on two out of the three Stannern grains (~ 1500-1800 ppm H$_2$O and δD around $\sim 20 \pm 100 \permil$; section 1 Ap1 and section 2 Ap4) analysed in this study are in close agreement with those reported by Sarafian et al. (2014) (~ 1500-2600 ppm H$_2$O and δD around $\sim 75 \pm 36 \permil$). Apatite in the other eucrites analysed here, however, show greater variability in H$_2$O contents and δD 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 intra-grain variability of 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 crystallisation 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 crystallised (Boyce et al., 2014), however, this was not directly observed as neither F nor Cl were measured in this study.
The weighted average δD 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 δD value of $-151 \pm 23 \%$ (95% confidence level, $n= 43$).

Apatite data also display some similarities with the preliminary work of Stephant et al. (2016) on pyroxene grains of four eucrites, three of which already have published apatite δD values and H$_2$O abundances. Results from this work give an abundance ranging from $\sim 40 - \sim 200$ ppm H$_2$O and a weighted average δD of $-241 \pm 64 \%$. The water content of these pyroxene grains are similar to most of the apatite data in this study. Interestingly, samples with higher pyroxene water content also contain apatite with higher water contents, however, there does not appear to be the same correlation between δD values (Sarafian et al., 2014; Stephant et al., 2016). The δD values of pyroxene from Stannern (Stephant et al., 2016) are in good agreement with the apatite values from this study, though they are more variable than the apatite data of Sarafian et al. (2014), whilst other pyroxene values are typically lower than apatite values. These pyroxene values are lower than Earth’s depleted mantle (Lécuyer et al., 1998) and most carbonaceous chondrites (Alexander et al., 2012) but is similar to the recently estimated deep mantle on Earth (δD < -218 \%; Hallis et al., 2015).

Data from this work can also be compared to the recent work of Sarafian et al. (2017d) on silicophosphates found in angrites. Silicophosphate is an extremely rare mineral both in terrestrial and extraterrestrial environments and currently not known in any other achondrite. In ‘quenched’ angrites such as D’Orbigny, however, it is a minor but common late-stage crystallisation product typically occurring at the rim of fassaitic (Al-Ti-rich) clinopyroxene (Mikouchi et al., 2010). These silicophosphates can contain up to 20 wt. % Si but have been
shown to still hold an apatite structure, leading some to name them silico-apatite (Mikouchi et al., 2009; 2010; 2011). Angrite silicophosphates in D’Orbigny and Sahara 99555 show a similar range of H₂O abundance and hydrogen isotope composition as eucrite apatite (Figure 4.3). Two data points in D’Orbigny, however, display high water content (~ 1700 and ~1890 ppm H₂O) as well as an enriched isotopic signature (δD +1034 ‰ and +1032 ‰ respectively; Sarafian et al., 2017d) at odds with eucrite data of comparable water contents. The authors argue that the parent melt of D’Orbigny experienced degassing of H₂; this would mean that the depleted results that match the isotopic composition of eucrites are higher than the true value.

### 4.4.5. 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 largely accreted dry (Boss, 1998; Lucey et al., 2006; Albarède, 2009). In this case, the ancient age of eucrites (typically 4547 Ma to 4559 Ma) argues in favour 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 homogenous reservoir whilst the Proto-Earth and Proto-Moon accreted largely dry. The impacts that delivered volatiles to the Earth and the Moon, as suggested by Bottke et al. (2010), could then be comprised of these smaller early planetesimals which have a homogenous D/H ratio. This would account for the seemingly different timings of accretion of volatiles to different parts of the inner Solar System while requiring a homogenous D/H 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 magma ocean stage of the planetesimal that degassing of volatile species could have led to elevated bulk D/H ratio (Sharp et al., 2013a). 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. Given the recent angrite data of Sarafian et al. (2017d), which demonstrates D’Orbigny underwent degassing and provides elevated H isotope compositions as well as those similar to eucrites, it would appear the degassing of planetesimals to the same uniform D/H ratio is increasingly unlikely.

Whilst the 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 δD value of −865 ‰ (Lellouch et al., 2001). If inner Solar System objects accreted water initially characterised 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 of D/H ratios from protosolar values is also a valid alternative. Objects formed at greater heliocentric distances, such as comets, seem to be characterised 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 characterised 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 highest 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 (Alexander et al., 2012).
The D/H signatures of water in apatite in eucrites measured in this study (weighted average δD value of $-34 \pm 67 \%$) and by Sarafian et al. (2014) (weighted average δD value of $-162 \pm 127 \%$) 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) (Figure 4.3). 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 crystallised 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 to 1800 ppm H$_2$O) and δD values similar to those measured in apatite in the eucrites (Figure 4.3). 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. The possible origin(s) of H in the inner Solar System is discussed in more detail in Chapter 6.

4.5. Conclusions

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 have 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 crystallisation ages (~4.5 Ga) of eucrites. Here, measurements of water (reported as equivalent H$_2$O abundances) and the hydrogen isotopic composition (δD) 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 δD value of $-34 \pm 67$‰. No systematic variations or correlations are observed in H$_2$O abundance or δD 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.

As such it can be concluded:

- Apatite from eucrites records the indigenous H-isotopic composition of the HED parent body.
- There is no resolvable difference between the H$_2$O content and δD values of apatite in the Stannern vs. the Main Group-Nuevo Laredo trends.
- Metamorphism on the HED parent-body appears to have had little effect on the H$_2$O content and δD values of apatite in eucrites.
- The δD results presented suggest that most eucrites were not affected by volatile degassing.
- The results from this study provide a fourfold increase in the number of δD/H$_2$O analyses available for apatite in eucrites.
- The results are consistent with previous studies and indicate that water in the HED parent body is characterised by a homogenous reservoir with a D/H signature similar to most types of carbonaceous chondrites, the Earth’s mantle and the Moon.
- There is no evidence for terrestrial alteration affecting the D/H ratio of apatite in the studied samples.
Chapter Five: Chlorine Isotope Variation in Apatite from Eucrites

5.1. Introduction

Chlorine is an important element being incompatible in nearly all silicates, extremely volatile and strongly hydrophilic (Sharp et al., 2010a). The Cl isotope composition ($^{37}\text{Cl}/^{35}\text{Cl}$) of meteorites, therefore, can provide useful information regarding the isotopic reservoirs of volatiles that were present in the early Solar System and any secondary processes that may have occurred on different parent bodies (Sharp et al., 2007; 2013b; Bellucci et al., 2017). There is relatively a narrow range in the Cl isotope compositions of terrestrial rocks, martian meteorites and chondritic meteorites ($\delta^{37}\text{Cl} \sim -5.6$ to $+1$ ‰ although one data point for a martian meteorite does reach $+8.6$ ‰) (Sharp et al., 2007; 2013b; 2016; Williams et al., 2016; Bellucci et al., 2017; Manzini et al., 2017), with eucrites ranging up to $\sim +12$ ‰ (Roszjar et al., 2015) and the lunar samples being an exception to this rule. Based on data that are currently available in the peer-reviewed literature, lunar samples display a significant range in Cl isotopic composition, especially lunar apatite, which is a common accessory mineral that can contain appreciable Cl (Sharp et al., 2007; 2013b), and which shows $\delta^{37}\text{Cl}$ values ranging from $\sim -4 \pm 2$ ‰, lighter than typical terrestrial values ($0 \pm 2$ ‰, e.g. Sharp et al., 2007), to extremely enriched values of $\sim +36 \pm 2$ ‰ (e.g. Sharp et al., 2010b; Boyce et al., 2015; Barnes et al., 2016).

The Howardite-Eucrite-Diogenite (HED) suite of meteorites is the largest suite of crustal and sub-crustal rocks available from a differentiated basaltic asteroid (most probably 4 Vesta) (McCord et al., 1970; De Sanctis et al., 2012b; McSween et al., 2013). The eucrites
are also some of the oldest igneous rocks in the Solar System, typically with crystallization ages from 4547 Ma to 4559 Ma (Misawa et al., 2005; Zhou et al., 2013; Touboul et al., 2015). Therefore, characterizing the volatile inventories of eucrites can help us understand the processes operating on asteroid parent bodies early in the Solar System history. For more details regarding the HED meteorites, see Chapter 1, section 1.3.

Apatite is a widely distributed accessory phase in planetary materials (Delaney et al., 1984b; Sarafian et al., 2013) and was the only known volatile-bearing mineral phase in eucrites until preliminary studies by Stephant et al. (2016) and Sarafian et al. (2017b) measured the H$_2$O abundance and H isotopic composition of eucritic pyroxenes. Currently the volatile inventory and isotopic composition of apatite in eucrites is limited, owing to a small number of studies (Sarafian et al., 2013; 2014; 2017; Roszjar et al., 2015; Barrett et al., 2016; Schneck et al., 2016). In order to investigate the history of volatiles in eucrites, the Cl isotopic composition of apatite from the cumulate eucrite Moore County and the basaltic eucrites Agoult, Dar al Gani (DaG) 844, DaG 945, Millbillillie, North West Africa (NWA) 2362 and Stannern were studied. Apatite grains in all samples except Agoult and NWA 2362 were previously analysed for their H isotopic composition and H$_2$O abundances (Barrett et al., 2016; See Chapter 4 for more details). Zinc isotopes were also analysed for sample DaG 945 specifically to test the hypothesis of Cl isotope fractionation via metal chlorides which is outlined below in section 5.3.2.

5.2. Results

A total of 33 measurements from 24 individual apatite grains from seven samples were obtained, the data for which are listed in Table 5.1 and plotted in Figure 5.1. EPMA data for apatite grains and the surrounding mesostasis phases are provided in the supplementary
material (Appendix A.3, Table 8.4 Table 8.5). Zinc isotope data for DaG 945 along with literature values for other samples analysed here are provided in Table 5.2.

The chlorine content of apatite grains studied here display a significant range, from ~ 24 to ~ 4900 ppm Cl. In basaltic eucrites, apatite grains contain similar amounts of Cl with Millbillillie having a relatively restricted range from ~ 1830 to ~ 2030 ppm Cl and both DaG 844 and Stannern containing ~ 1500 ppm Cl. For Stannern these results are comparable to SIMS results of Sarafian et al. (2017a) but ~ 500 ppm lower than EPMA results in Sarafian et al. (2013).

The cumulate eucrite Moore County displays a larger range in Cl content, from ~ 110 to ~ 690 ppm which are almost an order of magnitude lower than results of previous studies (Sarafian et al., 2013). Considerable intra-grain variability in Cl abundance is also observed.
in Moore County with a single grain having a range of ~ 360 ppm (Ap3). Residual eucrites Agoult and DaG 945 have the lowest Cl contents measured in this study and show restricted variation, both inter-grain as well as intra-grain, with values ranging from ~ 25 to ~ 60 ppm (Figure 5.1). NWA 2362, however, has the highest Cl content measured for any eucritic apatite as well as a significant inter-grain (~ 2320 to ~ 4900 ppm Cl) and intra-grain (~ 1000 ppm Cl in Ap4) variations.

The δ⁴⁰Cl values obtained for apatite from the basaltic eucrites are typically within error of terrestrial values and chondrites, however, one grain from Stannern does have a slightly enriched δ⁴⁰Cl value (Ap2, + 3.45 ± 1.39 ‰ 2σ) compared to the other basaltic eucrites in this study. This enriched grain is within error of other Stannern values from different grains (This study and Sarafian et al., 2017a), but resolvable from the terrestrial range and other basaltic eucrites studied here (Figure 5.1). Apatite grains within Millbillillie are very consistent with regards to their Cl isotope composition (ranging from –1.49 ± 1.13 ‰ to 0.34 ± 0.84 ‰ 2σ) and are also very consistent with the value –0.34 ± 1.15 ‰ (2σ) obtained for DaG 844.

The δ⁴⁰Cl values in Moore County are typically more enriched than those of basaltic eucrites, however, they also display larger uncertainties, owing to poorer counting statistics associated with the lower Cl contents of some apatite grains, and are typically within error of the basaltic eucrites (Fig. 5.1). Moore County does, however, have two grains which are more enriched (+ 6.62 ± 3.4 ‰ and + 13.1 ± 3 ‰ 2σ) than the terrestrial values which correspond to the lowest Cl content for this sample (113 and 130 ppm Cl respectively).

The residual eucrites display a wide range of chlorine isotope compositions. Agoult has the largest range of δ⁴⁰Cl values ranging from –3.98 ± 6.08 ‰ to + 11.64 ± 7.24 ‰ (2σ). Three
of the data points are within error of the Solar System range, however, two data points can be easily resolved from this group with enriched values (+ 8.96 ± 6.66 ‰ and + 11.64 ± 7.24 ‰) similar to those seen in the cumulate eucrite, Moore County. The residual eucrite NWA 2362, exhibits a resolvable enrichment in δ^{37}Cl values from the basaltic eucrites and terrestrial values, with results ranging from + 4.27 ± 0.87 to + 9.65 ± 1.52 ‰ (2σ) with one value even more enriched at + 13.58 ± 1.51 ‰ (2σ) (Figure 5.1). These values are similar to the two enriched points in Moore County and Agoult. DaG 945, on the other hand, shows a significant enrichment in δ^{37}Cl with values ranging from ~ + 27 ± 4.4 ‰ to ~ + 35 ± 6.2 ‰ (2σ). The δ^{37}Cl values of apatite from DaG 945 are amongst the highest chlorine isotopic compositions recorded for any Solar System material.

The data for δ^{66}Zn, δ^{67}Zn and δ^{68}Zn in DaG 945 are + 13.45, + 20.15 and + 26.70, respectively. These values are significantly enriched compared with other HED meteorites studied in Paniello et al. (2012) (Table 5.2).
Chapter Five: Chlorine Isotope Variation in Apatite from Eucrites

Table 5.1: Table of $\delta^{37}$Cl values and the associated uncertainties for apatite in eucrites.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\delta^{37}$Cl ($%$)</th>
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<th>$2\sigma$ (ppm)</th>
<th>Raster size ($\mu$m)</th>
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Chapter Five: Chlorine Isotope Variation in Apatite from Eucrites

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<tr>
<th>Sample</th>
<th>$\delta^{66}$Zn</th>
<th>$\delta^{67}$Zn</th>
<th>$\delta^{68}$Zn</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DaG 945</td>
<td>13.45</td>
<td>20.15</td>
<td>26.70</td>
<td>This Study</td>
</tr>
<tr>
<td>Millbillillie</td>
<td>-0.79</td>
<td>-1.37</td>
<td></td>
<td>(Paniello et al., 2012)</td>
</tr>
<tr>
<td>Stannern</td>
<td>1.19</td>
<td>2.48</td>
<td></td>
<td>(Paniello et al., 2012)</td>
</tr>
</tbody>
</table>

Table 5.2: Table displaying the zinc isotopic composition of samples studied in this thesis.

5.3. Discussion

5.3.1. Petrology, mesostasis mineral compositions and bulk elemental abundance

As mentioned in the previous section, the basaltic eucrites have apatite Cl isotopic compositions that cluster around 0 ‰ with an appreciable amount of Cl whilst cumulate and residual eucrites display a larger range in isotopic composition at relatively lower Cl contents (0.65 ‰ to 13.1 ‰ for Moore County and – 3.98 ‰ to 35.6 ‰ for residual eucrites). The mineral phases surrounding the apatite grains were analysed for mineral compositions and found to display no obvious systematic variations which could be correlated to $\delta^{37}$Cl values for any sample (Figure 5.2 and Appendix, Table 8.5). The surrounding mineral phases all have typical compositions for eucrites of their type and are broadly consistent with published literature values (e.g. Yamaguchi et al., 2009; and supplementary material of Mittlefehldt, 2015). No sample displays any form of metasomatism, meaning, therefore, this can be
effectively ruled out as a mechanism for fractionation. Interestingly, the basaltic eucrites all contain merrillite (though only in the DaG 844 section studied here was merrillite and apatite observed in close proximity to one another) which is not observed in the other samples in this study. All of these eucrites have consistently low and invariant δ^{37}Cl values and very similar Cl contents compared to the more variable Cl isotope signatures in residual and cumulate eucrites. When compared to the samples analysed by Sarafian et al. (2017a), no correlation between the presence and/or absence of merrillite and δ^{37}Cl is observed: NWA 1908 and NWA 5073 both have distinctly non-zero δ^{37}Cl values (average values of 7.10 ± 4.57 ‰ and −3.75 ± 1.14 ‰ respectively) and a much larger range in Cl content (988 ppm and 2058 ppm Cl respectively; Sarafian et al., 2017a). The metamorphic grade, indicated using the pyroxene classification of Takeda and Graham (1991) and expanded upon by Yamaguchi et al. (1996), also shows no correlation with either the Cl abundance or the Cl isotopic signature of the meteorite.
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Figure 5.2: Representative collection of back-scattered electron (BSE) images of each apatite grain analysed in this study. Ap = apatite, cr = chromite, FeO = iron oxide possibly weathering related, ilm = ilmenite, px = pyroxene, pl = plagioclase, si = silica phase, tr = troilite. The red and white squares represent the approximate location of Cl and H isotope NanoSIMS pits respectively. Hydrogen isotope data are taken from Barrett et al. (2016).
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Chapter Five: Chlorine Isotope Variation in Apatite from Eucrites

[Images of micrographs showing chlorine isotope variation in apatite from Eucrites samples. Each image contains labeled mineral phases and isotope data.]
The petrologic context of apatite grains in basaltic eucrite Millbillillie is similar across the entire sample, being associated with ilmenite and chromite, and all have similar isotopic compositions and abundance. The apatite grain analysed in DaG 844, however, occurs interstitial to two large pyroxene grains with minor amounts of chromite, in contrast to those in Millbillillie, and whilst it displays an identical Cl isotope composition, has a slightly lower Cl content (1444 ppm Cl compared to between ~ 1830 to ~ 2040 ppm Cl in Millbillie) comparable to Stannern (1490 and 1537 ppm Cl). The H\(_2\)O abundance of apatite in DaG 844 and two of three Stannern grains, are significantly higher than those seen in Millbillillie (Barrett et al., 2016). It has been suggested that the timing of apatite crystallisation affects the volatile content, with apatite displaying a clear preference for F over Cl and Cl over OH.
If the pre-requisite of McCubbin and Jones (2015) were met (see section 1.4.1), Millbillillie with its higher Cl content and lower, more variable H$_2$O content, may represent an earlier phase of crystallisation relative to DaG 844 and Stannern. This is in accordance with age data obtained by Miura et al. (1998) which provide an older age for Millbillillie compared to Stannern. Age dating of DaG 844 would help to further constrain this hypothesis.

One grain in Stannern (Ap2) has a noticeably different texture when compared to other apatite grains studied in this meteorite and the rest of basaltic eucrites. This grain appears to have co-crystallised with the silicates surrounding it even including small amounts of other minerals within the crystal (Figure 5.2). Whilst the grain has a similar Cl content to the other Stannern apatite analysed and to DaG 844, it has an elevated isotopic signature, with $\delta^{37}$Cl + 3.45 ± 1.39 ‰. Barrett et al. (2016) noted that this particular grain also contained less H$_2$O than other Stannern apatite analysed and could represent an earlier-formed apatite within Stannern, 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., 2015b). Moore County apatite grains, on the other hand, do not appear to show significant petrological differences between the two grains with heavier $\delta^{37}$Cl values (13.1 ‰ and 6.62 ‰) and the grain with $\delta^{37}$Cl ~ 0 ‰. Apatite grains here are similar in texture to those described by Sarafian et al. (2013) though the abundance of volatiles, both Cl and H$_2$O, are significantly lower than previously reported in literature.

The residual eucrites Agoult and DaG 945 share some petrological similarities but appear to be somewhat distinct from NWA 2362. Apatite in all of the samples are typically associated with relict mesostasis regions and consistent within each sample, but Agoult and DaG 945
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Apatite appear to have a stronger association with minerals such as chromite, ilmenite and a silica phase and the overall meteorites are more granulitic than NWA 2362. Ap2 in NWA 2362 stands out as anomalous with regards to its Cl content, almost 2000 ppm lower in abundance than the rest of the grains analysed. This grain however would appear to have a similar petrological context as the rest of the analysed grains, though it is closer to cracks filled with likely terrestrial FeO. Any removal of Cl from this apatite grain by terrestrial weathering, however, would likely have altered the Cl isotopic composition. As this grain has a consistent \( \delta^{37}\text{Cl} \) with respect to other grains within this sample it would seem unlikely terrestrial alteration caused the lower Cl abundance without compromising its isotopic composition. As the residual eucrites have all experienced high degrees of thermal metamorphism and the extraction of partial melts, it is possible that the degree of melt extraction could have affected the Cl content and isotopic composition, which is discussed later in section 5.3.3.

In a recent study, Sarafian et al. (2017a) observed a correlation between major and trace elements plus halogen content with \( \delta^{37}\text{Cl} \) and suggested that this was related to degassing of the vestan magma ocean or, alternatively, during emplacement or eruption after the magma ocean phase. Figure 5.3 displays the bulk rock abundances for various elements plotted against apatite \( \delta^{37}\text{Cl} \) values. The figure shows that there is no obvious correlation between bulk Mg, Cr, and Sc and \( \delta^{37}\text{Cl} \), however, there is a very weak negative correlation between K and \( \delta^{37}\text{Cl} \) if DaG 945 is excluded (DaG 945 is excluded based on its large leverage values in a simple linear regression model. See Appendix A.3.2). Whilst the relationship observed between K and \( \delta^{37}\text{Cl} \) is in keeping with Sarafian et al. (2017a), the Mg, Sc, and Cr data are not. Sarafian et al. (2017a) suggested a negative relationship between both Mg and Cr and \( \delta^{37}\text{Cl} \) owing to the crystallisation of olivine and spinel during magma ocean crystallisation,
respectively. Similarly their positive relationship between Sc and $\delta^{37}\text{Cl}$ implied that olivine rather than pyroxene was a major phases during magma ocean crystallisation. The weak correlation observed between K and $\delta^{37}\text{Cl}$ could represent the coupled loss of K and Cl during degassing as KCl. DaG 945, however, is an obvious outlier in Figure 5.3 with an appreciable amount of K and significant enrichment in Cl isotopic signature. This anomalous signature could potentially be caused by the degassing of KCl being supressed somehow by an element that is more reactive with Cl in this sample. As these samples are a mixture of meteorite finds and observed falls, it is unlikely that terrestrial weathering could be the cause of the observed correlation.

The data published by Sarafian et al. (2017a) also presents data for Pasamonte, a sample with a small, yet resolvable, difference in O isotopic composition from basaltic eucrites despite being otherwise petrologically and compositionally indistinguishable from them (Wiechert et al., 2004; Greenwood et al., 2005; Scott et al., 2009). This allows for comparison between anomalous eucrites and typical basaltic eucrites. The fact that Pasamonte has a similar volatile content and isotopic signature, for both hydrogen (Sarafian et al., 2014) and chlorine (Sarafian et al., 2017a), suggests that at least these two bodies may have a common source region for their volatiles and have undergone similar processes.
5.3.2. Degassing of metal chlorides

In the case of the Moon, there are currently two main models proposed for the fractionation of Cl isotopes: (i) the degassing of Cl in the absence of H as metal chlorides from lunar mare magmas (Sharp et al., 2010b; Ustunisik et al., 2015) and (ii) degassing of metal chlorides from the lunar magma ocean (Boyce et al., 2015) or urKREEP (Barnes et al., 2016). If degassing had played a significant role then there are several characteristic features that should be observed in apatite as outlined below (Sharp et al., 2010b; Boyce et al., 2015; Barnes et al., 2016):
- Elevated $^{37}\text{Cl}/^{35}\text{Cl}$ ratios should be inversely proportional to Cl abundance

- Elevated $^{37}\text{Cl}/^{35}\text{Cl}$ ratios should not be observed in samples with abundant H as degassing of HCl would not fractionate Cl (Schauble et al., 2003).

- Elevated $^{37}\text{Cl}/^{35}\text{Cl}$ ratios should be observed only in samples that have enrichments in D/H

Figure 5.4 shows the relationship between Cl and H for the eucrites analysed in this study. As presented in Figure 5.1, samples with low Cl content typically have higher $^{37}\text{Cl}/^{35}\text{Cl}$ ratios. There appears, however, to be no correlation between $\delta^{37}\text{Cl}$ and $\delta$D values of apatite (Fig. 5.4a) and Figure 5.4b demonstrates the lack of relationship between $^{37}\text{Cl}/^{35}\text{Cl}$ ratios and H$_2$O abundance. The third degassing characteristic is not observed. Unfortunately, there are no hydrogen isotope or H$_2$O content data available for Agoult or NWA 2362. In all samples, apatite grains display almost invariant $\delta$D values (Sarafian et al., 2014; Barrett et al., 2016) but a range of $\delta^{37}\text{Cl}$ values. This non-correlation is also observed in lunar basalts (Boyce et al., 2015). As shown in Figure 5.4b, low $\delta^{37}\text{Cl}$ values are seen throughout the entire range of H$_2$O abundances, but elevated values, however, appear only below 500 ppm H$_2$O. One apatite crystal in DaG 945 (Ap3) displays a 4-fold variation in H$_2$O abundance (60 and 229 ppm H$_2$O; Barrett et al., 2016), however, the Cl isotope analysis areas are spatially located next to only one of the H isotope analysis areas (Figure 5.2). The variation in H$_2$O abundance across a grain is probably caused by heterogeneity in the apatite crystal and so the value from the closest H isotope pit is used in Figure 5.4b (it should be noted that using either measurement would not change the conclusion presented here). DaG 844 and one of the two apatite grains in Stannern are characterised by high H$_2$O content (> 1100 ppm H$_2$O) and $\delta^{37}\text{Cl}$ values close to 0 ‰. As mentioned in the previous section, however, one
grain in Stannern (Ap2) studied here has a low H$_2$O content (~ 35 - 45 ppm H$_2$O; Barrett et al., 2016) and is characterised by a slightly enriched $\delta^{37}$Cl value of $+3.45 \pm 1.39$‰. The apatite in Moore County and DaG 945 are also characterized by low H$_2$O contents (typically < 200 ppm), with DaG 945 showing more variability than Moore County in terms of H$_2$O content. Both of these samples display some of the heaviest $\delta^{37}$Cl values. Repeat analysis of DaG 945 apatite in a separate session confirmed the heavy $\delta^{37}$Cl composition in this sample.

Additionally, there appears to be a positive correlation between apatite $\delta^{37}$Cl and bulk $\delta^{66}$Zn with no large leverage values to discount any sample (Figure 5.5). As Zn isotopes do not fractionate significantly during magmatic emplacement and differentiation (only 0.07 ‰, Chen et al., 2013) or through secondary processes, such as solar wind spallation or cosmogenic effects (Dhaliwal et al., 2017), any fractionation observed must arise from a different mechanism. The enriched $\delta^{66}$Zn and $\delta^{37}$Cl combined with low Cl and H$_2$O abundance of DaG 945 compared to basaltic eucrites which contain significantly more H$_2$O and Cl and display relatively unfractionated $\delta^{66}$Zn and $\delta^{37}$Cl values appears to support the hypothesis that Cl degassed as metal chlorides (Paniello et al., 2012; Sarafian et al., 2017a). GRA 98098, however, does not follow this trend containing the highest Cl abundance of eucrites to date but is enriched in heavy isotopes for both Cl and Zn. As such a different process is required to explain the $\delta^{37}$Cl values of GRA 98098.
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Figure 5.4: a) a plot of weighted average δD values versus average δ\textsuperscript{37}Cl values and b) plot of average δ\textsuperscript{37}Cl values versus H\textsubscript{2}O content. Solid symbols indicate apatite grains where both \textit{in-situ} δ\textsuperscript{37}Cl and hydrogen isotope measurements have been obtained from the same apatite grain. Open symbols indicate average values for the entire sample. \textsuperscript{1}Average δ\textsuperscript{37}Cl and non-weighted average δD values with associated 2σ uncertainties are taken from Sarafian et al. (2017a) and Sarafian et al. (2014) respectively. δD values and H\textsubscript{2}O abundances are from Barrett et al. (2016)
To test the degassing hypothesis further, simple degassing modelling was undertaken using the Rayleigh fractionation relationship $R = R_0 \times f^{(\alpha - 1)}$, where $R_0$ and $R$ are the initial and final $^{37}\text{Cl}/^{35}\text{Cl}$ ratios of chlorine in the melt, respectively, $\alpha$ is the fractionation factor and $f$ is the fraction of chlorine remaining in the melt. Figure 5.6 shows degassing curves for a variety of metal chloride species assuming an initial $\delta^{37}\text{Cl}$ of 0‰.

Based on this model basaltic eucrites appear to be relatively undegassed. The slightly $^{37}\text{Cl}$-enriched values observed in Pasamonte ($\delta^{37}\text{Cl} + 1.60 \pm 0.32$ ‰), Stannern ($\delta^{37}\text{Cl} + 1.69 \pm 2.30$ ‰), and Cachari ($\delta^{37}\text{Cl} 4.87 \pm 2.25$ ‰) require between roughly 10 – 40 % degassing depending on the metal chloride species. Experiments have recently demonstrated that during volatile-rich magma ascent, H is one of the earliest volatiles to degas and a H-rich
vapour would be lost at a faster rate than a Cl-rich vapour (Ustunisik et al., 2015). Once depleted in H, Cl would subsequently become the preferred volatile to degas (Sharp et al., 2013a; Ustunisik et al., 2015). This sequence of H degassing followed by subsequent Cl degassing would appear to fit the eucrites but fails to explain the occurrence of mare basalts rich in OH relative to Cl (Tartèse et al., 2013) given the significant preference of Cl over H when crystallising apatite (Boyce et al., 2014; McCubbin et al., 2015b). As the basaltic eucrites studied here contain appreciable H₂O with unfractionated D/H ratios it follows these samples would have fractionated Cl significantly.

![Graph showing degassing trajectories of various metal chloride species](image)

Figure 5.6: Calculated degassing trajectories of various metal chloride species: assuming an initial δ³⁷Cl value of 0‰. The calculation of these curves are outlined in the text.

The residual eucrite DaG 945 has δ³⁷Cl values of ~ + 30 ‰, implying that significant degassing of metal chlorides has occurred (Figure 5.6). Apatite grains in this sample have a low H₂O abundance (~ 50 - ~ 150 ppm H₂O; Barrett et al., 2016) and so, according to the models (Sharp et al., 2010b; Boyce et al., 2015; Barnes et al., 2016), must have degassed in
a H poor environment. Given that DaG 945 $\delta^{66}$Zn values are also significantly elevated, it would suggest ZnCl$_2$ was the dominant degassing phase for this sample and > 95 % degassing had occurred. It is difficult to ascertain whether Agoult has undergone any degassing owing to the large uncertainties associated with its $\delta^{37}$Cl values. Whilst the lightest Cl isotope value from this sample (-3.98 ± 6.08 ‰) does have the highest Cl content, at 44 ppm, and the heaviest value has the lowest Cl content (+11.64 ± 7.24 ‰ and 25 ppm Cl), the large uncertainties on all analyses from this sample precludes any meaningful correlation. Cl isotope values of ~ + 8 ‰, similar to that of NWA 2362 can be modelled by moderate amounts of degassing with a range from 38 % to 66 % Cl vapour loss, depending on the degassing species.

In contrast to the basaltic and residual eucrites, Moore County displays a more variable Cl isotope composition with a weak correlation between decreasing Cl content and increasing $\delta^{37}$Cl values. As this sample is a cumulate eucrite and is likely to have formed at depth, it is unlikely to have suffered any significant magmatic degassing. Recent work by Wales and Boyce (2016) documents the loss of H from apatite in terrestrial intrusions which could lead to fractionation. These authors suggest that caution is taken when interpreting intrusive rocks in terms of degassing. Owing to the aforementioned variability of the Cl isotope composition and negative correlation between Cl content and $\delta^{37}$Cl it is possible that Moore County may have degassed Cl. Similar to DaG 945, Moore County also has a low H$_2$O abundance (25 to ~125 ppm H$_2$O; Barrett et al., 2016) and may have degassed chlorine in a hydrogen-poor environment.

The timing of eucrite degassing may have been relatively early within the formation of Vesta. Paniello et al. (2012) suggested that unbrecciated eucrites represented an early eucritic crust shortly after differentiation and their heavy zinc isotopic signature was owing
to the volatilization of isotopically lighter zinc. Dhaliwal et al. (2017) model the loss of zinc during a lunar magma ocean (LMO) phase under various conditions. The first model yields a relatively homogenous bulk solid LMO $\delta^{66}$Zn value, while the second results in a stratification of $\delta^{66}$Zn values within the LMO sequence. This second model could be applied to account for the variation in zinc and chlorine isotopes observed in the eucrite parent body. However, as noted by Boyce et al. (2015), this would suggest later samples would be enriched in incompatible trace elements, something discussed in more detail below in section 5.3.3. Degassing during magmatic emplacement/eruption is an alternative hypothesis which can account for the variation seen in eucrites where each sample represents a different flow, some of which degassed (e.g. DaG 945) and some of which did not.

Overall the meteorites studied here appear to follow the degassing trend of zinc chloride, in keeping with the positive correlation between apatite $\delta^{37}$Cl and bulk $\delta^{66}$Zn shown in Figure 5.5. Given the strong correlation between Zn and Cl isotopes and low H abundance in measured apatite with heavy Cl isotope signatures, it is likely that the ZnCl$_2$ was the main degassing phase for Cl in a H poor environment. A potential minor component could be KCl owing to a weak negative correlation observed between K and $\delta^{37}$Cl (Fig. 5.3 and Sarafian et al., 2017a).

5.3.3. Contamination by ‘vKREEP’

An alternative hypothesis proposed by Boyce et al. (2015), postulated that in the case of lunar samples degassing occurred during crystallisation of the magma ocean. This would create early formed cumulates with low incompatible trace element abundances and unfractionated $\delta^{37}$Cl values. Cumulates that formed later (including the last dregs of the lunar magma ocean enriched in incompatible elements such as K, rare earth elements (REEs), and
P, collectively called KREEP and its primitive form – urKREEP) acquired heavier Cl isotopic signatures due to chlorine incompatibility within silicates. Barnes et al. (2016) proposed a variation of this model suggesting degassing of urKREEP, at a later stage than that proposed by Boyce et al. (2015). This would lead to an isotopically enriched reservoir that later mixed with the earlier formed, unfractionated cumulates and create the range of values observed among samples of different lunar lithological types. This contamination by an urKREEP component can be fingerprinted using bulk La/Sm or La/Yb ratios, where higher La/Sm and La/Yb ratios correspond to increasing contamination (Boyce et al., 2015; Barnes et al., 2016). Small fragments of a KREEP-like component discovered in two howardite meteorites suggest the possible existence of a ‘vestan KREEP’ or vKREEP which likely formed under similar conditions as lunar urKREEP (Barrat et al., 2012).

Figure 5.7 displays the bulk La/Yb ratio versus $\delta^{37}$Cl of apatite from eucrites. If eucrites were contaminated by a vKREEP component then we would expect to see similar enrichments in heavy Cl and REEs as the lunar samples. As Stannern and the Stannern trend eucrites are characterised by elevated incompatible trace elements, we would also expect these samples to follow the lunar trend and contain enriched Cl isotopic signatures. Stannern shows a slightly enriched bulk La/Yb ratio, compared to the other basaltic eucrites studied here (Fig. 5.7). GRA 98098 (a main group eucrite from Sarafian et al., 2017a) has a La/Yb ratio between Stannern and the main-group basaltic eucrite Millbillillie, but a heavier Cl signature than Stannern, in keeping with the $\delta^{37}$Cl range of Schneck et al. (2016).
Interestingly, NWA 5073 (a Stannern trend eucrite), which has the highest La/Yb ratio, has one of the lowest average \( \delta^{37}\text{Cl} \) observed.

![Figure 5.7: Plot of bulk La/Yb ratios (normalised to chondrites) versus average \( \delta^{37}\text{Cl} \) values of apatite.](image)

\(^1\)Average values from Sarafian et al. (2017a). The reference chondrite is from Lodders (2003). The lunar trendline is based on the data of Boyce et al. (2015) and Barnes et al. (2016).

From Figure 5.7 it is clear that most of eucrites do not show a significant positive correlation between La/Yb ratio and Cl isotope signatures to warrant assimilation of a \( ^{37}\text{Cl} \)-aenriched vKREEP element in their petrogenesis (Mittlefehldt and Lindstrom, 2003; Yamaguchi et al., 2009). There does, however, appear to be a negative relationship between La/Yb and \( \delta^{37}\text{Cl} \) values. The residual eucrites plus the cumulate eucrite Moore County, all display low La/Yb ratios and have significant variations in Cl isotopic compositions with DaG 945 having the lowest observed La/Yb ratio and most elevated \( \delta^{37}\text{Cl} \) values.
5.3.4. Partial melting and diffusion-controlled isotope fractionation

Yamaguchi et al. (2009) suggested that, as a result of extreme metamorphism residual eucrites lost a partial melt, which is indicated by their light REE depletion. The authors proposed that these partial melts could be the contaminant Barrat et al. (2007) required to form the Stannern trend eucrites. As partial melting is known to concentrate Cl at the Earth’s surface (Bonifacie et al., 2008) it is also possible that this process might cause isotopic fractionation. If so, then partial melting of these eucrites could have preferentially scavenged isotopically light Cl. Correlation between the δ$^{37}$Cl and La/Yb ratio in the case of cumulate and residual eucrites, could then be accounted for by differing degrees of partial melting or contamination, with DaG 945 having undergone the largest degree of partial melting and NWA 5073 having experienced the most contamination.

There are problems, however, with this mechanism: at high temperatures Cl is not expected to fractionate significantly (Schauble et al., 2003), and there is no experimental evidence for fractionating Cl isotopes during partial melting, unlike the case with Fe isotopes, where isotopically heavy iron preferentially enters the melt (Weyer and Ionov, 2007), contrary to what would be required of Cl. Another problem with fractionation during partial melting is that this model cannot easily account for Agoult which displays low bulk La/Yb but a range of apatite δ$^{37}$Cl from −3.98 ± 6.08 ‰ to 11.64 ± 7.24 ‰.

Instead of partial melting directly fractionating Cl, if the crust were partially melting and the melt was already saturated with respect to apatite, then the apatite could have exchanged volatiles by diffusion with the melt. Diffusion has the potential to lower the Cl content of the apatite and, assuming the system reached equilibrium, fractionate Cl isotopes, with $^{35}$Cl diffusing faster than $^{37}$Cl (Eggenkamp et al., 1994). Experiments conducted at low
temperatures in aqueous environments demonstrate that only minor fractionation, up to 2 ‰ could be produced by diffusion (Eggenkamp and Coleman, 2009), which decreases with temperature (Eggenkamp, 2014). Recent work, however, by Fortin et al. (2017) on Cl diffusion in dacite melts, suggests fractionations of up to ~ 5 ‰ are possible during convective bubble growth. This suggests that, even under the most favourable conditions, diffusion-controlled Cl fractionation would lead to < 5 ‰ variation of δ\textsuperscript{37}Cl values and could not account for the large variations (> 5 ‰) observed in some eucrites.

As no single process adequately explains the observations, it would suggest that more than one process was involved in establishing the final Cl isotopic composition of eucrites. The variation in δ\textsuperscript{37}Cl of residual eucrites also remains unexplained; discussion of this topic is revisited in Chapter 6, section 6.3.2.

5.3.5. Implications for volatiles in the inner Solar System

Whilst several works have suggested an inner Solar System Cl isotopic composition of ~ 0 ‰ (Magenheim et al., 1994; Sharp et al., 2007; 2013b), other, more recent, studies have considered the possibility that there might be a reservoir of isotopically lighter chlorine with δ\textsuperscript{37}Cl ~ - 4 ‰ (Bridges et al., 2004; Parnallee results in Sharp et al., 2013b; 2016; Williams et al., 2016; Sarafian et al., 2017a). This lighter reservoir was interpreted by Sharp et al. (2016) as representative of the primitive solar nebula, and as Mars is known to have accreted faster than the other terrestrial planets (Dauphas and Pourmand, 2011), it could have recorded the primary nebular value within its interior. Given the rapid accretion of Vesta (Touboul et al., 2015) and the \textsuperscript{37}Cl-depleted isotopic signature observed in this study and the work of Sarafian et al. (2017a) it is also possible that Vesta may have recorded this primary nebular value. The chlorine isotopic variation displayed could then be accounted for by
different degrees of degassing of a magma ocean. Smaller bodies, such as Vesta, would degass more efficiently than larger bodies owing to a greater surface area to volume ratio and coupled with the more rapid accretion time could preserve significantly more heterogeneity than larger, more slowly-forming planets. The Moon is thought to have formed significantly later than Vesta (e.g. Bottke et al., 2015), but still sufficiently early to have incorporated this primitive reservoir during accretion (as shown by the δ37Cl − 4 ‰ in lunar meteorite MIL 05035; Boyce et al., 2015). Most of the lunar samples display terrestrial-like or 37Cl-enriched compositions (e.g. Sharp et al., 2010b; Boyce et al., 2015; Barnes et al., 2016) though it is possible that material with lighter isotopic signatures, below the MIL 05035 data point, has yet to be discovered. Bellucci et al. (2017), however, show that the negative δ37Cl values (− 5.6 ‰ to − 2.7 ‰) observed in some martian meteorites are associated with core-rim relationships and increased concentrations in all halogens. These authors interpreted this as a rim resulting from reaction with martian brines and, therefore, no isotopically light nebula need be invoked. These authors also note that phosphates that do not show grain-scale heterogeneities record an isotope composition similar to Earth and chondrites, further calling into question the isotopically light nebula reservoir. As no core-rim zonation is observed in apatite from eucrites and non-zero δ37Cl values are not typically associated with increased Cl, reaction-rims do not appear to be a viable mechanism for Cl fractionation in eucrites, still leaving the isotopically light nebula reservoir a possibility.

The strikingly similar volatile content and isotopic composition of the anomalous eucrite Pasamonte (Sarafian et al., 2017a) with basaltic eucrites and terrestrial values, supports a common volatile reservoir and processes for the asteroid belt. This could be further strengthened by the analysis of other anomalous achondrites for their volatile content and isotopic compositions.
5.4. Conclusions

In general, most Solar System materials exhibit a relatively narrow range in bulk and apatite Cl isotope compositions, with terrestrial rocks, martian and chondritic meteorites having $\delta^{37}$Cl values of $\sim -5.6$ to $\sim +1.8$ ‰. Lunar rocks, however, appear to be an exception, displaying a significant range in their bulk and apatite $\delta^{37}$Cl values from $-4$ to $+36$ ‰. As the Howardite-Eucrite-Diogenite (HED) suite of meteorites represents the largest suite of crustal and sub-crustal rocks available from a differentiated basaltic asteroid, understanding the volatile inventories of the eucrites can help us to constrain the processes that operated on asteroid parent bodies early in the Solar System history.

Here the abundance and isotopic composition of Cl in apatite was determined for seven eucrites representing a broad range of textural and petrological characteristics. Apatite Cl abundances range from $\sim 25$ to $4900$ ppm and the $\delta^{37}$Cl values range from $-3.98$ to $+35.6$ ‰. Samples with lower measured $\text{H}_2\text{O}$ content typically were also enriched in $\delta^{37}$Cl but no correlation between $\delta^{37}$Cl and $\delta\text{D}$ values was observed. Modelled Rayleigh fractionation and a strong positive correlation between bulk $\delta^{66}\text{Zn}$ and apatite $\delta^{37}$Cl support the hypothesis that Cl degassed as metal chlorides, predominately as $\text{ZnCl}_2$, in a hydrogen poor environment. In the case of lunar samples, it has been noted that $\delta^{37}$Cl values of apatite increase with increasing bulk La/Yb ratio, this geochemical relationship is thought to have been established during the degassing history of the lunar magma ocean. Interestingly, most eucrites show a negative correlation with bulk La/Yb ratio. Recently, isotopically light Cl values have been suggested as recording the primary solar nebular signature. If this is the case then Vesta, which accreted rapidly and early in Solar System history, might also record this primary nebular signature corresponding to the most $^{37}$Cl-depleted values measured.
Chapter Five: Chlorine Isotope Variation in Apatite from Eucrites

...here. The significant variation in Cl isotope composition seen within the eucrites could then be related to magmatic processes, such as later degassing.

Based on the results presented here, the following conclusions can be drawn:

- The abundance and isotopic composition of Cl recorded by apatite from basaltic eucrites display a similar range in $\delta^{37}$Cl values to those reported previously for eucrites (Schneck et al., 2016; Sarafian et al., 2017a). Residual eucrites, particularly DaG 945, display a large range in compositions similar to lunar apatite (e.g. Boyce et al., 2015; Barnes et al., 2016).

- The results obtained here show a weak negative correlation between Cl abundance and $\delta^{37}$Cl values. Samples enriched in heavy Cl are also relatively H$_2$O poor. DaG 945 and Moore County display both of these trends and are in keeping with the degassing of metal chlorides in an H poor environment (Sharp et al., 2010b).

- There is no obvious correlation between $\delta^{37}$Cl and $\delta$D values of apatite.

- A strong positive correlation ($R^2 = 0.91$) between bulk $\delta^{66}$Zn and $\delta^{37}$Cl is observed suggesting that ZnCl$_2$ could have been the degassing metal chloride. A weaker, negative correlation is observed between bulk K content and $\delta^{37}$Cl which could suggest contemporaneous KCl degassing.

- When compared with $\delta^{37}$Cl of apatite, the bulk La/Yb ratios of eucrites appear to follow a trend opposite to that observed for the Moon (Boyce et al., 2015; Barnes et al., 2016), suggesting that contamination of eucritic magmas by a ‘vKREEP’ component (if that took place) is unrelated to the Cl isotope enrichments observed in apatite.
The data presented in this study would suggest that the mechanism of $^{37}$Cl isotope enrichment on Vesta is likely to have been heavily controlled by the degassing of Cl in the form of metal chlorides. The light isotopic signature seen in Agoult could potentially be recording the primary nebular Cl isotope composition which is eluded to in recent studies (e.g. Sharp et al., 2016; Williams et al., 2016) and the variation within the eucrites could be due to different degrees of degassing of metal chlorides, specifically ZnCl$_2$ and possibly KCl. Additional Zn isotope measurements of samples measured here could help to further constrain this hypothesis. The timing of degassing, however, remains unknown.
Chapter Six: Summary and Further Work

6.1. Introduction

The work presented in this thesis provides new insights into the origin and history of volatiles in eucrites whilst also presenting the first comprehensive characterisation of the mineral compositions, bulk major and trace elements and oxygen isotopic composition of the anomalous eucrite Emmaville. Findings from this research also have broader implications for the field of planetary science in general. The confirmation of Emmaville as an anomalous eucrite, derived from a separate parent body increases the number of possible basaltic parent bodies in the asteroid belt (Chapter 3). The hydrogen isotopic compositions of apatite studied here have implications for water source(s) and timing of volatile accretion in the inner Solar System (Chapter 4). Finally, the variation in chlorine isotopic composition of apatite within the eucrites, and especially the isotopically light signature observed in one sample, has ramifications for the evolution of the HED parent body as well as the chlorine isotopic composition of the solar nebula and the magmatic processes that operated on differentiated asteroids (Chapter 5).

At the start of this project, virtually no H or Cl isotope data existed in the published literature on apatite in eucrites and therefore, much was unknown about the history of these volatiles in eucrites and their parent body. At present only four (including one from this work) publications exists on H and Cl in eucrite apatite and, therefore, this field is relatively new and unexplored. This thesis has significantly expanded the existing, relatively limited dataset of volatile abundance and isotopic compositions for the mineral apatite found in the eucrites. The aim of the study was to include a diverse sample set, both in terms of metamorphic and
geochemical trends. The hydrogen abundance and isotopic composition data obtained for the studied eucrites is comparable to those observed in the lunar, terrestrial, and carbonaceous chondrite samples. Chlorine isotopes show significant fractionation in samples with low Cl and H$_2$O abundances, a feature similar to that observed in lunar samples. In the case of the Moon, this feature is thought to be caused by degassing of metal chlorides in a H poor environments. In eucrites samples that contain appreciable Cl and H$_2$O, little fractionation is observed. The data presented in this thesis points towards the presence of a homogenous inner Solar System volatile reservoir that existed early enough to be incorporated into the accreting HED parent body.

In this chapter the main findings of the previous chapters are synthesised, related to the original research questions of the PhD thesis (c.f. Chapter 1, section 1.5), and their broader implications for small bodies and the Solar System are discussed.

6.2. Summary of main findings

6.2.1. Chapter 3: Characterisation of Emmaville

It has long been known that several meteorites within the eucrite group display anomalous geochemical characteristics (e.g. Pasamonte, Ibitira; Wiechert et al., 2004; Mittlefehldt, 2005). The study of these anomalous eucrites allows us to understand more completely the number of parent asteroids represented by eucrite-like basalts, as well as further constrain the chemical and isotopic diversity represented within the HED meteorite suite. In Chapter 3 one such anomalous eucrite, Emmaville, is studied in detail in terms of its mineral composition, bulk major and trace elements, and oxygen isotopic composition. It was found that despite appearing texturally anomalous, being very fine-grained (< 60 µm)
compared to typical basaltic eucrites (50 - 100 µm for other fine-grained basaltic eucrites; Mayne et al., 2009), the mineral compositions and major and trace element abundances of Emmaville were almost indistinguishable from typical basaltic eucrites. The O isotopic composition of Emmaville, however, is anomalous: three separated fractions were analysed; two of these fractions had similar O isotope compositions to the bulk sample analysed by Greenwood et al. (2013; 2016) ($\Delta^{17}O = 0.139 \pm 0.016 \, \%_o \, 1\sigma$), with the third fraction having a slightly elevated $\Delta^{17}O$ (− 0.124 ‰) and higher $\delta^{18}O$ (+ 4.873 ‰) compared to the bulk Emmaville, possibly because this fraction has a higher feldspar content than the other two fractions. As no evidence for any exogenous material (e.g., chondritic clasts) was observed in the two thin sections studied, combined with a simple mixing model and striking similarity to typical basaltic eucrites, it was concluded that simple mixing of impactor material did not impart the anomalous O isotopic composition. On an oxygen isotope plot (See Chapter 3, Fig. 3.4) data from Emmaville also falls in a similar region to the anomalous meteorites Bunburra Rockhole, A-881394 and EET 92023. It would, therefore, seem plausible that all four of these samples are derived from a single HED-like parent body that is isotopically distinct (at least in terms of O isotopes) from the HEDs, but geochemically similar in composition.

This work was the first, comprehensive mineralogical and petrological study of the Emmaville eucrite, providing new and precise measurements of the mineral composition and bulk major, minor, and trace elements, as well as modal abundance data. During this study, mineral and bulk compositions were also collected for another less well studied eucrite, Tirhert, and these are amongst the first results for this sample. Additional samples were also analysed adding new geochemical data to the existing literature (e.g. for Roda; Birck and Allègre, 1978).
Chapter Six: Summary and Further Work

It was anticipated that suitable apatite grains would be found within the thin-sections of Emmaville studied here, for H and Cl isotope measurements, which would have allowed comparisons between anomalous achondrites and typical basaltic eucrites. Unfortunately, however, only a single apatite grain, too small to be analysed, was found in the Emmaville sections that were studied, and it was not possible to obtain additional thin sections for study.

6.2.2. Chapter 4: Hydrogen isotopes in eucrites

Whilst the volatile inventory of the Moon and Mars has been well studied for a range of lithologies and phases (e.g. Saal et al., 2008; 2013; McCubbin et al., 2010a; 2014; 2016; Hauri et al., 2011; Barnes et al., 2013; 2014; Filiberto et al., 2016; Robinson et al., 2016b), comparatively few data exist for the HED meteorites. With only one peer-reviewed study, almost contemporaneous to this work, for hydrogen isotopes (Sarafian et al., 2014) and chlorine isotopes (Sarafian et al., 2017a). Chapter 4 explores the abundance and isotopic composition of water in apatite in one cumulate eucrite and five basaltic eucrites one of which (Stannern) had also been studied previously by Sarafian et al. (2014). The present study provides approximately a fourfold increase in the number of δD/H₂O analyses available for apatite in eucrites and explores a broader range of petrological and geochemical trends compared to the previous study, including cumulate eucrites and residual basaltic eucrites. The results from this work record the indigenous H-isotopic composition of the HED parent body and significantly expand the previously reported range of H₂O abundance (previously ~ 650 to ~ 2600 ppm H₂O) with values ranging from ~ 30 to ~ 3500 ppm H₂O. These abundances are associated with a weighted average δD value of −34 ± 67 ‰ (n = 32; 95 % confidence), within uncertainties of the upper limit of the Sarafian et al. (2014) weighted average (δD of −162 ± 127 ‰). This work also demonstrated no resolvable
difference between the H$_2$O content and the δD values of apatite based on metamorphic grade or geochemical trend.

This study was also able to demonstrate that samples with low water contents such as DaG 945 and Moore County are similar in water content to the lunar highlands samples studied by Barnes et al. (2014). Based on results from previous H isotope studies of carbonaceous chondrites (Robert, 2006; Alexander et al., 2012), the Moon (Saal et al., 2013; Tartèse et al., 2013; 2014b; Anand et al., 2014; Barnes et al., 2014) and Earth (Lécuyer et al., 1998), it was concluded that there was a common source of water in the inner Solar System. Given the ancient ages of eucrites (typically 4547 to 4559 Ma; Misawa et al., 2005; Zhou et al., 2013), results from this study are consistent with the hypothesis that these volatiles must have accreted early in the history of the Solar System and could also have been added early to the Earth, rather than gained during a late accretion event. Results from this chapter are fully consistent with the hypothesis 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.

### 6.2.3. Chapter 5: Chlorine isotopes in eucrites

The final data chapter of this thesis (Chapter 5) reports new Cl isotope measurements in apatite in eucrites, to determine the variation in Cl isotopic composition among different eucrite groups. Five of the eucrites studied here were also analysed for H isotope composition (Barrett et al., 2016) and in some cases Cl analyses could be made on the same grain as previously used for the H measurements (Barrett et al., 2016). This has provided a combined dataset and helped to constrain more completely the volatile history of these particular apatite grains and samples. Because of the anomalous Cl isotope signature
observed in the residual eucrite DaG 945, two additional residual eucrites (Agoult and NWA 2362), not previously measured for H isotopes, were acquired for measurement of Cl isotopic composition. This enabled further investigation of the volatile history of the residual eucrites and any potential differences these samples may display compared with eucrites of different geochemical trends. A subsequent repeat analysis of DaG 945 apatite confirmed the very heavy $\delta^{37}$Cl composition detected in this sample.

The results of this study are among the first Cl isotope analyses for eucrites (a ~ 40 % increase on previous dataset; Sarafian et al., 2017a) and show that the apatite in eucrites display significant variation in terms of Cl content and isotopic composition. The basaltic eucrites form a tight cluster with Cl contents ranging from ~ 1440 to 2030 ppm Cl with $\delta^{37}$Cl values close to 0 ‰, though one apatite grain in Stannern has slightly elevated $\delta^{37}$Cl at + 3.45 ± 1.39 ‰. Data from these basaltic eucrites broadly agrees with the recent work of Sarafian et al. (2017a), although their basaltic samples have a larger range in Cl content (~ 650 pm in Juvinas to ~ 4000 ppm in Pasamonte). The cumulate eucrite Moore County typically displays a lower Cl abundance (~ 100 to ~ 700 ppm) than basaltic eucrites and with $\delta^{37}$Cl values ranging from near 0 ‰ to + 13.1 ± 3.01 ‰. The residual eucrites are the subgroup that show the most variation of chlorine in apatite; DaG 945 and Agoult have very low Cl contents (< ~ 60 ppm), whilst in contrast, NWA 2362 has the highest Cl content measured in this study, at ~ 4000 ppm Cl. The residual eucrites also display the widest range of chlorine isotopic compositions with values ranging from ~ − 4 ‰ to ~ + 36 ‰, some of the highest values recorded in Solar System materials and significantly more enriched in $\delta^{37}$Cl than the samples studied by Sarafian et al. (2017a) ($\delta^{37}$Cl of − 4.61 ‰ to + 8.94 ‰).

Where H isotope data are available, no obvious correlation was observed between $\delta^{37}$Cl and $\delta$D values of apatite. In all samples, apatite display consistent $\delta$D values (Sarafian et al.,
2014; Barrett et al., 2016) and varying of $\delta^{37}$Cl values. Such a lack of correlation is also observed in lunar basalts (Boyce et al., 2015). With regards to water content, however, unfractionated $\delta^{37}$Cl values (i.e. close to 0 ‰) are seen across the entire range of H$_2$O abundances, but elevated $\delta^{37}$Cl values are only present in apatite that contain < 500 ppm H$_2$O. This supports the prevalent theory that Cl degassed in a hydrogen-poor environment, where HCl was not the degassing phase (Sharp et al., 2010b). A strong positive correlation ($R^2 = 0.91$) between bulk $\delta^{66}$Zn and apatite $\delta^{37}$Cl is observed, suggesting that ZnCl$_2$ is probably the main phase pertinent to the degassing process. A weaker, negative correlation ($R^2 = 0.31$) is observed between bulk K content and apatite $\delta^{37}$Cl, which could suggest a minor component of KCl degassing contemporaneously with the ZnCl$_2$.

Study of lunar samples led to the suggestion that the relationship for apatite between REE content and Cl isotopic composition was the result of contamination of a degassed KREEP component (Boyce et al., 2015; Barnes et al., 2016). Here, it was found that the La/Yb ratio of eucrites appeared to follow a trend opposite to that observed for the Moon. This suggests that contamination of a ‘vKREEP’ component, with a fractionated signature from earlier degassing, is not the cause of the heavy Cl enrichment observed. Chapter 5 also outlines how this contamination process could be linked with the formation of the Stannern trend and residual eucrites through a process of partial melting of a main group basalt followed by contaminating of a second basalt magma by this crustal melt. This would result in a residual eucrite with an elevated Cl isotopic signature. The contaminated eucrite would have a light Cl isotope signature, with different levels of partial melting leading to differing levels of contamination (see Chapter Five Fig. 5.6). Partial melting, however, along with diffusion, cannot significantly fractionate Cl isotopes to the levels seen within samples such as DaG 945. The variation displayed within the eucrites on balance, therefore, appears to be mainly
caused by different degrees of degassing of metal chlorides owing to the significantly stronger correlation between bulk $\delta^{66}$Zn and apatite $\delta^{37}$Cl, supported by modelling of degassing curves for a variety of metal chlorides.

These results also have some interesting implications for the Cl inventory of the inner Solar System. Whilst several studies have suggested an inner Solar System Cl isotopic composition of $\sim$ 0 ‰ (Magenheim et al., 1994; Sharp et al., 2007; 2013b), others have suggested the possibility of a lighter isotopic reservoir for Cl with a $\delta^{37}$Cl of $\sim$ −4 ‰ (Bridges et al., 2004; Sharp et al., 2013b; Sharp et al., 2016; Williams et al., 2016; Sarafian et al., 2017a). This isotopically lighter reservoir was interpreted by Sharp et al. (2016) to be representative of the primitive solar nebula, and might be recorded in other planetary bodies. For example, since Mars is known to have accreted faster than the other terrestrial planets (Dauphas and Pourmand, 2011), it could have recorded the primary nebular value within its interior. Similarly given the rapid accretion of Vesta (Touboul et al., 2015) and the $^{37}$Cl-depleted isotopic composition observed in this study ($−3.98 ± 6.08$ ‰) and the work of Sarafian et al. (2017a), it is also possible that Vesta may have recorded this primary nebular signature. The wide range of isotopic compositions noted on Vesta and in the Moon (see Barnes et al., 2016) also point to a more heterogeneous inner Solar System than previously thought, with larger planetary bodies recording a rather homogenous signature whilst smaller bodies display a wide range of chlorine isotope values.

In a nutshell, this chapter provides some of the first Cl abundance and isotopic compositions for apatite in eucrites and the only data for cumulate and residual eucrites.

6.3. Implications for the evolution of minor bodies in the inner Solar System
6.3.1. Isotopically anomalous eucrites

6.3.1.1. Impact mixing and isotope anomalies

Chapter 3 (section 3.3.3) outlines how impact mixing could give rise to the anomalous O isotope signature observed in Emmaville. As discussed in that section, impact mixing of ordinary chondrite material (H or L) cannot simultaneously satisfy the Ni abundance and the O isotope signature. Impact mixing of an angrite-like component is also ruled out owing to the near identical bulk major and trace element abundances of Emmaville when compared with basaltic eucrites. An impact origin for Emmaville is possible, however, if the impactor had an as-yet-unknown oxygen isotopic composition. This impactor would possibly be non-chondritic (i.e. low siderophile element content) to keep the Ni content low and would require an elevated Δ^{17}O relative to the HEDs (> - 0.246 ± 0.014 ‰; Greenwood et al., 2014) to produce the observed oxygen isotopic composition.

Depending on the relative elevation in Δ^{17}O and Ni content, the percentage of admixed impactor could vary significantly. For example, mixing of a component with high Δ^{17}O and elevated Ni content would require very low percentages of mixing (< 1 %) and could possibly be why no exogenous material is observed within Emmaville. Smaller relative elevations in Δ^{17}O and Ni abundance would require the impactor to be chemically very similar to typical basaltic eucrites. The implications for this second hypothesis are outlined in section 6.3.1.2.

Impact mixing also has implications for other anomalous eucrites. With the exception of NWA 1240 and NWA 011 (and their pairs, e.g., NWA 2400), which plot below the eucrite fractionation line (EFL; see Chapter 1, Figure 1.11), all known anomalous basaltic achondrites plot between the EFL and the angrite fractionation line (AFL) (Greenwood et
For samples which lie just outside the 3σ envelope of the EFL (e.g. Pasamonte and Dhofar 007; Metzler et al., 1995; Yamaguchi et al., 2006) impact mixing is a viable solution to produce the observed oxygen isotope compositions especially when combined with highly elevated siderophile element contents, such as seen in Dhofar 007 and to a lesser extent Pasamonte (Dale et al., 2012; Day et al., 2012). Samples with oxygen values further from the EFL, but also with considerable siderophile element variations such as EET 92023 (Mittlefehldt and Lindstrom, 1996; Kaneda and Warren, 1998) could also be explained by impact-related mixing. Bunburra Rockhole displays a wide range in both $\Delta^{17}O$ and $\delta^{18}O$ which varies with lithological type (Benedix et al., 2017); however, the Ni content is depleted relative to typical eucrites (Spivak-Birndorf et al., 2015). This could suggest that Bunburra Rockhole, similar to Emmaville, would need a unique impactor; different lithologies within Bunburra Rockhole would require incorporation of different amounts of impactor to account for its O isotope variation and Ni depletion. However, for Bunburra Rockhole, its chromium isotopic composition (another powerful discriminator for parent body identification), is significantly different from HEDs, implying that an origin for Bunburra Rockhole involving some form of impact mixing on the eucrite parent body is unlikely.

### 6.3.1.2. Implications for the formation of minor bodies in the inner Solar System

With Chapter 3 concluding that Emmaville is likely to come from a separate parent body from that of the eucrites (i.e., not Vesta), the implications of this conclusion for the formation of minor bodies needs to be discussed. Despite appearing texturally anomalous, Emmaville is nearly indistinguishable from typical basaltic eucrites in terms of mineral compositions, major and trace element compositions, but is separated from them by its oxygen isotopic composition. This suggests that the formation of achondrite parent bodies must have
similarities in terms of formation processes and starting compositions. In terms of parent bodies, the most straightforward way to reconcile the major and trace element compositions of the eucrite-like achondrites is for the inner section of the asteroid belt, near Vesta, to be composed of Vesta-like planetesimals. Variation in oxygen isotopic composition may result from formation of parent objects at different heliocentric distance (Young and Russell, 1998). Separate parent bodies for the eucrites and anomalous eucrites could result from impact of elementally similar parent objects by isotopically distinct impactors, leading to a population of Vesta-like bodies with minimal major and trace element variation but different O isotope compositions.

6.3.2. Volatile inventory of minor bodies

Chapters 4 and 5 address the research questions 1 - 4 (question 4 is also discussed below) of the thesis (Chapter 1, section 1.5). The hydrogen and chlorine inventory and isotopic composition of several eucrites was established and secondary effects, particularly the potential effects of terrestrial alteration on H isotopes, were found to have no observable effect (answering questions one and two in section 1.5; Figure 6.1). As suggested in Chapter 4, this means that apatite grains are primary and unaltered allowing implications for Vesta, other small bodies, and the inner Solar System (see section 6.4 for more on the inner Solar System) to be considered.

With regards to the third question outlined in the introduction: from the results of this thesis and published literature (Sarafian et al., 2013; 2014; 2017b), the H isotopic signature of eucrites is homogenous, but H\textsubscript{2}O abundance is variable, though no correlation between H\textsubscript{2}O and metamorphic grade is observed. Cl isotopes, however, are variable and appear to be linked to a geochemical trend with cumulate and residual eucrites typically having lower Cl
abundances but elevated $\delta^{37}\text{Cl}$ values. The cause of this Cl isotope fractionation, at least for some samples (e.g. DaG 945), would appear to be the degassing of metal chlorides, specifically ZnCl$_2$. Agoult has very low Cl content (27 – 44 ppm) and variable $\delta^{37}\text{Cl}$ values ($-3.98 \%_o$ to $+8.96 \%_o$). For degassing to be the mechanism behind the observed fractionation in Agoult, it would be expected that apatite grains would need to contain variable H, potentially owing to multiple phases of apatite crystallisation. In this scenario, apatite with low $\delta^{37}\text{Cl}$ values would contain appreciable H$_2$O (possibly ~ 1000 ppm similar to basaltic eucrites with $\delta^{37}\text{Cl}$ values of 0 \%o), therefore buffering fractionation by degassing with the formation of HCl; once H had been depleted, degassing would fractionate Cl, accounting for the more enriched $\delta^{37}\text{Cl}$ values in Agoult. The hydrogen isotopic composition of Agoult would then be expected to vary with the amount of HCl degassing that has occurred in each apatite, with low $\delta D$ values giving near-undegassed signatures and severely degassed apatite having extremely elevated $\delta D$ values. Unfortunately, without hydrogen isotope data to support this hypothesis we cannot invoke degassing of ZnCl$_2$ to account for the chlorine data from Agoult. NWA 2362 data for Cl also cannot readily be explained by simple degassing, consequently, a different mechanism may be required to explain these results. Residual eucrites are believed to have experienced short, high temperature reheating events superimposed on the longer duration global metamorphism (Yamaguchi et al., 2009). These reheating events could have been caused by impact events and/or intrusions of hot magma (Fig. 6.1; Yamaguchi et al., 2009). If the residual eucrites experienced differing degrees/numbers of metamorphic events, then residual eucrites would have been altered to differing degrees, which could also have affected their isotopic compositions to differing extents. A problem with this scenario, however, is that partial melting is not known to fractionate Cl isotopes and, if it did, the degree to which it would fractionate the isotopes is likely to be small owing to the high temperatures involved (Schauble et al., 2003). If impacts
are the cause of these short metamorphic events, then it is not impossible that an impactor with a different $\delta^{37}\text{Cl}$ value could have contaminated the residual eucrites producing anomalous $\delta^{37}\text{Cl}$ values. Unfortunately, however, as none of the residual eucrites studied here appear to be shocked, nor contain any obvious exogenous material, this does not seem a viable option to explain the observed variation in chlorine data. Finally, another solution to the observed variation in Cl isotopes is that the meteorites are sampling different Cl isotope reservoirs within Vesta. This would, however, require the vestan magma ocean not to have homogenised; given the constancy of O and H isotopic compositions, (e.g.
Greenwood et al., 2014; Sarafian et al., 2014; Barrett et al., 2016) this does not seem to be a likely possibility.

Figure 6.1: A cartoon depicting a cross-section through Vesta displaying potential locations for different eucrite types and their corresponding volatile isotopic compositional ranges. Volatile data are taken from Sarafian et al. (2014; 2017b); Barrett et al. (2016). Crustal thickness from Mandler and Elkins-Tanton (2013)
The striking homogeneity of H isotopes in apatite from the suite of eucrites that were investigated in this thesis has implications for other minor bodies in the inner Solar System. With regards to anomalous eucrites, Sarafian et al. (2014; 2017a) measured the anomalous eucrite Pasamonte and found identical H and Cl isotope systematics to typical basaltic eucrites. As mentioned in chapters 4 and 5, this would suggest that the inner Solar System is indeed homogenous with regards to at least H and possibly Cl. If this is the case then we would expect Emmaville to be similar to basaltic eucrites with regards to its H and Cl systematics and volatile abundances. Samples with more variability, such as Bunburra Rockhole, should have homogenous H isotopes, but could display variability in Cl isotopes and volatile content (both H2O and Cl) based on the distinct coarse- and fine-grained lithologies within the sample. Recently, a study conducted by Sarafian et al. (2017c) measured silicophosphate grains within angrites to constrain further the timing and flux of water into the inner Solar System. Unfortunately, results from the angrite D’Orbigny suggest that silicophosphates in this sample had degassed, although the related angrite, Sahara 99555, had similar δD values to eucrites (Figure 4.3) (Sarafian et al., 2017d).

6.4. Implications for the inner Solar System

The volatile inventory and isotopic composition of eucrites has implications not just for small bodies, as discussed above, but also for the inner Solar System in general (research question 4 in Chapter 1, section 1.5). Given that HEDs formed very early in the history of the Solar System, their volatile inventories allow us to explore source(s) and processes affecting volatile elements at some of the earliest stages of the Solar System formation. Chapter 4 demonstrates that the H isotopic composition of eucrites appears to be homogenous and supports the hypothesis that water accreted to Vesta early (Sarafian et al., 2014). The H isotopic composition of Vesta is also similar to the rest of the inner Solar
System, particularly the Earth (Lécuyer et al., 1998), lunar highland samples (Barnes et al., 2014), and carbonaceous chondrites (Robert, 2006; Alexander et al., 2012), suggesting that there was a homogenous reservoir of hydrogen isotopes early on in inner Solar System history.

The distribution of volatiles, however, does not appear to be homogenous. Marrocchi et al. (2018) used the oxygen isotopic composition of aqueously-formed fayalite grains in carbonaceous chondrites to infer the water/rock ratio of the different groups. The low water/rock ratio (which increases with proximity to the snowline) and O isotopic composition indicate these groups formed in the main asteroid belt and accreted locally derived water (Figure 6.2). As the carbonaceous chondrites are part of the inner Solar System and have similar D/H ratios to the other bodies in the inner Solar System, delivery of these asteroids to the proto-Earth or proto-Vesta would only increase the water content of the bodies and not the D/H ratio. This would need to happen sufficiently early to fit with the date of formation of the eucrite parent body and so, does not require the late delivery of volatiles—but also does not preclude additional delivery at a later date (such as the late delivery of volatiles to the Moon; Bottke et al., 2010).

As chlorine is strongly hydrophilic it would be expected that the Cl abundance and isotopic composition of the inner Solar System would reflect similar patterns as water. There appears, however, to be no obvious correlation between δD and δ^{37}\text{Cl} in eucrites, a features also observed in lunar basalts (Boyce et al., 2015) (Chapter 5, section 5.3.2). Whilst a δ^{37}\text{Cl} value of ~ 0 ‰ has been suggested for the inner Solar System (Magenheim et al., 1994; Sharp et al., 2007; 2013b), other studies consider an isotopically lighter chlorine reservoir with δ^{37}\text{Cl} ~ − 4 ‰ (Bridges et al., 2004; Sharp et al., 2013b; Sharp et al., 2016; Williams et al., 2016; Sarafian et al., 2017a). This ^{37}\text{Cl}-depleted reservoir is disputed by Bellucci et al. (2017) for
Mars, who suggest that the isotopically light martian compositions are reaction rims caused by interactions with martian brines. As brines on Vesta are unlikely, given the conditions at the surface, and non-zero $\delta^{37}$Cl values are not generally associated with increased Cl (in fact the heaviest $\delta^{37}$Cl values are observed in one of the most Cl-poor samples, DaG 945) the production of isotopically light reaction rims is an unlikely process to explain the chlorine isotope compositions observed in eucrites (Sarafian et al., 2017a).
Figure 6.2: 1) Separation of non-carbonaceous chondrites (NCC) and carbonaceous chondrite (CC) reservoirs as depicted by Kruijer et al. (2017). Early Jupiter formation (~ 1 Ma after formation of Solar System) would act as a barrier against inward transport of solids, and therefore mixing, across the disk. 2) Key observations of O and H isotopic compositions in the protoplanetary disk at odds with Kruijer et al. (2017); (Marrocchi et al., 2018). 3) Scenario proposed by Marrocchi et al. (2018) for the preservation of $^{16}$O-rich and D-poor water in the inner Solar System. Jupiter acts as a barrier to significant inward transport of outer Solar System material. 4) Scenario proposed for chondrites studied in Marrocchi et al. (2018) for the accretion of $^{16}$O-rich D-poor water by hydrated carbonaceous asteroids. Increasing water/rock (w/r) ratios of the different chondrite groups...
reflect the different chondrite asteroids accreted close to the snow line, at increasing heliocentric distances. Vesta would likely have formed significantly further in than these groups. 5) Water rich chondrite asteroids provide Vesta its water whilst preserving a similar D/H ratio. Diagram modified after Marrocchi et al. (2018).

If $^{37}$Cl-depleted $\delta^{37}$Cl values do indeed represent the primordial nebula values then Jupiter, which formed within ~ 1 Ma of the formation of the Solar System and is believed to have captured the protosolar nebula D/H ratio ($- 865 \%$; Lellouch et al., 2001; Kruijer et al., 2017), should also have captured a primordial, isotopically light Cl composition and retained it, assuming no fractionation of Cl in its atmosphere. It would, therefore, be very interesting to acquire the Cl isotopic composition of Jupiter as a light primordial nebula would require some mechanism to fractionate the inner Solar System so that most of the data plot at ~ 0 \%.

6.5. Suggestions for further work

The work completed as part of this PhD thesis has highlighted the complexity of the volatile inventory of eucrites. With the study of the history of volatiles in HEDs in its infancy, more data are required to further constrain the volatile inventory of the HED parent body to understand the origin of volatiles in the inner Solar System. As such, there are plenty of avenues that can be explored.

An obvious starting point is to expand on the current data sets for hydrogen isotopes (Sarafian et al., 2014; Barrett et al., 2016) and chlorine isotopes (Sarafian et al., 2017a), specifically for samples with well understood lithological histories that are part of petrological and geochemical trends that are underrepresented in the current data set (e.g., Stannern trend and cumulate eucrites). Additional data would further test the hypothesis that these distinct subgroups of eucrites have broadly similar $\delta$D values and potentially shed more
light into the variation observed in $\delta^{37}$Cl. Obtaining the cosmic-ray exposure ages for samples DaG 945 and DaG 844 would prove useful to constrain more fully the role of spallogenic D present in these samples. Currently, the oldest exposure age for HED meteorites of 38 Ma has been used for these samples to provide a maximum correction for spallogenic D and, therefore, H isotope data for these samples may have been overcorrected.

Another logical extension to this work would be the inclusion of in situ measurements of apatite in the diogenite and howardite groups, therefore, encompassing the entirety of the HED suite. Apatite, however, is rare in diogenites and additional care must be taken in the analysis of apatite in howardites to ensure that the grains are indigenous and not from an exogenous source. Analysis of diogenites would provide insight into samples which are believed by some to be more primitive than the eucrites (Barrat et al., 2008; Mandler and Elkins-Tanton, 2013). Given the nature of howardites, it is possible these samples contain clasts of diogenitic and eucritic material which are not commonly seen. Data from within clasts could also be compared to any apatite found in the matrix, provided it can be identified as indigenous. Analysis of anomalous eucrites (e.g. Bouvante, Pasamonte) and anomalous achondrites believed to be from distinct HED-like parent bodies (e.g. Bunburra Rockhole, Emmaville) would allow for comparison between these groups and typical basaltic eucrites and provide additional constraints to the volatile inventory and source(s) not only of the HED parent body, but potentially common or distinct volatile reservoirs in the asteroid belt as well the inner Solar System. This could then be followed up, where possible, by investigating the volatile composition of apatite in other achondrite groups e.g. Angrites (Sarafian et al., 2017c).

As has been recently demonstrated by Boyce et al. (2014), volatile partitioning into apatite is more complex than previously thought, therefore, it cannot be reliably used to calculate
the volatile inventory of the parental magma from which the apatite crystallised. Nominally anhydrous early-formed minerals such as pyroxene, however, do not have this problem and can, therefore, be used to calculate the volatile inventory of the parental melt. Preliminary work conducted by Stephan et al. (2016) on four eucrite pyroxenes provide a weighted average δD of (∼ 241 ± 64 ‰) and an estimate for the maximum H₂O content of eucrite parent melts of ≤ 0.2 wt.%. These pyroxene measurements come from samples where apatite data has already been acquired and the apatite grains are typically ‘wet’. There also appears to be a correlation between the H₂O abundance of the apatite and pyroxene grains which could warrant further study.

Another possible avenue of exploration could be the analysis of other light volatile systems as well as noble gases in HED meteorites. Specifically, C, N, and noble gas measurements could complement the H and Cl isotopic data. Currently there is little data in the way of C, N and noble gases for HED meteorites (Miura and Sugiura, 1993; Grady et al., 1997; Miura et al., 1998; Abernethy, 2014) and additional data would allow for the investigation of the evolution of these elements and their response to factors such as pressure, temperature and melt composition on small asteroidal bodies, as well as the interrelations between different isotopic groups. It was noted in Chapter 5, during Cl isotope analysis, that there is a strong correlation between bulk δ⁶⁶Zn and apatite δ³⁷Cl. Currently, limited data are available for bulk δ⁶⁶Zn (Paniello et al., 2012) and additional analyses of samples either with Cl isotope measurements available for Zn or samples with Zn measurements available for Cl, would be invaluable for further constraining this correlation, which would help confirm the hypothesis laid out in chapter five and identify the fractionation mechanism(s) of Cl in eucrites.

It was also discussed in Chapter 3 that the Cr isotopic composition of Emmaville would be an invaluable additional indicator of the provenance of this anomalous meteorite. If the ε⁵⁴Cr
value for Emmaville were to be similar to Bunburra Rockhole and A881934, with which Emmaville shares similar O isotope values, it would add significant weight to these samples being from the same parent body. If the $\epsilon^{54}$Cr values are similar to the HEDs it would have implications for the impactor hypothesis for the generation of anomalous eucrite-like samples and, potentially, the homogeneity of Vesta.

In conclusion, the emerging field of extra-terrestrial volatiles has made significant progress over the last decade. The new and improved analytical techniques which have become available have allowed for new components within samples and new research areas to be explored. It is because of this pioneering research that there are now possibly even more questions to be answered than before and as such this is an exciting time for research in the field of Solar System volatiles.
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A.1. Chlorine isotope calibrations
A.2. Supplementary material for Chapter 3

A.2.1. Standard values and associated errors

The accuracy of our trace element data is assessed as a percentage relative standard deviation for the BIR-1 reference material, dissolved up in this study, compared to published values using the following formula:

\[
\text{Deviation from reference value} = \left( \frac{\text{Measured Value} - \text{Reference Value}}{\text{Reference Value}} \right) \times 100
\]

The precision of our measurements is assessed by the relative standard deviation from the mean measurement of Tinhert, analysed 4 times throughout the course of the sample run. Uncertainties are presented in Table 8.1 and Table 8.2 and major, minor, and trace elements respectively.

Table 8.1: Measured major element standard values (in wt. % unless otherwise specified). Also shown for comparison are published values for BIR-1 (Flanagan, 1984) converted from wt. % oxide to elemental abundance and the percentage deviation of our measurements from these values.

<table>
<thead>
<tr>
<th>Element</th>
<th>BIR-1 Mass (g)</th>
<th>Published values converted from oxides (Flanagan, 1984)</th>
<th>BIR-1 deviation from published values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.09834</td>
<td>6.02 5.85</td>
<td>2.97</td>
</tr>
<tr>
<td>Al</td>
<td>7.89</td>
<td>8.20 -3.87</td>
<td>-3.87</td>
</tr>
<tr>
<td>K (µg/g)</td>
<td>257</td>
<td>249 3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Ca</td>
<td>9.61</td>
<td>9.51 1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Mn</td>
<td>0.13</td>
<td>0.14 -6.22</td>
<td>-6.22</td>
</tr>
<tr>
<td>Fe</td>
<td>8.06</td>
<td>7.92 1.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Table 8.2: Average values (in µg/g unless otherwise specified) for BIR-1 from this study (n=4). Also shown for comparison are published values for BIR-1 (Eggins et al., 1997) and the percentage deviation of our average from these values.

<table>
<thead>
<tr>
<th></th>
<th>BIR-1 average (n = 4)</th>
<th>Published Values (Eggins et al., 1997)</th>
<th>BIR-1 deviation from published values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
<td>0.09834</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>3.61</td>
<td>3.40</td>
<td>6.15</td>
</tr>
<tr>
<td>Sc</td>
<td>46.8</td>
<td>44</td>
<td>6.26</td>
</tr>
<tr>
<td>Ti (mg/g)</td>
<td>5.75</td>
<td>5.76</td>
<td>0.00</td>
</tr>
<tr>
<td>V</td>
<td>322</td>
<td>313</td>
<td>2.85</td>
</tr>
<tr>
<td>Cr (mg/g)</td>
<td>0.38</td>
<td>0.38</td>
<td>-0.32</td>
</tr>
<tr>
<td>Co</td>
<td>52.0</td>
<td>51.0</td>
<td>2.00</td>
</tr>
<tr>
<td>Ni</td>
<td>163</td>
<td>166</td>
<td>-1.79</td>
</tr>
<tr>
<td>Cu</td>
<td>124</td>
<td>126</td>
<td>-1.56</td>
</tr>
<tr>
<td>Zn</td>
<td>71.6</td>
<td>71.0</td>
<td>0.86</td>
</tr>
<tr>
<td>Ga</td>
<td>15.4</td>
<td>16</td>
<td>-3.90</td>
</tr>
<tr>
<td>Rb (ng/g)</td>
<td>211</td>
<td>240</td>
<td>-12.2</td>
</tr>
<tr>
<td>Sr</td>
<td>111</td>
<td>110</td>
<td>1.32</td>
</tr>
<tr>
<td>Y</td>
<td>17.2</td>
<td>16.5</td>
<td>3.96</td>
</tr>
<tr>
<td>Zr</td>
<td>15.4</td>
<td>14.5</td>
<td>6.00</td>
</tr>
<tr>
<td>Ba</td>
<td>6.72</td>
<td>6.40</td>
<td>4.93</td>
</tr>
<tr>
<td>La</td>
<td>0.62</td>
<td>0.58</td>
<td>6.79</td>
</tr>
<tr>
<td>Ce</td>
<td>1.86</td>
<td>1.85</td>
<td>0.60</td>
</tr>
<tr>
<td>Pr</td>
<td>0.37</td>
<td>0.37</td>
<td>1.22</td>
</tr>
<tr>
<td>Nd</td>
<td>2.44</td>
<td>2.35</td>
<td>3.96</td>
</tr>
<tr>
<td>Sm</td>
<td>1.15</td>
<td>1.10</td>
<td>4.18</td>
</tr>
<tr>
<td>Eu</td>
<td>0.53</td>
<td>0.52</td>
<td>2.22</td>
</tr>
<tr>
<td>Gd</td>
<td>1.81</td>
<td>1.97</td>
<td>-8.15</td>
</tr>
<tr>
<td>Tb</td>
<td>0.38</td>
<td>0.38</td>
<td>-0.18</td>
</tr>
<tr>
<td>Dy</td>
<td>2.57</td>
<td>2.50</td>
<td>2.92</td>
</tr>
<tr>
<td>Ho</td>
<td>0.59</td>
<td>0.57</td>
<td>3.83</td>
</tr>
<tr>
<td>Er</td>
<td>1.87</td>
<td>1.70</td>
<td>9.96</td>
</tr>
<tr>
<td>Yb</td>
<td>1.66</td>
<td>1.60</td>
<td>3.50</td>
</tr>
<tr>
<td>Lu</td>
<td>0.25</td>
<td>0.25</td>
<td>-1.28</td>
</tr>
<tr>
<td>Hf</td>
<td>0.63</td>
<td>0.56</td>
<td>11.7</td>
</tr>
<tr>
<td>Pb (ng/g)</td>
<td>2813</td>
<td>3000</td>
<td>-6.24</td>
</tr>
<tr>
<td>Th (ng/g)</td>
<td>32.8</td>
<td>30</td>
<td>9.18</td>
</tr>
<tr>
<td>U (ng/g)</td>
<td>9.54</td>
<td>10</td>
<td>-4.63</td>
</tr>
</tbody>
</table>
A.2.2. Confirmation of mineral quartz via Raman spectroscopy

Subsequent to the Raman analysis of Emmaville, the generated data were compared to database spectra using the CrystalSleuth program (Figure 8.1).

Figure 8.1: Example raman spectra for the silica phase of Emmaville. The blue quartz line represents archive data taken from CrystalSleuth.
A.3. Supplementary material for Chapter 5

A.3.1. References associated with Figure 5.3

References for bulk data are as follows: Agoult (Yamaguchi et al., 2009), Cachari (Bogard et al., 1985), DaG 945 (Yamaguchi et al., 2009), GRA 98098 (Warren et al., 2009), Juvinas (Barrat et al., 2007), Millbillille (Barrett et al., 2017), Moore County (Barrat et al., 2000; Bogard and Garrison, 2003), NWA 2362 (Yamaguchi et al., 2009), NWA 5073 (Roszjar et al., 2011), Pasamonte (Metzler et al., 1995), Stannern (Barrat et al., 2007).

A.3.2. Fits and Diagnostics for linear regression models.

For Figures 5.2 and 5.4 simple linear regression models were calculated to investigate correlation. Where observations returned large leverage values (HI > 3p/n where p is the number of parameters and n is number of observations) these samples were removed and the regression re-calculated (see Table 8.3). Leverage is a measure of the distance from an observations’s x value to the average of the x-values for all observations in a data set. A large leverage value indicates an unusual predictor value compared to the remaining data and could potentially skew a linear regression.
Table 8.3: Table of $R^2$ values with and without the inclusion of sample DaG 945 along with their associated HI values. The threshold HI value for data to be considered anomalous for these data is 0.054.

<table>
<thead>
<tr>
<th>K</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$ (inc. DaG 945)</td>
<td>0.23</td>
</tr>
<tr>
<td>$R^2$ (excl. DaG 945)</td>
<td>0.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Large HI values</th>
<th>$\delta^{37}Cl$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DaG 945 Ap1a</td>
<td>0.091</td>
</tr>
<tr>
<td>DaG 945 Ap1b</td>
<td>0.079</td>
</tr>
<tr>
<td>DaG 945 Ap2a</td>
<td>0.111</td>
</tr>
<tr>
<td>DaG 945 Ap2b</td>
<td>0.133</td>
</tr>
<tr>
<td>DaG 945 Ap3a</td>
<td>0.168</td>
</tr>
<tr>
<td>DaG 945 Ap3b</td>
<td>0.081</td>
</tr>
<tr>
<td>DaG 945 Ap4</td>
<td>0.107</td>
</tr>
</tbody>
</table>
A.3.3. Additional material

![Truncated pyroxene ternary for mesostasis regions surrounding apatite grains.](image)

Figure 8.2: Truncated pyroxene ternary for mesostasis regions surrounding apatite grains.
Table 8.4: Representative apatite compositions measured by EPMA. Atoms per formula unit are calculated based on 25 oxygen.

<table>
<thead>
<tr>
<th></th>
<th>Agoult Basaltic</th>
<th>DaG 844 Basaltic</th>
<th>DaG 945 Basaltic</th>
<th>Millbillillie Basaltic</th>
<th>Moore County Cumulate Basaltic</th>
<th>NWA 2362 Basaltic</th>
<th>Sioux County Basaltic</th>
<th>Stannern Basaltic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. % n = 9</td>
<td>n = 3</td>
<td>n = 7</td>
<td>n = 10</td>
<td>n = 5</td>
<td>n = 10</td>
<td>n = 9</td>
<td>n = 18</td>
</tr>
<tr>
<td>P_{2}O_{5}</td>
<td>41.86</td>
<td>40.03</td>
<td>42.31</td>
<td>41.64</td>
<td>42.47</td>
<td>41.16</td>
<td>41.81</td>
<td>42.56</td>
</tr>
<tr>
<td>SiO_{2}</td>
<td>0.25</td>
<td>0.44</td>
<td>0.08</td>
<td>0.09</td>
<td>0.11</td>
<td>0.20</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>SO_{2}</td>
<td>0.03</td>
<td>0.00</td>
<td>0.06</td>
<td>0.02</td>
<td>0.02</td>
<td>0.08</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>Y_{2}O_{3}</td>
<td>0.06</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
<td>0.08</td>
<td>0.02</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>Ce_{2}O_{3}</td>
<td>0.03</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.16</td>
<td>0.06</td>
<td>0.05</td>
<td>0.08</td>
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Table 8.5: Representative compositions of mesostasis phases measured by EPMA. Atoms per formula unit are calculated based on the follow number of oxygen: 6 – Pyroxene, 8 – Plagioclase, 3 – Ilmenite, 4 – Chromite

Agoult

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| <strong>Ti</strong>        | 0.003    | 0.004    | 0.011  | 0.021  | Ti     | 0.000 |       |       |       |       |       |       |       |
| <strong>Al</strong>        | 0.029    | 0.035    | 0.042  | 0.059  | Al     | 1.795 |       |       |       |       |       |       |       |
| <strong>Cr</strong>        | 0.020    | 0.012    | 0.010  | 0.012  | Cr     | 0.000 |       |       |       |       |       |       |       |
| <strong>Fe</strong>        | 0.756    | 0.761    | 0.859  | 0.568  | Fe     | 0.019 |       |       |       |       |       |       |       |
| <strong>Mn</strong>        | 0.023    | 0.024    | 0.026  | 0.017  | Mn     | 0.000 |       |       |       |       |       |       |       |
| <strong>Mg</strong>        | 1.148    | 1.130    | 0.987  | 0.713  | Mg     | 0.003 |       |       |       |       |       |       |       |
| <strong>Ca</strong>        | 0.023    | 0.035    | 0.070  | 0.631  | Ca     | 0.828 |       |       |       |       |       |       |       |
| <strong>Na</strong>        | 0.001    | 0.001    | 0.002  | 0.004  | Na     | 0.170 |       |       |       |       |       |       |       |
| <strong>Total</strong>     | 3.988    | 3.988    | 3.986  | 3.985  | Total  | 5.011 |       |       |       |       |       |       |       |</p>
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269
## Stannern

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Appendix