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Basaltic volcanism on the Angrite Parent Body: comparison with 4 Vesta
Feergus A. J. Abernethy, A. B. Verchovsky, I. A. Franchi and Monica M. Grady

Abstract – Carbon and nitrogen data from stepped combustion analysis of eight angrites, seven eucrites and two diogenites, alongside literature data from a further nine eucrites and two diogenites, have been used to assess carbon and nitrogen incorporation and isotope fractionation processes on the angrite parent body, for comparison with volatile behaviour on the HED parent body (4 Vesta). A sub-set of the angrite data has been reported previously (Abernethy et al., 2013). Two separate families of volatile components were observed: (1) Moderately Volatile Material (MVM), mostly combusting between $\sim 500 - 750$ °C and indistinguishable from terrestrial contamination and (2) Refractory Material (RM), mainly released above 750°C and thought to be carbon (as CO_3^{2-}) and nitrogen (as N_2 or NH_4^+) dissolved within the silicate lattice, fitting with the slightly oxidised ($\sim \text{IW}$ to $\text{IW} + 2$) angrite $f\text{O}_2$ conditions. Isotopic fractionation trends for carbon and nitrogen within the plutonic and basaltic (quenched) angrites suggests that the behaviour of the two volatile elements is loosely-coupled, but that the fractionation process differs between the two angrite sub-groups. Comparison with results from eucrites and diogenites implies similarities between speciation of carbon and nitrogen on 4 Vesta and the Angrite Parent Body, with the latter being more enriched in volatiles than the former.

Introduction

Angrites are a small group (28 classified samples, including pairings, as of March 2017; *Meteorite Database*; <http://www.lpi.usra.edu/meteor/>) of 4.53 - 4.56 billion year-old achondrites (Jagoutz et al. 2002; Amelin, 2008a). They are notable for their depletion in silica and volatile alkalis (Na and K) and enrichment in calcium (Warren & Kallemeyn, 1995; Bischoff et al, 2000; Mittlefehldt et al, 2002). Their mineralogy

consists of almost equal proportions of calcic plagioclase (An_{99.6}), high aluminium, titanium diopside (fassaite) and a distinctive Ca-rich olivine (kirschsteinite) (Floss et al. 2003; Burbine et al. 2006). Surprisingly, the ‘type specimen’, Angra dos Reis (AdoR), differs from the rest of the group and is composed almost entirely (93 vol. %) of pyroxene (Prinz et al. 1977). Angrites show a broadly bimodal distribution in terms of age and texture: the finer-grained (~ 0.5 mm) Angrites have formation ages of ~ 4.564 Ga, whilst the more coarse-grained samples (~ 2 mm) are slightly younger, with ages closer to ~ 4.558 Ga (e.g., Baker et al. 2005; Markowski et al. 2007; Amelin 2008a, b; Wadhwa et al. 2009; McKibbin et al. 2015). The age data suggest at least two separate angrite formation events, possibly more, given the time intervals found between coarse-grained Angrites by Amelin (2008a). Oxygen (Greenwood et al. 2005) and strontium isotopic compositions (Tonui et al. 2003) appear to constrain the group to a single parent body. Siderophile element depletion (Kleine et al. 2012; Riches et al. 2012) and remnant magnetization (Weiss et al. 2008) suggest that the original parent body was fairly large (> 70 km in diameter). Reflectance spectroscopy of Angrites has suggested that they may emanate from Asteroid 5261 Eureka (Rivkin et al. 2007), a Mars Trojan, estimated to be about 1.3 km across, supporting an inference that the low number of Angrites known on Earth is because the (current) Angrite parent body (APB) is small. Unusually for achondrites, Angrites as a group display very little evidence for brecciation or metamorphism (Keil et al. 2012). Two basaltic quenched Angrites, D’Orbigny and Sahara 99555, are characterised by numerous vesicles (up to several mm in size). Water and CO₂ are the dominant vesicle-forming gases in terrestrial basalts (e.g., King and Holloway, 2002), but vesiculation in basaltic meteorites is believed to be controlled by CO₂ and CO (McCoy et al. 2006) with the ratio of CO/CO₂ moderated by oxygen fugacity (*f*O₂). Since Angrites are relatively oxidised (up to IW+2), CO₂ is

likely to be the most significant vesicle-forming gas (McCoy et al. 2006). On the basis of the size and number density of the vesicles within D'Orbigny and Sahara 99555, McCoy et al. (2006) calculated that ~ 12.5 ppm CO_2 (equating to 3.4 ppm C) was required in the melt to produce the observed textures. In an investigation of the light element content of a small subset of angrites, Abernethy et al. (2013) found up to ~ 100 ppm in some of the samples, an order of magnitude more carbon than required for the bubble nucleation process. In an attempt to reconcile these findings with the McCoy et al. (2006) model, and to compare angrite petrogenesis with that of igneous rocks from a body of known size (eucrites and diogenites, thought to be sourced from the ~ 520 km diameter asteroid 4 Vesta; McSween et al., 2013), we have extended our study of carbon and nitrogen in angrites. We address the question of whether basaltic and plutonic angrites exhibit different behaviours that could be related to their depth of origin and whether degassing of the angrite parent body was a catastrophic or gradual process. This will provide a view of the range of magmatic regimes in existence during the earliest period of Solar System history.

Materials and Methods

The carbon and nitrogen abundances and isotopic compositions of a suite of 8 angrites, 7 eucrites and 2 diogenites, were determined by incremental oxidation (stepped combustion) of milligram-sized aliquots of meteorite. The samples analysed, and their sources, are listed in Table 1; a basic overview of the sample textures is given in Table 2. A reservoir of powder (around 100 μm in grain-size, smaller than the mean grain-size of the meteorites) was produced for most specimens by gentle crushing of whole-rock chips of $\sim 300 - 500$ mg using an agate mortar and pestle. The chips were taken to be as representative as possible of the whole rock meteorites, a reasonable assumption since the angrites are unbrecciated at this scale. Although only D'Orbigny

has been identified as having fluid inclusions (King et al., 2012), crushing was kept to a minimum to avoid losing trapped volatiles. Three angrites, NWA 1296, NWA 4590 and NWA 4801, were obtained as (μm grain-sized) powders from the Australian National University (ANU). Pt foil, 25 μm in thickness, was used to prepare small envelopes ($\sim 3 \times 3$ mm in size) in a class 10,000 clean room. These were subsequently placed in a quartz tube containing CuO and evacuated to 10^{-7} mbar for approximately 30 minutes before being sealed and removed. The sealed tube was placed in a furnace for approximately 12 hours at 900 °C before being returned and opened in a class 1000 clean room. The purpose of this step was to reduce the blank contribution of the foil to a minimum by oxidising any contaminant material on the foil itself. Sample size was variable, depending on the mass of material available (1 – 10 mg, exact masses are given in Table 3); samples were weighed into the cleaned Pt envelopes in a class 100 clean room. They were analysed on the stepped combustion gas extraction mass spectrometry system FINESSE at the Open University (OU). Incremental heating in 100°C (200 – 500 °C and 1100 – 1400 °C) and 50 °C (500 – 1000 °C) steps was performed in the presence of oxygen derived from the decomposition of copper (II) oxide at 850 °C. Carbon dioxide and nitrogen produced on combustion were separated cryogenically; CO₂ abundance was measured on a capacitance manometer (Chell MK 3934 Baratron), whilst nitrogen yield was determined from calibration of the mass spectrometer ion current at $m/z = 28$. Uncertainty on the yield was about ± 1 % of the total number of nanograms measured for carbon and ± 5 % for nitrogen. Carbon isotopic measurements were made on a triple-collector mass spectrometer; nitrogen isotopes were measured on a combined dual-focusing mass spectrometer and quadrupole, all operating in a static-vacuum mode. Details of the techniques and instrumentation have been published previously (Swart et al., 1983; Yates et al, 1992; Boyd et al, 1998;

Mikhail, 2011). Isotopic compositions are reported in the delta (δ) notation as parts per thousand (‰) deviation from Vienna Peedee Belemnite (vPDB) for carbon, and terrestrial air for nitrogen using the following equation:

$$\delta (\text{‰}) = \left(\frac{\text{Sample ratio}}{\text{Standard ratio}} - 1 \right) * 1000$$

Empty Pt foil envelopes were run before and after each analysis to determine the blank level for data correction. Blank levels were ~ 10 ng of carbon and 1 - 2 ng of nitrogen per step at low temperatures, dropping to 2 - 3 ng and 0.5 ng respectively at temperature steps above 600 °C. Uncertainties in the isotopic composition were determined through error propagation and are largely influenced by the significance of the blank contribution.

Several angrites, D'Orbigny being the most spectacular example, contain void spaces lined with carbonates. Because the samples that exhibit these features are meteorite 'finds', it is unclear whether the carbonates are terrestrial weathering products, or from re-condensed magmatic gases on the angrite parent body. In order to distinguish between a terrestrial and an extraterrestrial origin for the carbonates, their carbon and oxygen isotopic compositions were determined on CO₂ released following dissolution in 99 % orthophosphoric acid. Flakes of material were hand-picked from D'Orbigny (BM2001,M10 from the Natural History Museum, London); two generations of carbonates were present, distinguishable by differences in colour and texture: a hard, creamy-coloured plaque lining the interior surface of visible void spaces, and a softer, whiter layer usually found either overlying the harder material or on the external surface of the main mass. The acid dissolution experiments also included analysis of ~ 20 mg samples of whole-rock powder taken from homogenised reservoirs of D'Orbigny, NWA 4590 and NWA 4801 in order to compare the separate samples to a bulk rock acid dissolution. The D'Orbigny powder was taken from the same reservoir used in the

stepped combustion experiments, while both NWA samples were obtained from additional ~ 100 mg-sized chips provided by Arizona State University. All samples were analysed using a Thermo-Fisher Scientific Finnigan DELTAplusAdvantage gas-bench instrument at the OU. The samples were sealed inside sample tubes and flushed with He gas to remove atmosphere. Samples were dosed with 20 drops of 99 % orthophosphoric acid using a needle through a resealing bung on the sample tube, and left to react for 30 minutes at 72 °C. Carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopic compositions were measured on the resulting CO_2 gas. Standards of NIST limestone and marble were also run at the same time and used to calculate measurement uncertainties.

Results

Surface volatiles and complex organics that are typically attributable to contamination, combust below ~ 500 °C (Swart et al., 1983; Grady et al. 2004), although they can persist up to ~ 600 °C. The cut-off for nitrogen contamination is considered to be 700 °C (Miura & Sugiura, 1993). In order to ensure capture of indigenous components and elimination of most of the contamination, only data from temperatures greater than 500 °C are considered. Above 500 °C, there appears to be, at most, two discrete families of components present, based on maxima in the volatile release profiles associated with changes in isotopic composition. The components combust at different temperatures: the first appears at ~ 500 – 750 °C and is referred to as Moderately Volatile Material (MVM). The second set of components combusts at temperatures greater than ~ 750 °C and is referred to as Refractory Material (RM). Since identification of the phases is based on maxima in the volatile abundance profiles rather than a specific temperature range, there are slight differences in the observed combustion temperature ranges between components in different samples, and not all samples contained both families

of components. We employ the terms MVM and RM until we can be more certain of the identification of the components, or their hosts. Table 3 summarises the combustion temperatures of volatiles from each sample, including replicate analyses. Data for the first run of NWA 2999 were rejected (and are not reported here) as the sample had been heavily contaminated by washing in ethanolamine thioglycolate (EATG; the sample had been prepared for oxygen isotope analysis). A second sample of NWA 2999 was obtained that had not experienced EATG pre-treatment. For several samples, yields of carbon and/or nitrogen above 750 °C were at blank levels. One analysis of NWA 1296 produced measurable amounts of carbon, but a problem with the mass spectrometer precluded analysis of its isotopic composition. Results are given in Tables 4 and 5, and plotted in Figures 1 and 2. Two angrites (carbon and nitrogen data; Wright et al., 1989) plus 6 eucrites and two diogenites (carbon data only; Grady et al., 1997) had been analysed in earlier studies, using Finesse-like precursor systems. The data have been re-evaluated are also included in Tables 4 and 5.

Carbon

Summaries of the abundance and isotopic composition of carbon in the MVM and RM components in angrites, eucrites and diogenites are presented in Tables 4 and 5 and plotted in Figures 1a and 2a, respectively. The Tables and Figures also include an updated version of the deconvoluted components from the supplementary information of Abernethy et al. (2013). Not all samples contained both MVM and RM.

MVM carbon occurs in concentrations of around 0 – 400 ppm with $\delta^{13}\text{C}$ between about – 25 ‰ and 0 ‰ for most of the samples (Table 4). New data from this study show (Figure 1a) that 6 of the 7 meteorites containing MVM with carbon isotopic compositions towards the more ^{13}C -enriched end of the range (i.e., $\delta^{13}\text{C} > -10$ ‰) are hot desert finds – we call this population Cluster A. Two results from non-desert

meteorites fall in Cluster A, from a whole rock sample and a glass separate from D'Orbigny; the anomalous eucrite Ibitira is also on the edge of the cluster, with $\delta^{13}\text{C} \sim -11 \text{ ‰}$

The population of samples that make up Cluster B, with $\delta^{13}\text{C} < -15 \text{ ‰}$, includes Antarctic angrites and eucrites, as well as the non-desert meteorite fall, Angra dos Reis and a replicate analysis of NWA 4590. A replicate analysis of whole rock D'Orbigny, with $\delta^{13}\text{C} \sim -16 \text{ ‰}$, is the only sample that sits between the clusters. The associated differences in $\delta^{13}\text{C}$ of up to 20 ‰ between the replicates (Figure 1a) are well outside the expected range of experimental reproducibility. There is no relationship between petrogenesis (basaltic or cumulate) with cluster, either in abundance or isotopic composition, for angrites or for eucrites and diogenites.

Refractory material (RM) is carbon mainly released above 750 °C. Unlike the MVM, there is no bimodal distribution in carbon abundance or isotopic composition: most of the samples contain < 30 ppm carbon, with $\delta^{13}\text{C}$ between -30 ‰ and -20 ‰ (Table 5; Figure 2a). Two of the analyses of AdoR and the first run of Sahara 99555 have higher carbon abundances (60 – 90 ppm) than the other meteorites; the three analyses of D'Orbigny have $\delta^{13}\text{C}$ between -17 ‰ and -10 ‰ , as does NWA 2999 ($\delta^{13}\text{C} \sim -15 \text{ ‰}$). The analysis of NWA 4590 has both an elevated carbon abundance (44.4 ppm) and slightly elevated $\delta^{13}\text{C}$ (-15 ‰). Reproducibility of the carbon data from RM is a bit better than that for the MVM.

Nitrogen

Nitrogen data are summarized in Tables 4 and 5 and plotted in Figures 1b and 2b. There are considerably fewer nitrogen than carbon results, mainly because most of the eucrites and diogenites appeared to contain no measureable nitrogen.

The abundance of nitrogen in MVM in angrites is ≤ 3.5 ppm, with $\delta^{15}\text{N}$ from 0 ‰ to + 15 ‰ (Figure 1b). Exceptions are NWA 1296, with $\delta^{15}\text{N}$ equal to $+ 38.7 \pm 3.4$ ‰ and the glass from D’Orbigny, with $\delta^{15}\text{N}$ of $+ 28.9 \pm 1.5$ ‰. One of the two eucrites that yielded nitrogen (ALHA81001) had a higher abundance than any of the angrites (5.0 ppm), whilst Ibitira had an elevated $\delta^{15}\text{N}$ value ($+ 22.2 \pm 3.0$ ‰). There is no relationship between angrite petrogenesis (plutonic vs. quenched) with either nitrogen abundance or isotopic composition of MVM. **There is also no** correspondence between the two clusters identified in the carbon data and nitrogen results.

Most of the RM nitrogen is released on combustion above 800 °C (Table 5, Figure 2b). The refractory nitrogen component is low in abundance, generally < 2 ppm, with $\delta^{15}\text{N}$ between $- 5$ ‰ and $+ 20$ ‰. One run of Sahara 99555 has an elevated nitrogen abundance (9.9 ppm), around 2 – 5 times more than any other sample – the same run that had an elevated carbon abundance. There are two outliers in isotopic composition: the angrite NWA 1296 ($\delta^{15}\text{N} = + 58.1 \pm 5.0\%$) and one of the whole rock analyses of D’Orbigny ($\delta^{15}\text{N} = + 34.8 \pm 10.7$ ‰). Data from the RM seem to be more reproducible than from the MVM: replicate analyses of samples are within, or close to, the uncertainties of the measurements, although the dataset is small. One exception is Sahara 99555, in which there was a 20-fold difference in nitrogen yield between the two runs, with a difference in $\delta^{15}\text{N}$ only just outside the precision of the analyses.

Carbonate

With the exception of the D’Orbigny carbonate plaque results and those from the whole rock experiment of NWA 4590, the acid dissolution experiments (Table 6) yield $\delta^{13}\text{C}$ values of close to 0 ‰. The oxygen isotope results cluster around $\delta^{18}\text{O} \sim + 30$ ‰, again with the exception of NWA 4590 ($+24$ ‰).

Discussion

(i) Moderately Volatile Material (MVM)

MVM carbon shows a broadly bimodal distribution in terms of $\delta^{13}\text{C}$ (Figure 1a), with one group of $\delta^{13}\text{C}$ values of -11 ‰ to + 10 ‰ (Cluster A; $n = 10$, nine angrites plus the eucrite Ibitira) and a second of four angrites plus five eucrites and four diogenites with $\delta^{13}\text{C}$ of -16 ‰ to -26 ‰ (Cluster B; $n = 15$). Assuming the two clusters are discrete components, they are considered separately.

Cluster A contains plutonic and basaltic angrites found in hot desert environments, plus one sample of whole rock D'Orbigny, the glass separate from it and the Ibitira eucrite. The mean value of $\delta^{13}\text{C}$ in Cluster A is -0.9 ± 5.2 ‰. The 500 – 750 °C temperature range has been linked to carbonate decomposition (Grady et al. 2004) and since the $\delta^{13}\text{C}$ values almost completely overlap the data from the carbonate dissolution experiments (Table 6), decomposition of a carbonate is almost certainly the source of the carbon in Cluster A MVM. Terrestrial soil carbonates have a range of $\delta^{13}\text{C}_{\text{VPDB}}$ from - 10 ‰ to + 5 ‰ and $\delta^{18}\text{O}_{\text{SMOW}}$ (converted from vPDB using the equation of Coplen et al. 1983) of + 15 ‰ to + 30 ‰ (Cerling, 1984; Cerling & Quade, 1993). As there appears to be minimal difference between the results from the desert angrites, those from D'Orbigny and terrestrial soil carbonates, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results suggest a terrestrial, rather than an extraterrestrial origin for any carbonates.

Cluster B includes plutonic and basaltic angrites, eucrites and diogenites. The meteorites have a similar range in carbon abundance to that of Cluster A, but lower and slightly more tightly grouped isotopic composition ($\delta^{13}\text{C} \sim -22.5 \pm 2.2$ ‰). Combustion temperatures and carbon isotopic compositions of Cluster B MVM are close to those of terrestrial organic matter (Gilmour & Pillinger, 1985; Grady et al. 2004). The combustion temperature is also characteristic of amorphous carbon and

poorly crystalline graphite (Grady et al. 2004), depending on the grain size of the material, and whether or not it was directly exposed to oxygen for combustion, or shielded by trapping within mineral grains. The range in $\delta^{13}\text{C}$ from -28‰ to $+18\text{‰}$ is also typical of carbon in terrestrial igneous rocks, graphite (Faure, 1986), HED (Grady et al. 2004) and martian (Grady et al. 1997) magmatic carbon, as well as terrestrial organic matter. It is unlikely that the Cluster B component is magmatic carbon, as it is released below the $> 800\text{ °C}$ onset of silicate softening (Grady et al. 2004). The combustion temperature is also not sufficient to indicate crystalline graphite, such as that found in the martian orthopyroxenite ALH 84001 (Steele et al. 2012a). There is currently no petrographic evidence for indigenous amorphous carbonaceous material of a similar nature to that found in some martian meteorites (Steele et al. 2012b) or chondrites (Busemann et al. 2007; Starkey et al. 2013) in any of the meteorites studied. This does not preclude the presence of amorphous carbonaceous material, but there is no compelling evidence to support the presence of such a component.

Up to 3.5 ppm nitrogen is associated with MVM in angrites, with $\delta^{15}\text{N}$ mainly between 0‰ and $+20\text{‰}$ (Table 4). MVM in Cluster A meteorites contains marginally less N with higher $\delta^{15}\text{N}$ than that in Cluster B specimens, but there are insufficient data to determine whether this is a real difference. The nitrogen isotopic composition of MVM falls within the nitrogen isotopic composition of CO, CV and CM chondrites, but with at least an order of magnitude lower abundance (Kerridge, 1985). Nitrogen released at low temperatures from ordinary chondrites has a similar abundance and isotopic composition to that described here, and was characterised as from terrestrial contamination (Hashizume & Sugiura, 1995). MVM nitrogen has an isotopic composition within the range of terrestrial atmospheric and organic nitrogen ($\delta^{15}\text{N} \approx 0$

± 20 ‰; Hoefs, 2004), including biologically fractionated nitrogen ($\delta^{15}\text{N} \approx +5$ to $+20$ ‰; Boyd et al. 1993). The data suggest that nitrogen in the MVM is largely a mixture of contamination from organic compounds and atmospheric adsorption with the possible exceptions of NWA 1296, D’Orbigny and Ibitira.

On the basis of the carbon and nitrogen data, there is no strong evidence to suggest an indigenous component within the MVM in angrites. Data are sparse for eucrites and diogenites, but where present, the MVM has similar characteristics to angrites. The MVM is thus considered mostly to be terrestrial contamination, and will not be discussed further. The remainder of the paper focuses on the occurrence of refractory C- and (or) N-bearing components in angrites, and comparison with such material in eucrites and diogenites.

(ii) Refractory Material (RM)

Carbon oxidised by combustion at temperatures above 750 °C is labelled ‘Refractory Material’, or RM. It does not have the bimodal distribution in carbon isotopic composition exhibited by the MVM and there is very little relationship between carbon abundance and isotopic composition (Figure 2a) on the basis of petrogenesis (quenched vs. slowly cooled angrites, or eucrites vs. diogenites). Nor does the presence of vesicles in D’Orbigny or Sahara 99555 appear to have led to any substantial difference in isotopic composition.

Carbon release temperatures above 750 °C may indicate the presence of specific phases such as crystalline graphite and lattice-bound carbon in minerals (Grady et al. 2004). In stepped combustion analyses, graphite combustion is usually characterised by a sharp maximum in carbon yield, i.e., increased amounts of CO₂ released in a narrow temperature interval of 100 – 150 °C centred around ~ 800 °C. In contrast, CO₂ produced from carbon held within a mineral lattice is liberated over much broader temperature

ranges. Inspection of the combustion ranges for RM carbon (Table 3) show that in all cases, carbon dioxide is released over a broad temperature range. This observation, combined with the lack of any obvious signs of a discrete carbonaceous phase such as well-crystalline graphite, suggests that the high-temperature carbon is hosted within minerals.

Speciation of carbon as a ‘solid’ phase differs from the previous characterisation of angrite volatiles (mainly through study of the vesicles within D’Orbigny and Sahara 99555; McCoy et al. 2006) as a vapour phase. The presence of a gas within an angrite melt is feasible, given the relatively high fO_2 of angrites (Brett et al. 1977; Ma et al. 1977; McKay et al. 1994; Jurewicz, 1993; 2004; Kuehner & Irving 2007). It is currently thought that the main mechanism of carbon dissolution in terrestrial basalts is through the formation of CO_3^{2-} ions by a combination of CO_2 with non-bridging oxygen atoms (NBOs) in (mafic) silicate melts (Fine & Stolper, 1985; Pawley et al. 1992; Brooker et al. 2001; Nowak et al. 2003; Iacono-Marziano et al. 2012; Dasgupta et al. 2013). This proposed mechanism of dissolution, whereby the relative concentrations of network forming (e.g., Al^{3+} , Si^{4+}) and complexing (e.g., Ca^{2+} , Mg^{2+} , Fe^{2+} , Na^+ , K^+) cations determine the availability of NBOs and therefore the solubility of CO_2 (Lowenstern, 2000), also means that the Ca-rich, Si-poor chemistry of the angrites is suitable for carbon incorporation to produce CO_3^{2-} ions.

One potential location for carbon in igneous meteorites is in glassy melt inclusions within olivine and pyroxene. A second mineral host is within apatite grains. These occur in angrites and eucrites, and are known to contain hydroxyl and/or halide ions (Sarafian et al., 2013, 2015; McCubbin et al., 2015; Barrett et al., 2016). Several angrites contain silicophosphates, in which the tetrahedral SiO_4^{4-} anion substitutes for PO_4^{3-} (Mittlefehldt et al., 2002). It is entirely possible that the CO_3^{2-} anion also acts in a similar

way. Indeed, carbonate-rich hydroxyl apatite is one of the main constituents of bone; it is thought that the CO_3^{2-} anion may substitute in the hydroxyl ion site, as well as for the PO_4^{3-} tetrahedra within the apatite lattice (Wopenka and Pasteris, 2005).

Refractory nitrogen, generally < 2 ppm, occurs in a few of the angrites analysed, and one eucrite (Figure 2b); in most cases, the levels of nitrogen produced were hardly above blank levels (Table 5). When nitrogen is present, its isotopic composition is variable, most samples having total $\delta^{15}\text{N}$ between -5 ‰ and $+20$ ‰. Analysis of 5 eucrites by Miura and Sugiura (1993), employing an order of magnitude more material (included in Figure 2b), yielded similar results. Whilst some of the RM nitrogen has the same range in $\delta^{15}\text{N}$ as the MVM, the release temperature is too high to support interpretation as the RM being a contaminant.

Given the inferred IW to IW+2 oxygen fugacity conditions of formation in the angrites, it seems unlikely that the nitrogen is the result of decomposition of phases present in more reduced meteorites such as sinoite ($\text{Si}_2\text{N}_2\text{O}_2$) or osbornite (TiN). Indeed, the relatively high oxygen fugacity of the angrites should make any kind of chemical process of nitrogen dissolution into the original melt unlikely (Libourel et al., 2003; Miyazaki et al., 2004). Graphite is stable at APB oxygen fugacities (Hirschmann & Withers, 2008), so could host the nitrogen, although, as discussed above, no graphite has been observed petrographically or identified as a significant contributor to the carbon inventory. Where graphite does occur in meteorites, e.g., in ureilites, nitrogen associated with the graphite tends to be isotopically light, with $\delta^{15}\text{N} < -50$ ‰ (Downes et al., 2015). Acapulcoites and lodranites also contain graphite, and nitrogen is partitioned between graphite, metal and silicates in these meteorites. The three reservoirs have different nitrogen isotopic compositions, with that released from graphite and metal being much lighter ($\delta^{15}\text{N} \approx -150$ ‰ to -100 ‰; Kim & Marti,

1994; El Goresy et al., 2005) than that released from silicates ($\delta^{15}\text{N} \approx 0 \text{ ‰}$ to $+ 30 \text{ ‰}$; Grady et al. 1993, Kim and Marti, 1993). Angrites, eucrites and diogenites are metal- and sulphide-poor, and the observed range of $\delta^{15}\text{N}$ compositions suggest affinity to silicates rather than metal. A further factor that militates against nitrogen being hosted in graphite is the difference in combustion (or release) temperature of carbon and nitrogen. If nitrogen were solely in graphite, it would be mobilised when the graphite burnt. Since there is not always a coincidence between the temperature ranges within which carbon and nitrogen yields reach a maximum (Table 3), it is unlikely that the main host of nitrogen is carbonaceous.

In terrestrial rocks nitrogen occurs as the NH_4^+ ion (Boyd et al. 1993), substituting for monovalent cations (e.g., Na^+ , K^+). Despite the significant depletion of these components within Angrites, there still remains sufficient abundance for such NH_4^+ substitution to take place within the plagioclase, should there have been an accessible source of NH_4^+ ions. However, if this were the case one would expect some correlation between the plagioclase abundance and the nitrogen abundance and for plagioclase free samples such as Angra dos Reis (Mittlefehldt et al. 1998) to also be more depleted in nitrogen. As this does not appear to be the case, alternative explanations must be considered. Libourel et al. (2003) found that nitrogen in silicate melts with a high oxygen fugacity would become physically incorporated into cavities in the silicate network as an N_2 molecule. This could then partition from the melt into mineral phases via the same mechanism as noble gases (Miyazaki et al., 2004). Under these circumstances the initial melt solubility, as with the carbon, is thought to be controlled by the balance of network-forming and network-modifying cations. As the abundance of cations such as Ca^{2+} and Mg^{2+} increases, nitrogen solubility decreases (Miyazaki, 2004). The high calcium (in silicates) abundance within the Angrites compared with

other meteorite groups might then provide a reasonable explanation as to why they have such a low abundance of high-temperature nitrogen. However, cation abundance cannot be the sole control on volatile content: if it were, eucrites and diogenites, with lower total Ca abundances than angrites, should have higher N contents. Results from Table 5 and Figure 2 show that this is not the case.

Volatile loss mechanisms

Assuming that carbon and nitrogen are both dissolved in the initial silicate melts from which the angrites crystallised, it is possible that their abundances might be linked. However, when carbon and nitrogen yields are plotted against one another (Figure 3a) it is clear that there is no obvious relationship between the two elements. If Sahara 99555(1), an apparent outlier, is omitted, then there is a weak correlation between carbon and nitrogen abundance ($r = 0.66$), but it relies on a single data point from Angrados Reis. Since the basaltic and plutonic angrites have different ages and petrogeneses, and therefore did not evolve as a single continuous sequence (Amelin, 2008a, b), it is perhaps not surprising that there are differences in volatile complements between the two angrite sub-groups. All five points from the quenched angrites, including the apparent S99-1 outlier, can be fit well to an exponential curve ($r = 0.98$), suggesting that, with its high volatile abundance, Sahara 99555 might retain a record of the initial parent body gas composition. The plutonic angrites scatter round either a linear ($r = 0.86$) or an exponential curve ($r = 0.91$), indicating that there is a poorly-defined relationship between carbon and nitrogen. Figure 3b shows how the isotopic composition of nitrogen varies with that of carbon. Again, as for the abundance data, there is a weak relationship between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ when the angrites are treated as a single group ($r = 0.74$, $n = 10$). Taking the quenched angrites alone, there is a good linear correlation between increasing $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ($r = 0.98$, $n = 4$), but the dataset is

very small. At face value, the association suggests that the fractionation of carbon and nitrogen may be linked within the rapidly-cooled angrites. There is a similar relationship between carbon and nitrogen isotopic composition in plutonic angrites, although it is less well-defined than in the quenched meteorites ($r = 0.90$, $n = 6$). The ‘correlations’, such as they are, do imply a relationship between the hosts of carbon and nitrogen, as might be expected if they were in the silicate lattice and were able to diffuse out.

Variation in carbon and nitrogen isotopic composition of the angrites is explicable if several different components with different isotopic compositions are mixed in different proportions. A possible component includes species implanted from exposure to cosmic radiation (Becker, 1980). The effect of cosmic radiation is to produce ^{15}N (and ^{13}C) leading to a heavier isotopic composition, depending on the length of time for which the samples have been exposed. Comparing published cosmic ray exposure (CRE) ages of the angrites (Lugmair & Marti, 1977, Eugster et al. 1991, Kurat et al. 2004, Nakashima et al. 2008, Keil, 2012) with nitrogen isotopic composition shows that there is no relationship between the two parameters, indicating that exposure on the surface of the APB or in space does not have a major role in moderating volatile composition in angrites. The paucity of the dataset means that it is difficult to reach the same conclusion regarding eucrites and diogenites, although Miura and Sugiura (1993) inferred the presence of spallogenic nitrogen in the eucrites they analysed.

If we continue with the supposition that volatile species are held within minerals, then fractionation by partial degassing of the melt during angrite formation is the most likely process to explain the observed distinctions in angrite isotopic composition. Figure 3b shows that there is not a single simple relationship between carbon and nitrogen in the plutonic and quenched angrites, but as discussed above, there are separate linear trends

of increasing $\delta^{15}\text{N}$ with $\delta^{13}\text{C}$ in each angrite subgroup. Within the very limited dataset of quenched angrites, vesiculation (2.08 vesicles/cm³) of D'Orbigny (McCoy et al. 2006) implies significant gas loss. The ^{13}C - and ^{15}N -enrichment of residual carbon and nitrogen in D'Orbigny relative to those in Sahara 99555 (the other vesiculated angrite for which data are available) is consistent with fractionation through degassing. One inference that may be drawn from Figure 3b is that the two sub-groups of angrites degassed at different rates from a common source of volatile material. The isotopic compositions of this common source had $\delta^{13}\text{C} \approx -24 \text{ ‰}$ and $\delta^{15}\text{N} \approx +1 \text{ ‰}$, (the isotopic compositions where the two linear trends cross, marked with the dotted lines in Figure 3b). Gas loss from a source with $\delta^{13}\text{C} \approx -24 \text{ ‰}$ and $\delta^{15}\text{N} \approx +1 \text{ ‰}$ is broadly compatible with data for the quenched angrites. However, two of the plutonic angrites have $\delta^{13}\text{C}$ much less than -24 ‰ ($\delta^{13}\text{C} \sim -27.3 \text{ ‰}$ for AdoR-2 and -30.5 ‰ for NWA 4801-2), so simple degassing cannot be the complete explanation for the range in isotopic compositions.

We can model how light element isotopic composition changes as a magma cools because volatile species are fractionated in a predictable fashion, depending on whether the system is closed or open. In a closed system, volatiles cannot escape directly, but undergo back reactions with the cooling magma, eventually leading to equilibrium between the different reservoirs. In an open system, the volatiles escape, and the isotopic composition of the residual species depends on the loss mechanism.

Catastrophic Degassing

If degassing is very rapid (catastrophic), most of the volatiles are lost in a single episode, there is no reaction between solid and gas, and any residual volatiles retain the isotopic composition of the starting material. Catastrophic degassing is dependent on formation and coalescence of vapour bubbles within a cooling magma, and the ability

of the vapour to escape. On a planetary body, when a melt becomes oversaturated with respect to volatiles, bubble growth can be extremely rapid, leading to sudden vapour escape (Suckale and Elkins-Tanton, 2010). However, analysis of D'Orbigny and Sahara 99955 by McCoy et al. (2006) suggests that such a mechanism might not be applicable on the angrite parent body. The two samples are vesicular, showing that the magma body within which they formed must have been either at a reasonable depth within the parent body, or sufficiently crystallised, in order to generate sufficient confining pressure to prevent bubble escape. The continued presence of vesicles in D'Orbigny and Sahara 99955 show that bubble coalescence prior to a catastrophic release of gas did not occur. The cooling rate of quenched angrites (up to 50 °C per hour; Scott & Bottke, 2011) implies that degassing, although not catastrophic, must have been rapid if volatiles were to escape before parent body solidification. In contrast to the basaltic angrites, plutonic angrites cooled much more slowly, at rates as low as 1.4 °C per year (McKay et al. 1998), allowing gradual escape of volatiles, so catastrophic degassing is also not an applicable process for these meteorites.

Open System Degassing

If volatile loss is more gradual, as the magma cools, the final isotopic composition is controlled by temperature-dependent fractionation between the volatile and solid reservoirs. The fractionation can be modelled by assuming a Rayleigh-type distillation of the escaping volatiles (Hoefs, 2004). For the carbon system, we used the CO₂ – graphite fractionation factor at 1000 °C from Bottinga (1968, modified by Polyakov & Kharlashina, 1995) and the temperature-independent CO₂ – melt fractionation factor from Matty (1991) to produce a family of curves tracing how carbon isotopic composition might evolve during open system degassing of a basaltic melt. Three representative curves are shown in Figure 4a based on starting isotopic compositions of

$\delta^{13}\text{C} - 35 \text{ ‰}$ (lowermost curves), $\delta^{13}\text{C} - 25 \text{ ‰}$ and $\delta^{13}\text{C} - 20 \text{ ‰}$ (uppermost curves). For nitrogen, degassing curves for N_2 and NH_4^+ were calculated (Rouilleau et al. 2012), assuming initial $\delta^{15}\text{N}$ values of -30 ‰ and 0 ‰ (Figure 4b). The starting isotopic compositions were selected either to be close to the postulated initial values of the source material, as derived from Figure 3b, or to be a (better) fit to the data.

There was little match between the data for carbon in the more rapidly-cooled angrites to any single calculated fractionation pathway. Replicate analyses of two of the quenched angrites show that there is a very heterogeneous distribution of volatiles in the samples and that their abundance and isotopic composition has not been set by equilibrium fractionation. The high nitrogen abundance in S99-1 (2 – 3 times that of the other samples) is unlikely to be from terrestrial atmosphere, even though its $\delta^{15}\text{N}$ is close to zero, because the release temperature ($T > 900 \text{ °C}$) is too high and the associated carbon too light (terrestrial atmospheric CO_2 has $\delta^{13}\text{C} \sim -7 \pm 2 \text{ ‰}$). If the nitrogen in S99-1 is indigenous to the angrite parent body, it may be contained within closed gas-rich vesicles that ‘popped’ during analysis. It also has the closest carbon and nitrogen isotopic compositions to those posited for the original volatiles held within the angrite parent body ($\delta^{13}\text{C} \approx -24 \text{ ‰}$; $\delta^{15}\text{N} \approx +1 \text{ ‰}$).

Even though the plutonic angrites cooled much more slowly than the basaltic samples, and so might be expected to demonstrate a more regular relationship between $\delta^{13}\text{C}$ and extent of gas loss, the model curves in Figure 4 do not show a convincing relationship. Most of the plutonic angrites have lost more than 80% of their original predicted complement of carbon and nitrogen. An alternative explanation may be the presence of multiple distinct mantle sources, as suggested by Kleine et al. (2012) on the basis of existing Pb-Pb ages and examination of ^{182}Hf - ^{180}Hf systematics. If this is the case, then multiple groupings by source region would be expected as opposed a continuous

isotopic trend. Unfortunately, the dataset and indeed the number of available angrites is likely currently insufficient to evaluate this fully.

Comparison with Eucrites and Diogenites

Angrites are very similar in age to the largest group of differentiated meteorites, the eucrites (Amelin, 2008a). They are also close in oxygen isotopic composition (Greenwood et al., 2005, 2006), implying that angrites and eucrites formed at almost the same time in similar locations in the solar nebula. Eucrites are derived from the 520 km diameter asteroid 4 Vesta (e.g., McSween et al., 2013). The source of angrites is not known, although, based on the size distribution of main belt asteroids, the angrite parent body must be smaller than that of the eucrites, and so the petrogeneses of the two groups of achondrites are likely to differ. Nonetheless, examination of the carbon and nitrogen chemistry of eucrites may help in interpretation of the angrite data (and vice versa).

There have been very few measurements of carbon in HEDs: Grady et al. (1997) analysed 4 eucrites and 2 diogenites, and inferred that they contained very little indigenous carbon (< 30 ppm), and what was present was isotopically light ($\delta^{13}\text{C} \approx -25$ ‰). The main conclusion of Grady et al. (1997) was that if indigenous carbon did occur in eucrites and diogenites, it was very difficult to distinguish from terrestrial organic contamination on the basis of isotopic composition. An additional 7 eucrites and 2 diogenites were analysed as part of this study; results (Table 5) confirm the findings of Grady et al. (1997), that there is very little carbon and even less nitrogen in eucrites and diogenites. Whilst 8 of the 11 eucrites and 5 of the 6 diogenites yielded sufficient carbon to analyse, only one eucrite and none of the diogenites gave sufficient nitrogen to measure. In the samples where carbon was present, its abundance and isotopic composition was generally within the spread of values from the earlier study (Grady et al., 1997). Carbon abundance (2 – 30 ppm) tended to be towards the lower

end of the angrite range; carbon isotopic composition was also similar to angrites, with most of the samples having $\delta^{13}\text{C} \approx -30\text{‰}$ to -20‰ (Figure 2a).

A lack of nitrogen in the eucrites that were studied makes it difficult to compare results with those from angrites, therefore nitrogen data from five eucrites analysed by Miura and Sugiura (1993) have been included in Figure 2b. As with the carbon, nitrogen appears to be broadly similar between angrites and eucrites, mainly falling between 0.2 – 1 ppm abundance and $\delta^{15}\text{N}$ of 0 to + 100 ‰.

On average, eucrites and diogenites contain only half to one third as much carbon as angrites: mean carbon abundances are 32.4 ppm, 22.5 ppm, 12.5 ppm and 7.4 ppm for, respectively, plutonic and quenched angrites, eucrites and diogenites. They are also isotopically lighter: mean $\delta^{13}\text{C}$ are -21.7‰ , -17.0‰ , -26.0‰ and -26.3‰ for, respectively, plutonic and quenched angrites, eucrites and diogenites. There are insufficient nitrogen data to make a similar absolute comparison between HED and angrites, but that in itself shows that nitrogen is depleted in the former compared with the latter.

Eucrites are the largest group of asteroidal basalts. Angrites, much fewer in number, have similar crystallization ages to eucrites (e.g. Keil, 2012). Both groups of meteorites solidified from melts, requiring **variable degrees** of melt extraction, equilibrium partial melting and fractional crystallization. Even though the two parent bodies aggregated and differentiated almost contemporaneously, differences in oxygen isotopic composition indicate that their formation locations were separate (Greenwood, 2005). Eucrites, and their cumulate partners, diogenites, originate from 4 Vesta, over 500 km in diameter. The size of the angrite parent body is debated, but, as summarised by Keil (2012), several lines of argument lead to the conclusion that the original APB must have been > 100 km in diameter. This would have been sufficiently large to produce the suite

of quenched and plutonic angrites analogous in relative formation location to the fine and coarse-grained basaltic eucrites respectively. Age-dating of eucrites shows that magmatic activity on 4 Vesta started very early in Solar System history (within $\sim 1 - 3$ Ma of CAI formation; Touboul et al., 2015) and continued for up to 50 Ma (Zhou et al. (2013). The time line of angrite evolution is similar to eucrites (e.g., Markowski et al. 2007; Amelin 2008a, b; Wadhwa et al. 2009; Kleine et al. 2012; McKibbin et al. 2015), and assuming that 4 Vesta and the APB experienced similar magmatic processes, their volatile reservoirs could likewise have evolved in comparable ways. However, on the basis of textural evidence, the later histories of the angrite and eucrite parent bodies diverged. Angrites are practically unshocked, unbrecciated and unmetamorphosed, whereas eucrites have experienced brecciation, shock and thermal metamorphism. If 4 Vesta is the parent body of the eucrites and diogenites that have landed on Earth as meteorites, then it is a truism to observe that the HED parent is still present in the Asteroid Belt, and is of a significant size. The same is not the case for angrites. Spectroscopic matches between angrites and asteroids have identified at least 3 bodies that might be the source of angrites: 3819 Robinson (Burbine et al., 2006), 3628 Božněmcová (Cloutis et al. 2006) and 5261 Eureka (Rivkin et al. 2007). These asteroids are less than 10 km in diameter and have mean orbital parameters quite different from that of 4 Vesta: 3819 Robinson and 3628 Božněmcová have semi-major axes of 2.78 AU and 2.54 AU respectively, which places them in the Middle Main Belt. This contrasts with 4 Vesta, which has a semi-major axis of 2.36 AU, and is in the Inner Main Belt. The different locations place two of the potential APB on the far side of the 3:1 Kirkwood Gap, whilst 4 Vesta is on the nearside. 5261 Eureka is a Mars Trojan, with semi-major axis of 1.52 AU, again, very different from 4 Vesta. Whichever asteroid is the APB, it is clearly no longer > 100 km in diameter. Scott and Bottke

(2011) suggested that collisional break-up of a larger APB might have produced much smaller objects, of the order of 10 km in diameter some of which may still be present, although there has been no conclusive identification to date.

The implications of the carbon and nitrogen data from eucrites and diogenites – or rather, the lack of it – are that 4 Vesta was pretty thoroughly degassed of volatiles, although there is some recent recognition of at least some residual water, chlorine and fluorine (Sarafian et al., 2013; Barrett et al., 2016). It is clear from existing geochemical data that the origins of the volatiles within the angrite and HED groups are different (Greenwood et al., 2005). However, it is not clear whether this represents fractionation from a similar initial abundance and isotopic composition or whether the starting compositions were significantly different. Under the conditions of a comparable starting composition, it is unlikely that 4 Vesta could have produced the relative difference in carbon isotopic composition by simply having a greater degree of simple degassing. A simple explanation for the difference can be found in the brecciated nature of the HED group. While care was taken to select unbrecciated samples, the fact that the majority of HED meteorites have suffered brecciation implies substantial modification of the volatile reservoirs within the body and thus even relatively undisturbed individual samples may show traces of disruption. Perhaps more importantly, the strong evidence for extensive thermal metamorphism within the eucrite group (e.g. Metzler et al., 1995; Kleine et al., 2005) makes it exceptionally likely that volatiles would have been remobilised after formation. Again however, it is important to mention that this is based on the assumption of a comparable starting composition. It is entirely possible that the HEDs evolved from an entirely different starting composition and have arrived at their current composition by chance only. In this way, the implications for the angrites in

Figure 3b may prove useful. There is a hint of a link between the carbon and nitrogen isotopes within the angrites and it would be interesting to see whether the same relationship is found within the HED group, which may be traceable back to an initial composition. At present this comparison is not possible due to the paucity of simultaneous carbon and nitrogen data but it is possible that an additional study with larger aliquot sizes would be able to produce this information.

Conclusions

Angrites contain several different carbon- and nitrogen-bearing components, the most abundant of which is released on combustion at temperatures around 500 – 750 °C. This Moderately Volatile Material (MVM) is clearly a mixture of two separate phases, one of which is inorganic in nature (Cluster A, up to 400 ppm carbon with $\delta^{13}\text{C}$ of -11 ‰ to +10 ‰), the other, organic (Cluster B up to 200 ppm carbon with $\delta^{13}\text{C}$ of -26 ‰ to -16 ‰). Cluster A has a carbon isotopic composition within the range of carbonates in terrestrial soils, whilst Cluster B falls within the isotopic values of terrestrial organic matter. We conclude that the MVM is a combination of terrestrial contaminants. Flakes of calcium carbonate scraped from cavities within D'Orbigny have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ indistinguishable from terrestrial soil carbonates, so it is not possible, on the basis of their light element composition, to infer that the carbonates were native to the angrite parent body.

Above ~ 750 °C, much lower quantities of carbon and nitrogen are released on combustion: mean carbon abundance of 30 ppm and $\delta^{13}\text{C} - 20.0 \pm 6.7$ ‰; mean nitrogen abundance of 2 ppm and $\delta^{15}\text{N} + 12.7 \pm 16.8$ ‰. The extended and variable range in release temperature (in some cases up to 1300 °C), plus the observation that graphite has never been petrographically identified in angrites, together with the presence of vesicles in some of the angrites, suggests that carbon and nitrogen are dissolved in the

silicate lattice, rather than occurring as specific, discrete components. The match in carbon content and isotopic composition between whole rock D'Orbigny and a glass separate hand-picked from the sample also supports this conclusion. The carbonate anion might also substitute within phosphate minerals. Nitrogen may be physically dissolved in the silicate matrix, either as N_2 or as NH_4^+ : results from combustion are unable to distinguish between the two possibilities. Substitution of the ammonium ion within apatite is also an intriguing potential locality for nitrogen storage in igneous meteorites.

Eucrites and diogenites are less oxidised than angrites, and, if their parent asteroid **began** with a similar complement of volatiles to the angrite parent body, **they** are far more degassed. From the angrite results and comparison with those obtained from unbrecciated and anomalous eucrites and diogenites, some interesting inferences can be made regarding the state of carbon and nitrogen in the Solar System. The apparent correlation between ^{13}C and ^{15}N enrichment within the angrite group points towards a simple, possibly linked, mass-dependent fractionation process. Carbon in eucrites and diogenites is less abundant and isotopically lighter than carbon in angrites, suggesting a greater degree of degassing. However it is not clear from the data whether this is the result of different processes from a source of similar composition or the result of similar processes, taken to a greater extent, from a significantly different starting composition.

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Figure Captions

Figure 1: Moderately Volatile Material (MVM) released from angrites, eucrites and diogenites by stepped combustion (Table 4). (a) Carbon. The range in $\delta^{13}\text{C}$ of angrite carbonates (Table 6) is shown by the uppermost shaded region, whilst that for soil carbonates (Cerling, 1984; Cerling & Quade, 1993) also incorporates the lower pale shaded region. Cluster A is signified by the rectangular box (b) Nitrogen. The shaded region is the range of $\delta^{15}\text{N}$ for terrestrial organic contaminants (Boyd et al. 1993; Miura & Sugiura, 1993); the dashed line is terrestrial atmosphere. Error bars are smaller than the symbols unless shown otherwise. Closed symbols: data from this study and from Abernethy et al. (2013); Open symbols: angrites – Wright et al., 1989; eucrites and diogenites – Grady et al., 1997.

Figure 2: Refractory Material (RM) released from angrites, eucrites and diogenites by stepped combustion (Table 5). (a) Carbon and (b) Nitrogen. Error bars are smaller than the symbols unless shown otherwise. Closed symbols: data from this study and from Abernethy et al. (2013); Open symbols: angrites – Wright et al., 1989; carbon in eucrites and diogenites – Grady et al., 1997; nitrogen in eucrites – Miura and Sugiura, 1993. Note the logarithmic scale for abundance data.

Figure 3: Variation of carbon with nitrogen in RM in angrites. (a) Abundances. The upper line is an exponential fit to the data from quenched angrites (including S99-1). Although the fit has $r = 0.98$, because there are only 5 points, the significance of the fit is poor. The lower line is an exponential fit to the data from plutonic angrites ($r = 0.91$, $n=6$). The dashed line is an exponential fit to abundance data from all angrites, $r = 0.69$, $n = 11$. In all three populations (quenched angrites, plutonic angrites and all angrites), the data fit better to an exponential curve than a monotonic linear trend.

(b) Isotopic compositions. The steep line is a linear fit to the data from quenched angrites ($r = 0.98$, $n = 4$); again, the significance of the apparent correlation is poor because of the low number of data points. The shallow line is a linear fit to data from plutonic angrites ($r = 0.90$, $n = 6$). The dashed line is a linear fit to abundance data from all angrites ($r = 0.74$, $n = 10$).

Figure 4: Rayleigh fractionation curves to assess open system degassing as a mechanism for volatile evolution on the APB. (a) Carbon. The solid lines are calculated assuming CO₂-graphite fractionation at 1000 °C (Bottinga, 1968) and the dashed lines assuming temperature-independent CO₂-melt fractionation (Matty, 1991), from starting $\delta^{13}\text{C}$ values of –35 ‰, –25 ‰ and –20 ‰. (b) Nitrogen. The curves are calculated assuming diffusion as molecular nitrogen (solid line) or as atomic nitrogen or NH₄⁺ (dashed line) from starting $\delta^{15}\text{N}$ values of –30 ‰ and 0 ‰. Closed symbols: data from this study and from Abernethy et al. (2013); Open symbols: Wright et al., 1989.

Figure 1

Figure 2

Figure 3

Figure 4

Table 1: Samples analysed in this study

Sample	Source	Sample	Source	Sample	Source
Angrites		Eucrites		Diogenites	
Angra dos Reis	1	ALHA 81001	2	GRA 98108	2
D'Orbigny	1	Asuka 881394	6	GRO 95555	2
LEW 86010	2	Caldera			
NWA 1296	3	GRA 98098	2		
NWA 2999	4	Ibitira			
NWA 4590	3	PCA 91007	2		
NWA 4801	3	QUE 97053	2		
Sahara 99555	5				

Source: (1) Natural History Museum, London (D'Orbigny BM 2001, M10; Angra dos Reis BM 63233); (2) Antarctic Meteorite Working Group, Houston, USA; (3) Dr Yuri Amelin, Australia National University, Canberra; (4) A. Hupé; (5) Dr A. Bischoff, Universität Münster, Münster; (6) National Institute of Polar Research, Tokyo, Japan.

Table 2: Basic textural characteristics of samples analysed

Sample	Texture	Grain size	Ref
Quenched Angrites			
D’Orbigny	Vesicular, abundant glass, contains alternate dense and vesicular layers	< 2 mm	1
Sahara 99555	Ophitic, vesicular	~ 0.5 mm	1
NWA 1296	Vesicular, spinifex olivines	< 0.5 mm	1, 2
Plutonic Angrites			
Angra dos Reis	Cumulate	< 5 mm	3
LEW 86010	Granular with euhedral to subhedral grains	< 2.5 mm	1
NWA 2999	Granular, possibly partially metamorphosed	Mostly 0.1–0.5 mm but up to 6 mm	1, 4
NWA 4590	Igneous cumulate	0.6–1.6 mm	1
NWA 4801	Granular, cumulate	0.1–1.2 mm	1
Eucrites			
ALHA81001	Basaltic, glassy, heterogeneous, unbrecciated	Mostly < 0.2 mm	5
Asuka 881394	Granulitic, cumulate	0.4–2 mm	10
Caldera	Gabbroic, monomict breccia	Few mm	5, 6
GRA 98098	Granoblastic, unbrecciated	~ < 1 mm	5
Ibitira	Granoblastic, vesicular	~ < 0.2 mm	5, 8
PCA 91007	Brecciated, vesicular	~ 0.05–0.1 mm	9
QUE 97053	Sub-ophitic, shocked, unbrecciated	~ < 1.5 mm	5
Diogenites			
GRA 98108	Moderately shocked		
GRO 95555	Granular aggregate, anhedral crystals	0.3–2.4 mm	7

References: ¹Keil (2012) ²Jambon et al. (2005) ³Prinz et al. (1977) ⁴Kuehner et al. (2006) ⁵Mayne et al. (2009) ⁶Wadhwa & Lugmair (1996) ⁷Papike et al. (2000) ⁸Wilkening & Anders, (1975) ⁹Warren et al. (1996) ¹⁰Nyquist et al. (2003)

Table 3: Combustion temperatures for carbon and nitrogen components

Sample	Moderately Volatile Material		Refractory Material	
	[C]	[N]	[C]	[N]
Quenched Angrites				
D'Orbigny-1 ¹	600 - 700	600 - 800	750 - 950	850 - 1200
D'Orbigny-2	500 - 650	nm	700 - 1200	nm
D'Orbigny Glass ¹	600 - 800	500 - 650	900 - 1200	900 - 1100
NWA 1296-1	600 - 800	700 - 800	950 - 1400	800 - 1200
NWA 1296-2	550 - 650	na	na	na
Sahara 99555-1 ¹	650 - 700	600 - 800	750 - 950	900 - 1200
Sahara 99555-2	650 - 800	550 - 750	850 - 1000	800 - 1100
Plutonic Angrites				
Angra dos Reis-1 ¹	650 - 750	650 - 700	850 - 1100	900 - 1100
Angra dos Reis-2	nm	nm	750 - 1000	nm
Angra dos Reis-3 ²	500 - 700	na	900 - 1200	na
Angra dos Reis-4 ²	na	500-600	na	900 - 1100
LEW 86010-1 ¹	600 - 700	nm	750 - 1100	950 - 1000
LEW 86010-2	600 - 700	700	750 - 800	900 - 1100
LEW 86010-3 ²	500 - 600	na	800 - 900	na
LEW 86010-4 ²	na	550 - 700	na	800 - 1100
NWA 2999	550 - 750	550 - 750	800 - 900	800 - 1000
NWA 4590-1	600 - 750	nm	nm	nm
NWA 4590-2	700 - 750	nm	750 - 1000	750 - 1100
NWA 4801-1	550 - 700	500 - 700	nm	nm
NWA 4801-2	600 - 700	550 - 800	750 - 1100	750 - 800
Eucrites				
ALHA76005 ³	500 - 700	nm	750 - 1000	nm
ALHA81001	550 - 700	600 - 700	1200 - 1300	750 - 850
Asuka 881394	nm	nm	nm	nm
Caldera	nm	nm	nm	nm
GRA 98098	nm	nm	1300 - 1400	nm
Ibitira-1	nm	nm	nm	nm
Ibitira-2	550 - 600	550 - 600	nm	nm
Juvinas ³	500 - 700	nm	800 - 1200	nm
Pasamonte ³	500 - 700	nm	750 - 1200	nm
PCA 91007	nm	nm	750 - 1000	nm
QUE 97053	nm	nm	1100 - 1400	nm
Sioux County ³	500 - 700	nm	750 - 1200	nm
Diogenites				
EETA 79002 ³	500 - 700	nm	750 - 900	nm
GRA 98108	nm	nm	nm	nm
GRO 95555	nm	nm	750 - 1200	nm
Johnstown ³	500 - 700	nm	800 - 1200	nm
Shalka ³	500 - 700	nm	750 - 850	nm
Tatahouine ³	500 - 700	nm	750 - 850	nm

na – not analysed; nm – not measurable (i.e., no volatiles released above blank levels)

¹Abernethy et al. (2013); ²Wright et al. (1989); ³Grady et al. (1997)

Temperature ranges are based on the step profiles of each combustion experiment. They are associated with a noticeable maximum in yield or a rapid shift in isotopic composition to a plateau value around the temperatures of ~ 500-700 °C for MVM and greater than 750 °C for RM.

Table 4: Carbon and Nitrogen characteristics of Moderately Volatile Material (MVM) in angrites, eucrites and diogenites

Sample	Mass (mg)	[C] (ppm)	±	$\delta^{13}\text{C}$ (‰)	±	[N] (ppm)	±	$\delta^{15}\text{N}$ (‰)	±
Quenched Angrites									
D'Orbigny-1 ¹	5.112	3.6	0.0	7.9	1.0	2.9	0.1	8.4	1.6
D'Orbigny-2	5.683	260.9	0.1	-15.9	1.1	nm		nm	
D'Orbigny Glass ¹	4.778	62.9	1.0	-3.0	1.2	1.7	0.1	28.9	1.5
NWA 1296-1	6.358	267.2	2.7	na		0.7	0.0	38.7	3.4
NWA 1296-2	1.214	170.6	1.7	-2.8	1.2	nm		nm	
Sahara 99555-1 ¹	10.695	57.8	1.9	-10.4	0.4	2.3	0.3	3.9	2.6
Sahara 99555-2	9.257	15.3	0.2	-8.2	2.8	0.7	0.0	13.4	1.0
Plutonic Angrites									
Angra dos Reis-1 ¹	5.241	32.9	0.3	-20.3	0.4	1.1	0.1	0.1	3.6
Angra dos Reis-2	3.025	nm		nm		nm		nm	
Angra dos Reis-3 ²	4.123	94.3	0.9	-25.1	0.7	na		na	
Angra dos Reis-4 ²	5.365	na		na		2.1	0.2	8.1	1.0
LEW 86010-1 ¹	3.779	6.0	0.1	-21.5	1.4	nm		nm	
LEW 86010-2	5.04	37.1	0.2	-19.1	1.5	3.5	0.2	12.7	0.3
LEW 86010-3 ²	5.062	108.0	1.1	-17.1	2.8	na		na	
LEW 86010-4 ²	5.682	na		na		1.3	0.4	8.2	1.1
NWA 2999	5.966	129.3	1.3	-6.5	0.5	1.5	0.1	13.4	1.6
NWA 4590-1	7.19	21.3	0.2	-1.2	2.0	nm		nm	
NWA 4590-2	4.838	38.2	0.4	-22.9	1.2	nm		nm	
NWA 4801-1	6.249	208.3	2.1	5.8	0.2	1.7	0.1	13.9	1.8
NWA 4801-2	2.894	385.7	3.9	0.5	0.8	2.7	0.1	8.9	1.9
Eucrites									
ALHA76005 ³	10.414	12.9	0.2	-24.5	1.2	na		na	
ALHA81001	5.056	187.8	1.9	-22.2	0.6	5.0	0.1	-5.3	0.5
Asuka 881394	4.331	nm		nm		nm		nm	
Caldera	5.144	nm		nm		nm		nm	
GRA 98098	5.535	nm		nm		nm		nm	
Ibitira-1	6.615	nm		nm		nm		nm	
Ibitira-2	7.924	13.9	0.5	-11.0	0.6	0.4	0.1	22.2	3.0
Juvinas ³	15.483	62.9	0.1	-22.2	0.2	na		na	
Pasamonte ³	10.787	86.7	0.1	-21.4	0.2	na		na	
PCA 91007	5.108	nm		nm		nm		nm	
QUE 97053	5.094	nm		nm		nm		nm	
Sioux County ³	28.804	203.4	0.1	-23.6	0.2	na		na	
Diogenites									
EETA 79002 ³	10.557	162.1	0.1	-24.9	0.2	na		na	
GRA 98108	6.110	nm		nm		nm		nm	
GRO 95555	5.365	nm		nm		nm		nm	
Johnstown ³	16.591	126	0.1	-22.1	0.5	na		na	
Shalka ³	10.777	46.8	0.2	-25.0	0.5	na		na	
Tatahouine ³	10.159	53.3	0.2	-23.2	0.2	na		na	

na – not analysed; nm – not measurable (i.e., no volatiles released above blank levels);

¹Abernethy et al. (2013); ²Wright et al. (1989); ³Grady et al. (1997)

Table 5: Carbon and nitrogen characteristics of Refractory Material (RM) in angrites, eucrites and diogenites

Sample	Mass (mg)	[C] (ppm)	±	$\delta^{13}\text{C}$ (‰)	±	[N] (ppm)	±	$\delta^{15}\text{N}$ (‰)	±
Quenched Angrites									
D'Orbigny-1 ¹	5.112	11.9	0.1	-10.3	0.7	0.7	0.1	34.8	10.7
D'Orbigny-2	5.683	15.6	0.1	-17.2	5.5	nm		nm	
D'Orbigny Glass ¹	4.778	14.7	0.2	-14.8	3.6	1.3	0.1	20.3	3.6
NWA 1296-1	6.358	27.5	0.3	na		0.4	0.2	58.1	5
NWA 1296-2	1.214	nm		nm		nm		nm	
Sahara 99555-1 ¹	10.695	57.7	0.6	-23.4	2.3	9.9	0.5	4.6	0.4
Sahara 99555-2	9.257	7.8	0.1	-19.2	2.6	0.5	0.1	9.4	3.4
Plutonic Angrites									
Angra dos Reis-1 ¹	5.241	61.8	0.6	-21.4	0.5	2.6	0.1	-1.1	1.9
Angra dos Reis-2	3.025	17.6	0.2	-27.3	0.6	nm		nm	
Angra dos Reis-3 ²	4.123	88.3	0.9	-25.1	0.8	na		na	
Angra dos Reis-4 ²	5.365	na		na		3.9	0.3	-0.0	0.8
LEW 86010-1 ¹	3.779	13.1	0.1	-25.4	0.8	0.4	0.1	2.2	3.0
LEW 86010-2	5.04	24.5	0.2	-20.3	0.4	1.2	0.1	-0.7	4
LEW 86010-3 ²	5.062	1.5	0.1	-25.4	8.2	na		na	
LEW 86010-4 ²	5.682	na		na		0.4	0.1	11.3	0.7
NWA 2999	5.966	21.4	0.2	-5.2	0.8	0.6	0.1	16.3	2.0
NWA 4590-1	7.19	nm		nm		nm		nm	
NWA 4590-2	4.838	44.4	0.4	-14.9	5.4	0.8	0.1	9.1	3.3
NWA 4801-1	6.249	nm		nm		nm		nm	
NWA 4801-2	2.894	18.7	0.2	-30.5	0.7	0.4	0.2	-1.7	1.0
Eucrites									
ALHA76005 ³	10.414	11.8	0.2	-24.9	1.2	na		na	
ALHA81001	5.056	2.9	0.5	-23.8	4.0	1.0	0.1	-2.6	8.8
Asuka 881394	4.331	nm		nm		nm		nm	
Caldera	5.144	nm		nm		nm		nm	
GRA 98098	5.535	5.7	0.2	-27.8	4.8	nm		nm	
Ibitira-1	6.615	nm		nm		nm		nm	
Ibitira-2	7.924	nm		nm		nm		nm	
Juvinas ³	15.483	15.3	0.1	-23.8	1.0	na		na	
Pasamonte ³	10.787	11.6	0.2	-22.4	1.5	na		na	
PCA 91007	5.108	7.2	0.6	-30.0	1.7	nm		nm	
QUE 97053	5.094	17.0	0.1	-27.3	1.1	nm		nm	
Sioux County ³	28.804	27.0	0.1	-28.5	0.8	na		na	
Diogenites									
EETA 79002 ³	10.557	3.5	0.2	-21.2	2.1	na		na	
GRA 98108	6.110	nm		nm		nm		nm	
GRO 95555	5.365	2.2	0.5	-30.2	4.6	nm		nm	
Johnstown ³	16.591	22	0.1	-28.6	1.0	na		na	
Shalka ³	10.777	7.0	0.2	-26.6	2.2	na		na	
Tatahouine ³	10.159	2.5	0.5	-25.0	2.2	na		na	

na – not analysed; nm – not measurable (i.e., no volatiles released above blank levels);

¹Abernethy et al. (2013); ²Wright et al. (1989); ³Grady et al. (1997)

Table 6: Results from dissolution of carbonates in orthophosphoric acid

Sample	$\delta^{13}\text{C}$ (‰) (vPDB)	$\pm$	$\delta^{18}\text{O}$ (‰) (vSMOW)	$\pm$
D'Orbigny:				
Whole Rock-1	+ 1.00	0.17	+ 31.64	0.20
Whole Rock-2	- 0.86	0.09	+ 28.31	0.14
Powder-1 *	- 0.48	0.08	+ 28.96	0.06
Powder-2	- 0.40	0.20	+ 29.14	0.14
Powder-3	- 0.86	0.15	+ 28.73	0.18
Plaque-1 *	+ 5.37	0.05	+ 30.09	0.02
NWA 4590	- 6.94	0.28	+ 23.56	0.14
NWA 4801	+ 1.64	0.07	+ 28.29	0.08

*Data from Abernethy et al. (2013).

All D'Orbigny material came from specimen BM2001,M10 from the Natural History Museum, London. The powder was picked from several locations across the exterior surface of the approx. 5 x 4 x 3 cm-sized specimen, and the plaque removed from the interior of an open vesicle on the exterior surface.