



The oxygen isotope composition of diogenites: Evidence for early global melting on a single, compositionally diverse, HED parent body



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ABSTRACT

Oxygen isotope measurements of a suite of 22 diogenites demonstrate that they have a restricted range of $\Delta^{17}\text{O}$ values: -0.246 ± 0.014 (2σ). These results indicate that the diogenites form a single population consistent with a single parent body source, rather than multiple sources as has recently been suggested. Our previously published analysis of eucrites and cumulate eucrites ($n = 34$) give very similar results to the diogenites, with $\Delta^{17}\text{O} = -0.241 \pm 0.016\text{‰}$ (2σ) and confirm that diogenites and eucrites are from the same parent asteroid. The isotopic homogeneity displayed by diogenites, eucrites and cumulate eucrites, provides strong evidence for an early large-scale melting event on the HED parent body, possibly resulting in the formation of a magma ocean. The paradox, whereby diogenites show isotopic evidence in favor of global melting, but also geochemical features indicative of late stage interaction with eucritic crust, may reflect a rapid transition from global to serial magmatism on their parent body. The fact that all the lithologically varied HED units have an isotopically homogeneous composition supports the proposal that they are derived from a single, large, diverse asteroid, most likely 4 Vesta. The recent suggestion that the HEDs are not from Vesta, but instead represent material from the same asteroidal source as the main-group pallasites and IIIAB irons can be excluded by our oxygen isotope data.

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1. Introduction

The early solar system was populated by a multitude of small differentiated planetesimals, which by a process of collisional mergers, formed the building blocks of the larger terrestrial planets (Bottke et al., 2006a; Chambers, 2004; Russell et al., 2012; Walsh et al., 2011). Iron meteorites are predominantly samples from the cores of between 26 to 60 small differentiated asteroids (Chabot and Haack, 2006; Scott, 1972; Wasson, 2013a) and yield ages within 1–2 Myr of solar system formation (Kleine et al., 2005). However, silicate-rich material from the overlying mantle and crust of these bodies is much less common in both the asteroid population and meteorite record (Burbine et al., 1996). This most likely reflects the greater physical strength of iron meteorites and asteroids (Burbine et al., 1996), which commonly have much longer cosmic ray exposure ages than silicate-rich meteorites (Eugster, 2003).

The 525 km diameter asteroid 4 Vesta is the largest surviving differentiated protoplanet (Russell et al., 2012). A range of evidence, including: spectral data, orbital dynamics and recent remote sensing observations by the NASA Dawn spacecraft indicates that the Howardite–Eucrite–Diogenite (HED) group of meteorites originated from 4 Vesta (Binzel and Xu, 1993; De Sanctis et al., 2012; McCord et al., 1970; McSween et al. 2011, 2013). However, this link has been disputed by some (Schiller et al., 2011; Wasson, 2013a). The HEDs are the most abundant group of differentiated meteorites arriving on Earth, comprising roughly 6% of all witnessed falls (statistics from Meteoritical Bulletin Database; see also Burbine et al., 2002). Eucrites are basaltic rocks that formed either as lava flows or intrusions, diogenites are coarser-grained igneous cumulates and howardites are complex impact breccias containing both diogenitic and eucritic fragments.

Despite showing significant mineralogical and geochemical diversity (McSween et al., 2011; Yamaguchi et al., 2011), the majority of diogenites and eucrites display relatively restricted variation with respect to $\Delta^{17}\text{O}$ (Scott et al., 2009). The level of oxygen isotope homogeneity shown by the HEDs is equivalent to that in the SNCs and lunar rocks (Greenwood et al., 2012a) and has been cited as evidence that their parent body underwent early,

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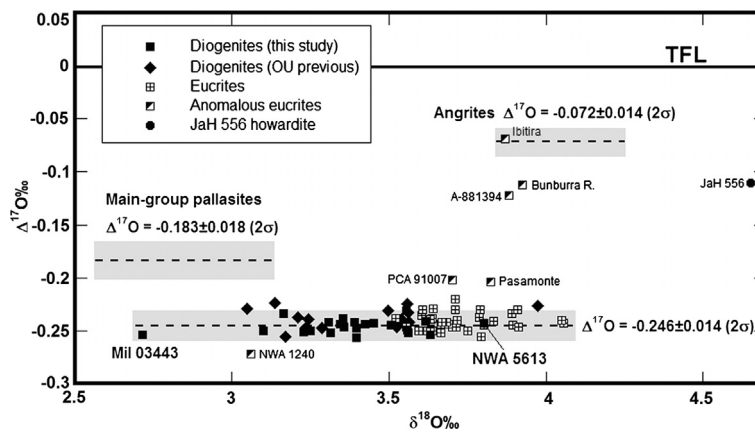


Fig. 1. Oxygen isotope composition of diogenites shown in relation to isotopically normal and anomalous eucrites. Diogenites this study (squares); previous Open University diogenite analysis (diamonds) (Barrat et al., 2006, 2008; Greenwood et al., 2005; Scott et al., 2009); eucrites and cumulate eucrites (squares with crosses) (Barrat et al., 2007; Greenwood et al., 2005; Gardner-Vandy et al., 2011; Llorca et al., 2009; Moggi-Cecchi et al., 2008; Roszjar et al., 2011; Scott et al., 2009; Yamaguchi et al., 2009); anomalous eucrites (diagonal-filled square) (Bland et al., 2009; Greenwood et al., 2005; Scott et al., 2009); JaH 556 howardite (Janots et al., 2012). Grey boxes show the $\Delta^{17}\text{O} \pm 2\sigma$ variation for the diogenites, main-group pallasites (Greenwood et al., 2006) and angrites (Greenwood et al., 2005). Horizontal dashed lines are the mass fractionation lines for the diogenites, main-group pallasites and angrites. The isotopically anomalous basaltic achondrite NWA 011 (Yamaguchi et al., 2002) is not shown on the diagram for reasons of scale. TFL = Terrestrial Fractionation Line. Errors are 2σ .

large-scale melting, resulting in the development of a magma ocean (Greenwood et al., 2005). However, in contrast to the bulk of HEDs, a relatively small group of basaltic achondrites (Fig. 1) have anomalous oxygen isotope compositions (i.e. at least 3σ outside the mean $\Delta^{17}\text{O}$ value of isotopically normal samples) (Greenwood et al., 2012a; Scott et al., 2009). Three possible explanations have been proposed to explain the origin of these anomalous HEDs: (i) both normal and anomalous samples come from a single heterogeneous parent body (Wiechert et al., 2004), (ii) anomalous samples are from non-HED parent bodies (Scott et al., 2009), and (iii) isotopic heterogeneity may be the result of impact mixing (Greenwood et al., 2005; Janots et al., 2012).

One approach to test these models further would be to look in detail at the oxygen isotope composition of diogenites. These coarse-grained orthopyroxenites are likely to have crystallized at deeper structural levels in their parent body than the basaltic eucrites, and as a result are less likely to be modified by impact mixing processes. While diogenites are not immune to the effects of impact processing, with most showing evidence of brecciation, only a small subset are polymict, including the important falls Aïoun el Atrouss, Garland and Pecklsheim (Mittlefehldt, 1994; Mittlefehldt et al., 1998; Meteoritical Bulletin Database). Warren et al. (2009) estimate that only 4% of diogenite meteorites are polymict, compared to 30% for the eucrites.

A recent study by Day et al. (2012) reported higher levels of oxygen isotope variation in the diogenites than had previously been recognized and as a result it was suggested that they may be derived from multiple parent bodies. In view of the importance of trying to understand whether the HEDs are derived from a single or multiple parent bodies and to better resolve the levels of isotopic heterogeneity present within this important group of achondrites, we have undertaken a detailed study of a representative suite of 22 diogenites.

2. Materials, methods and sample selection

Oxygen isotope analysis was carried out at the Open University using an infrared laser-assisted fluorination system (Miller et al., 1999). All analyses were obtained on approximately 2 mg whole rock aliquots drawn from larger homogenized sample powders (see below). Oxygen was released from the sample by heating in the presence of BrF_5 . After fluorination, the oxygen gas released was purified by passing it through two cryogenic nitrogen traps and

over a bed of heated KBr. Oxygen gas was analyzed using a MAT 253 dual inlet mass spectrometer. Published analytical precision (2σ) for our system, based on replicate analysis of international (NBS-28 quartz, UWG-2 garnet) and internal standards, is approximately $\pm 0.08\text{‰}$ for $\delta^{17}\text{O}$; $\pm 0.16\text{‰}$ for $\delta^{18}\text{O}$; $\pm 0.05\text{‰}$ for $\Delta^{17}\text{O}$ (Miller et al., 1999). Changes to analytical procedures implemented subsequent to the system description given by Miller et al. (1999) have resulted in improvements to precision such that 39 analyses of our internal obsidian standard undertaken during six separate sessions in January, February and September of 2013 gave the following combined results: $\pm 0.05\text{‰}$ for $\delta^{17}\text{O}$; $\pm 0.09\text{‰}$ for $\delta^{18}\text{O}$; $\pm 0.02\text{‰}$ for $\Delta^{17}\text{O}$ (2σ). All sample powders analyzed in this study were prepared by crushing whole rock chips with a mass of between 20 mg and 1.3 g. Details of the exact mass for each sample are given in Table 1. Sample powders were prepared either at the Open University or the University of Brest (Table 1). Samples prepared at the Open University were crushed to a fine powder in an agate pestle and mortar and likewise at the University of Brest using a boron-carbide mortar. A number of the samples (NWA 1877, NWA 4223, NWA 4664, NWA 5613) were leached in 6 M HCl to remove weathering products following the procedures described in Barrat et al. (2010). All samples were subsequently leached in a solution of ethanolamine thioglycollate (EATG), which has proved to be efficient at removing terrestrial weathering products, without significantly disturbing the primary oxygen isotope composition of the sample (Greenwood et al., 2012b). The mass of homogenized powder that was treated with EATG varied between 15.3 and 79.1 mg (see Table 1 for details). In all cases the 2 mg aliquot loaded for fluorination was drawn from the EATG-leached material. The precision (1σ) quoted for individual meteorite samples analyzed in this study is based on replicate analyses.

Oxygen isotopic analyses are reported in standard δ notation, where $\delta^{18}\text{O}$ has been calculated as: $\delta^{18}\text{O} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{ref}} - 1] \times 1000$ (‰) and similarly for $\Delta^{17}\text{O}$ using the $^{17}\text{O}/^{16}\text{O}$ ratio (where ref is VSMOW: Vienna Standard Mean Ocean Water). $\Delta^{17}\text{O}$, which represents the deviation from the terrestrial fractionation line, has been calculated using a linearized format (Miller, 2002):

$$\Delta^{17}\text{O} = 1000 \ln(1 + \delta^{17}\text{O}/1000) - \lambda 1000 \ln(1 + \delta^{18}\text{O}/1000)$$

where $\lambda = 0.5247$, which was determined using 47 terrestrial whole rock and mineral separate samples (Miller et al., 1999; Miller, 2002).

Table 1

#	Sample	Lithology	Source	Low-Ca pyroxene		Mass (g)	EATG (mg)	N	$\delta^{17}\text{O}$ (‰)	1 σ	$\delta^{18}\text{O}$ (‰)	1 σ	$\Delta^{17}\text{O}$ (‰)	1 σ
				FeO/MgO	(Dy/Yb) _n									
1	A-87147,111	Diogenite	NIPR	0.59	0.64	~0.2	20.5	2	1.454	0.071	3.250	0.130	-0.250	0.003
2	A-880785,91	Diogenite	NIPR	0.62	0.44	~0.2	20.2	2	1.533	0.070	3.395	0.130	-0.247	0.002
3	A-881526,111	Diogenite	NIPR	0.58	0.61	~0.2	18.6	2	1.491	0.008	3.306	0.035	-0.242	0.010
4	ALHA 77256,169	Ol-diogenite	MWG	0.58	0.67	0.050	27.1	2	1.655	0.081	3.616	0.153	-0.241	0.001
5	MET 00424,26	Diogenite	MWG	0.74	0.01	0.039	16.3	3	1.593	0.062	3.507	0.123	-0.245	0.006
6	MET 00425,18	Diogenite	MWG	0.34	0.70	0.047	31.0	3	1.565	0.170	3.450	0.329	-0.243	0.004
7	MET 00436,33	Diogenite	MWG	0.72	0.80	0.050	23.4	2	1.513	0.106	3.356	0.202	-0.246	0.001
8	MIL 03443,21	dunitic diogenite	MWG	0.52	0.62	0.050	27.3	4	1.169	0.074	2.714	0.156	-0.254	0.020
9	MIL 07001,36	Ol-diogenite, unbr.	MWG	0.55	0.69	0.051	26.0	3	1.632	0.026	3.554	0.048	-0.231	0.002
10	MIL 07003,15	Diogenite	MWG	0.98	0.74	0.040	25.7	2	1.534	0.018	3.388	0.021	-0.242	0.007
11	MIL 090105,11	Diogenite	MWG		0.80	0.522	24.4	2	1.520	0.043	3.353	0.084	-0.238	0.001
12	MIL 090159,5	Diogenite	MWG		0.82	0.534	33.2	2	1.524	0.023	3.396	0.039	-0.256	0.003
13	NWA 1877	Ol-diogenite	UBO	0.55	0.52	0.652	37.0	2	1.425	0.044	3.164	0.091	-0.234	0.004
14	NWA 4223	Ol-diogenite, unbr.	UBO	0.62	0.64	0.889	79.1	5	1.441	0.120	3.227	0.226	-0.251	0.005
15	NWA 4664	Polymict diogenite	UBO	0.35–0.84	0.88	1.056	35.7	2	1.616	0.091	3.558	0.160	-0.249	0.007
16	NWA 5480	Ol-diogenite (IMB)	UBO	0.59	0.28	1.036	36.8	2	1.375	0.006	3.099	0.007	-0.250	0.010
17	NWA 5613	Diogenite	UBO	0.71	0.81	1.254	28.7	3	1.750	0.069	3.803	0.130	-0.243	0.002
18	NWA 6927	Diogenite	UBO		0.83	0.895	16.6	2	1.614	0.045	3.561	0.107	-0.252	0.011
19	SAN 03473,11	Diogenite	MWG	0.56	0.69	0.523	29.1	2	1.485	0.018	3.312	0.027	-0.252	0.004
20	Y-74013,146	Diogenite	NIPR	0.65	0.38	~0.2	20.2	2	1.508	0.034	3.343	0.057	-0.244	0.004
21	Y-981710,66	Diogenite	NIPR	0.55–0.84	0.87	~0.2	29.2	2	1.650	0.050	3.631	0.100	-0.254	0.002
22	Y-981956,81	Diogenite	NIPR	0.58	0.47	~0.2	15.3	2	1.550	0.096	3.424	0.185	-0.244	0.000
		Mean values (1 to 22)							1.527	0.118	3.382	0.222	-0.246	0.007
		Diogenites previously analyzed at the Open University (Greenwood et al., 2005; Barrat et al. 2006, 2008; Scott et al., 2009)												
23	Bilanga	Diogenite (Fall)		0.45	0.67			4	1.616	0.189	3.538	0.381	-0.239	0.022
24	Johnstown	Diogenite (Fall)		0.57	0.70			4	1.602	0.104	3.497	0.154	-0.231	0.026
25	Tatahouine	Diogenite (Fall), unbr.		0.53	0.26			4	1.461	0.180	3.243	0.328	-0.239	0.015
26	Shalka	Diogenite (Fall)		0.59	0.36			2	1.626	0.074	3.563	0.171	-0.242	0.016
27	Manegaon	Diogenite (Fall)		0.4				2	1.368	0.095	3.047	0.130	-0.229	0.027
28	Roda	Ol-diogenite (Fall)		0.61	0.71			2	1.476	0.041	3.287	0.121	-0.247	0.022
29	Aioun al Atrouss	Diogenite polym. (Fall)		0.56				2	1.420	0.006	3.137	0.036	-0.224	0.013
30	Dhofar 700	Diogenite, unbr., unequilibrated		0.57–0.84	0.61			2	1.856	0.031	3.973	0.100	-0.226	0.021
31	NWA 4272	Diogenite			0.78			2	1.633	0.028	3.561	0.012	-0.233	0.022
32	A-881548	Olivine diogenite		0.50	0.80			4	1.639	0.117	3.557	0.209	-0.225	0.016
33	GRA 98108,24	Ol-diogenite		0.53				2	1.447	0.020	3.233	0.030	-0.247	0.004
34	GRO 95555,35	Diogenite, unbr.		0.55	0.48			4	1.407	0.145	3.171	0.255	-0.255	0.015
35	NWA 1461	Diogenite		0.3	1.01			2	1.602	0.021	3.524	0.035	-0.246	0.002
36	Y-75032,55	Diogenite		0.89	0.81			2	1.446	0.053	3.210	0.123	-0.237	0.011
37	NWA 4215	Diogenite, unbr., unequilibrated		0.53–0.63	0.45			2	1.431	0.102	3.203	0.205	-0.248	0.005
		Mean values (1 to 37)							1.530	0.122	3.382	0.228	-0.243	0.009

References for the orthopyroxene chemical features: [Mittlefehldt \(1994\)](#), [Fowler et al. \(1994\)](#), [Barrat et al. \(2006, 2010\)](#), [Domanik et al. \(2004\)](#), [Mittlefehldt et al. \(2012\)](#). Abbreviations: UBO: University of Brest; NIPR: National Institute of Polar Research; MWG: Meteorite Working Group; (Dy/Yb)_n: CI normalized bulk ratio.

In Section 3.2 we compare our oxygen isotope results on diogenitic samples with those obtained at the Geophysical Laboratory and published in Day et al. (2012). In making a comparison between the two datasets it is important to note that both laboratories have in the past undertaken an extensive inter-laboratory comparison study, the results of which were published in Rumble et al. (2007). The results obtained by the Rumble et al. (2007) study clearly demonstrated that both laboratories achieve comparable levels of precision and despite some minor differences in analytical procedures, essentially make use of the same technique for the analysis of oxygen isotopes. As a consequence, it is important to bear in mind that the comparison between the two diogenite datasets developed in Section 3.2 is sample specific and has no wider applicability.

The 22 samples analyzed in this study were selected using a number of criteria. The principal aim was to have a sample suite that encompassed the full lithological and geochemical diversity currently known amongst the diogenites. In terms of lithological variation, the samples studied include unbrecciated, monomict and polymict diogenites and olivine diogenites (Table 1). With respect to their geochemistry, the samples have FeO/MgO ratios that range from 0.34 to 0.98 and cover the diversity of REE abundances and patterns, with CI normalized Dy/Yb ratios $(Dy/Yb)_n$ varying from 0.01 to 0.87 (Table 1) (Barrat et al. 2008, 2010). The samples analyzed in this study complement those previously analyzed at the Open University (Barrat et al. 2006, 2008; Greenwood et al., 2005; Scott et al., 2009) and so provide a combined suite of 37 diogenite fall and find samples, all analyzed under closely similar calibration conditions (Table 1).

3. Results

3.1. Results from this study

Full results are given in Table 1 and plotted in Fig. 1. The diogenites show a restricted range of $\Delta^{17}O$ values: $-0.246 \pm 0.014\%$ (2σ) (Fig. 1). In terms of $\delta^{18}O$, with the exception of two outliers (NWA 5613 and MIL 03443), the data forms a relatively tight array with values ranging from 3.0‰ to 3.6‰ (Fig. 1). The desert find NWA 5613 has a somewhat heavier $\delta^{18}O$ value than the other diogenites measured in this study. One explanation for this might be that, despite ethanalamine thioglycollate (EATG) treatment, not all the terrestrial weathering products were removed from the sample. NWA 5613 also contains approximately 5 vol% plagioclase feldspar and this may in part account for its higher $\delta^{18}O$ value. In contrast, MIL 03443 is significantly lighter with respect to $\delta^{18}O$ than the other diogenite samples. MIL 03443 is a brecciated dunite containing over 91 vol% olivine (Beck et al., 2011). Our analysis of MIL 03443 is somewhat lighter with respect to $\delta^{18}O$ than that of Beck et al. (2011), i.e. 2.71‰ compared to 3.09‰. MIL 03443 is a relatively coarse-grained, brecciated rock and the difference in $\delta^{18}O$ between the two analyses may reflect variation in modal olivine content. Our mean $\Delta^{17}O$ value for 4 replicate analyses of MIL 03443 is $-0.254 \pm 0.040\%$ (2σ), which is within error of the mean value for all the diogenites analyzed in this study i.e. $-0.246 \pm 0.014\%$ (2σ), consistent with MIL 03443 being an HED.

3.2. Comparison with the results of previous studies

Previous high-precision laser fluorination studies have generally yielded results indicating that diogenites show restricted variability with respect to $\Delta^{17}O$ and have values similar to other HED lithologies. Thus, if the diogenite data obtained in our previous studies (Barrat et al. 2006, 2008; Greenwood et al., 2005; Scott et al., 2009) is combined with the current data, there is only

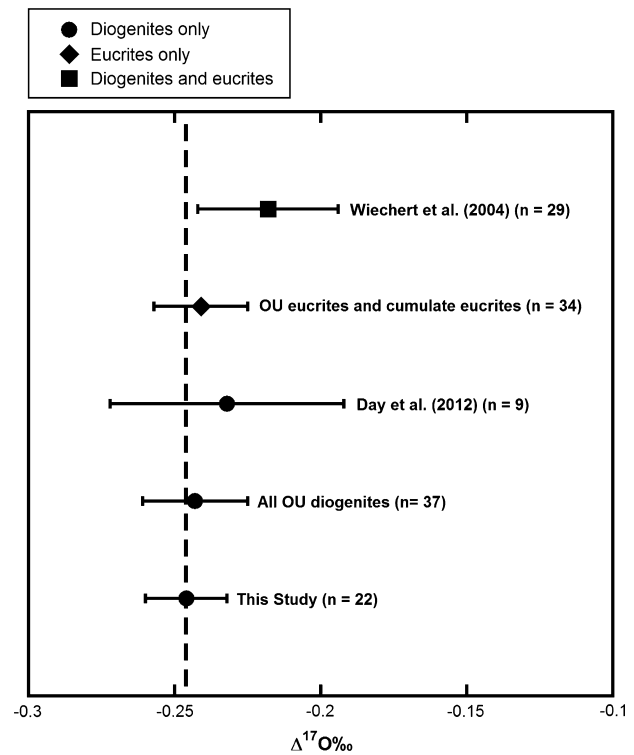


Fig. 2. Comparison of the mean $\Delta^{17}O$ values obtained in various studies of diogenites and eucrites. For references see text and caption of Fig. 1. Vertical dashed line is the average $\Delta^{17}O$ value obtained in the present study. Error bars are 2σ .

a moderate shift in the mean $\Delta^{17}O$ value and a small decrease in precision i.e. $\Delta^{17}O = -0.243 \pm 0.018\%$ (2σ) ($n = 37$) compared to $\Delta^{17}O = -0.246 \pm 0.014\%$ (2σ) ($n = 22$) (Table 1, Fig. 2). Our previously published analysis of 34 eucrites and cumulate eucrites (references given in the caption to Fig. 1) also give very similar results to the diogenites with $\Delta^{17}O = -0.241 \pm 0.016\%$ (2σ) (Fig. 2). These results would appear to confirm the generally held view that diogenites and eucrites are from the same parent asteroid (McSween et al., 2013).

Day et al. (2012) obtained a mean $\Delta^{17}O$ value of $-0.232 \pm 0.040\%$ (2σ) for seven diogenite samples combined with analyses of two additional samples from previous studies (Fig. 2). They suggested that these nine diogenites could be resolved into two distinct groups having $\Delta^{17}O$ values of $\sim -0.25\%$ and -0.21% (Fig. 3). Six of the samples run by Day et al. (2012) have also been analyzed by us (Fig. 3). Our results for these samples give a $\Delta^{17}O$ value of $-0.242 \pm 0.016\%$ (2σ), which is close to that obtained for our full suite of 22 diogenite samples. A number of the samples analyzed by Day et al. (2012) have relatively large uncertainties that appear to compromise their proposed groupings (Fig. 3). Thus, comparison of our results with those obtained by Day et al. (2012) does not support their view that the diogenite meteorites: “represent mantle and crustal materials from two or more differentiated asteroids.” The data obtained in this study indicates that diogenites are from a single isotopically homogeneous parent body. A study of various HED lithologies by Wiechert et al. (2004) gave a mean $\Delta^{17}O$ value which is somewhat shifted in comparison with the results obtained here i.e. $-0.218 \pm 0.024\%$ (2σ) (Fig. 2). This probably reflects calibration differences between the two laboratories (Scott et al., 2009).

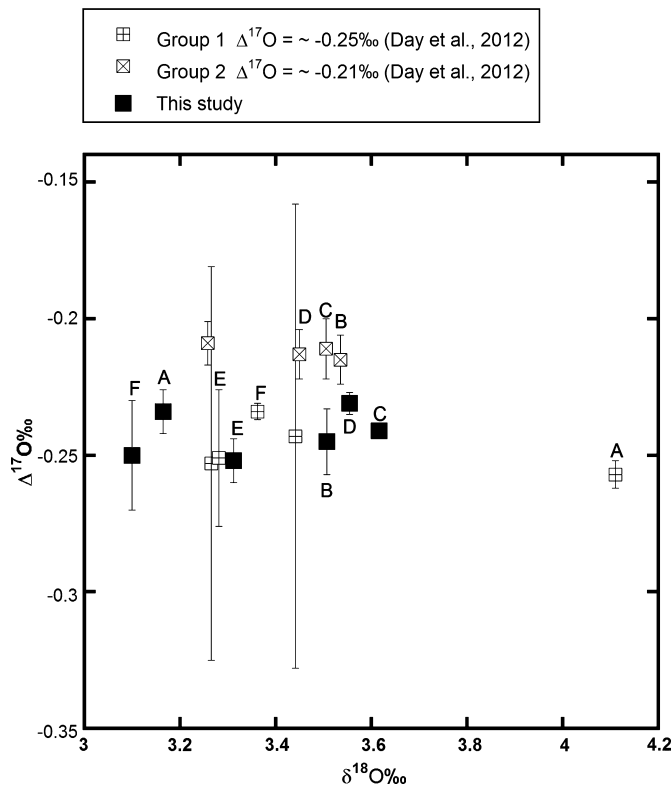


Fig. 3. Oxygen isotope composition of nine diogenite samples as determined in the study of Day et al. (2012). Samples were allocated to one of the two groups as defined in the text of Day et al. (2012). Error bars (2σ) taken from Table S1 of Day et al. (2012). Six of the Day et al. (2012) diogenites were also run during the present study. These are also shown on the diagram (2σ errors as per Table 1). Letters refer to individual sample names: A = NWA 1877; B = MET 00424; C = ALHA 77256; D = MIL 07001; E = SAN 03473; F = NWA 5480.

4. Discussion

4.1. The oxygen isotope composition of the HEDs: homogeneous or heterogeneous?

4.1.1. Diogenites

When attempting to evaluate the intrinsic oxygen isotope variation present in a meteorite group it is important to bear in mind that calibration conditions can vary somewhat between laboratories. This is less of a problem for groups which show significant isotopic variation, such as primitive chondrites and achondrites. However, for groups such as the HEDs, which display an extremely narrow range of $\Delta^{17}\text{O}$ values, it is important that data is collected under consistent analytical conditions. Studies that use data compiled from a range of literature sources risk overestimating the intrinsic isotopic variation present in the HEDs. Day et al. (2012) obtained a value for $\Delta^{17}\text{O}$ of $-0.232 \pm 0.040\text{‰}$ (2σ) for nine diogenites, which they combined with literature data to calculate a $\Delta^{17}\text{O}$ value for the diogenites of $-0.235 \pm 0.029\text{‰}$ (2σ) ($n = 26$). They suggest that this value exceeds analytical uncertainties and indicates higher levels of intrinsic variation within the diogenites than has been previously recognized. However, since this value was obtained by combining data from different laboratories it is likely to exaggerate the intrinsic variability of the diogenites. The problems associated with combining data for the HEDs measured in different laboratories were discussed by Scott et al. (2009), who point out that, even when data is normalized to the same slope factor for the calculation of $\Delta^{17}\text{O}$ values, this can make discrepancies between differing datasets (Greenwood et al., 2005; Wiechert et al., 2004) even greater. It is clear from the analysis of

Scott et al. (2009) that caution needs to be exercised when combining data from different investigators where small differences in $\Delta^{17}\text{O}$ are important, as is the case for the HEDs. The results of the present study, based on 53 replicate analyses of 22 samples (Table 1), indicate that the diogenites are extremely homogeneous with respect to $\Delta^{17}\text{O}$ i.e. $-0.246 \pm 0.014\text{‰}$ (2σ), i.e. about half the level of intrinsic variation estimated by Day et al. (2012). This evidence indicates that diogenites are derived from a parent body that experienced a high level of oxygen isotope homogenization.

4.1.2. Why no anomalous diogenites?

As noted in Section 3.2, our previously published oxygen isotope analyses of eucrites and cumulate eucrites give very similar results to the diogenites with respect to $\Delta^{17}\text{O}$ (Figs. 1, 2). This lends support to the view that all of the major HED lithologies are derived from a single parent asteroid (McSween et al., 2013). However, a small group of basaltic achondrites (Fig. 1) have $\Delta^{17}\text{O}$ that lie at least 3σ outside the mean value defined by the majority of eucrites and cumulate eucrites (Greenwood et al., 2012a; Scott et al., 2009). As pointed out by McSween et al. (2013), the degree of emphasis given to these anomalous samples has resulted in significant differences in the interpretation of HED oxygen isotope data. Thus, Wiechert et al. (2004) proposed that both normal and anomalous samples come from a single heterogeneous parent body. In contrast, Scott et al. (2009) suggested that the isotopically anomalous samples may have come from distinct asteroidal sources, while Greenwood et al. (2005) and Janots et al. (2012) highlighted the possible role of impact processes as a mechanism for producing isotopic heterogeneity.

In the case of a few anomalous eucrites such as NWA 011 (Yamaguchi et al., 2002), Ibitira (Mittlefehldt, 2005), and A-881394 (Nyquist et al., 2003) a range of evidence would seem to indicate that they are not from the same parent body as the majority of HED samples (Scott et al., 2009). However, the situation is less clear cut for the others, with at least some showing significant degrees of brecciation e.g. Bunburra Rockhole (Bland et al., 2009) and Pasamonte (Metzler et al., 1995), while Pasamonte shows elevated HSE contents compared to most eucrites and diogenites (Dale et al., 2012; Day et al., 2012). While it is likely that some anomalous eucrites are derived from distinct parent bodies, a number may be the products of impact mixing on the surface of the HED parent body.

That isotopically anomalous rocks were formed by impact processes on the surface of the HED parent asteroid is demonstrated by the howardite JaH 556 (Janots et al., 2012). JaH 556 is composed of highly shocked clasts set in a finely recrystallized vesicular matrix. The bulk oxygen isotope composition of JaH 556 is anomalous, with a $\Delta^{17}\text{O}$ value of -0.11‰ (Fig. 1). In contrast, EATG-washed clasts in JaH 556 have normal HED $\Delta^{17}\text{O}$ values. 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 of JaH 556 and its bulk oxygen isotope composition point to it containing a 10–15% H chondrite component (Janots et al., 2012).

An interesting observation from the present study is the fact that so far no diogenite samples have been identified which have an anomalous oxygen isotope composition. As discussed in Section 1, the diogenites have experienced impact processing and many are brecciated. On the basis of their highly variable HSE abundances Day et al. (2012) suggest that a chondritic component was added to some diogenites after core formation, but prior to crystallization (see Section 4.3). However, the level of siderophile contamination is lower than in polymict eucrites and howardites (Warren et al., 2009). Compared to the eucrites, diogenites are coarser-grained lithologies and so are likely to have crystallized at

greater depths in their parent body. This is also reflected in the scarcity of polymict diogenites (Warren et al., 2009).

The lack of isotopically anomalous diogenites could be used as an argument against distinct asteroidal sources for the anomalous eucrites. If such anomalous eucrites were formed on distinct asteroids to normal HEDs, then it might be reasonable to anticipate finding equivalent anomalous cumulates i.e. diogenites with non-HED oxygen isotope compositions. The fact that none have so far been identified might suggest that the number of basaltic asteroids sampled by the anomalous eucrites is limited, or that they are the products of impact processing on the HED parent asteroid. However, such an argument ignores the special circumstances that seem to have been required to liberate diogenites from the HED parent body. It appears likely that diogenites were mixed onto the surface of their parent body by a single large impact that predated the collisional event that finally ejected them into space (Warren et al., 2009). This hypothesis is supported by recent numerical modeling of the Rheasilvia basin on Vesta which suggests that a single large impact event would not have liberated mantle material from the asteroid, but instead at least two events were required (Ivanov and Melosh, 2013). While such a multiple strike scenario favors Vesta as the source of the diogenites (see Section 4.4), the lack of anomalous diogenites probably does not exclude distinct parent body sources for anomalous eucrites, on the basis that surface material is more easily liberated from an asteroid than deeper lithologic units. However, what is important from the perspective of this discussion is that the diogenites provide clear evidence that the HED parent body was isotopically homogeneous, except with respect to its regolith, and that there is therefore no need to invoke intrinsic heterogeneity (Wiechert et al., 2004), or multiple diogenite parent bodies (Day et al., 2012).

4.2. Evidence for early global-scale melting on the HED parent body

The HED parent body is generally considered to have formed from a chondritic precursor (Boesenberg and Delaney, 1997; Righter and Drake, 1997; Ruzicka et al., 1997; Toplis et al., 2013). Chondrites are mixtures of materials with diverse oxygen isotopic compositions (including isotopically distinct ice). Thus for example, the CV_{3oxA} subgroup shows variability with respect to $\Delta^{17}\text{O}$ that is approximately two orders of magnitude greater than that displayed by the HEDs ($\Delta^{17}\text{O}$ of CV_{3oxA} = $-3.86 \pm 1.58\%$ (2σ), Greenwood et al., 2010). Homogenization of chondritic precursor materials clearly required some form of large-scale mixing process.

The results presented here demonstrate that the diogenites form a single population consistent with a single parent body source. Further, it is clear from comparison with the results of our previous studies that, despite showing considerable geochemical diversity, all of the main HED lithologies have virtually identical $\Delta^{17}\text{O}$ compositions (Figs. 1, 2). The important questions that arise from these observations concern the exact nature and timing of the event(s) that so effectively homogenized the primordial oxygen isotope variation of the HED precursor materials.

Based on moderately siderophile element abundances (Ni, Co, Mo, W and P), it has been suggested that Vesta experienced an early global-scale melting event, possibly leading to the development of some form of magma ocean (Righter and Drake, 1997). The extremely low highly siderophile element (HSE) abundances (Os, Ir, Ru, Pt, Pd, Re) in HEDs are also consistent with early global-scale melting, resulting in rapid, efficient, low-pressure core formation (Dale et al., 2012; Day et al., 2012). Using a range of possible chondritic source compositions, Righter and Drake (1996, 1997) calculated a percentage core mass for the HED parent body of between 5% and 25%. More recent modeling by Toplis et al. (2013) derived values of between 10% and 30%. The large uncertainties

inherent in such modeling relate to the fact that the precursor material from which the HEDs formed is unknown. The preferred HED precursor composition of Toplis et al. (2013) (75% H chondrite: 25% CM chondrite mix) gives a calculated core radius of 114.2 km, which is a close match to that derived from Dawn observations (110 ± 3 km) (Russell et al., 2012).

While moderately and highly siderophile element abundance data indicates that the HED parent body underwent core formation, this evidence alone does not unambiguously demonstrate that a phase of global melting was involved. Taylor (1992) concluded that high degrees of partial melting ($\sim 50\%$) were required for metal “to drain away and form a core”. While partial melting exceeding 50% has been generally accepted by most recent modeling studies (Hevey and Sanders, 2006; Moskovitz and Gaidos, 2011), core formation at lower degrees of melting may also be possible (Neumann et al., 2012). However, the extended period for core formation in models with lower degrees of melting and the formation of unmelted chondritic crusts suggest that these models are not appropriate for Vesta. The magma ocean model developed by Righter and Drake (1997) indicates that the HED mantle may have been between 65% to 77% molten (1500–1530 °C) and would have undergone turbulent convection during its initial stages. At such elevated temperatures, high degrees of partial melting and turbulent mixing, global-scale homogenization of oxygen isotopes would have taken place extremely rapidly i.e. in less than 400 000 yr (Greenwood et al., 2005).

Development of an early magma ocean on Vesta has also been invoked as a model to explain the Mg isotope systematics of diogenites (Schiller et al., 2011). Using this data Schiller et al. (2011) derive an age for the onset of magma ocean crystallization on the HED parent body of 0.6 Myr after CAI condensation and infer that it was completely solidified within the following 2–3 Myr. However, they argue that such rapid crystallization is inconsistent with 4 Vesta as the source of the HEDs, based on a comparison with the much longer timescales inferred from modeling studies of planetesimals heated by decay of ^{26}Al (Gupta and Sahijpal, 2010). The ages calculated by Schiller et al. (2011) are essentially based on a specific model for the evolution of a hypothetical HED magma ocean. In view of the uncertainties inherent in such a model, this evidence would seem to be less persuasive in pinpointing the HED parent body than the more direct observations made by the Dawn spacecraft (McSween et al., 2013) (see Section 4.4 below).

The possibility that the HED parent body had an early magma ocean has been criticized by Wasson (2013b), who suggests instead that HED magmatism is better explained in terms of impact-driven, local-scale, melting. One of the main objections to large-scale melting on early-formed asteroids cited by Wasson (2013b) relates to the efficacy of ^{26}Al as a heat source (Kunihiro et al., 2004). Based on a study of Mg isotopes in five chondrules from the CO3 chondrite Y-81020, Kunihiro et al. (2004) concluded that the decay of ^{26}Al would not have produced enough heat to cause significant melting. These authors assumed that igneous differentiation and core formation occurred after the known chondrites had accreted. There is, however, strong evidence that the differentiated bodies accreted before the parent bodies of the chondrites, and that most chondrules formed later when levels of ^{26}Al had fallen below those needed to cause melting (e.g., Bizzarro et al., 2005; Hevey and Sanders, 2006; Kleine et al., 2005; Kruijer et al., 2012; Sanders and Scott, 2012). A recent thermal modeling study concluded that ^{26}Al is a viable heat source for the differentiation of Vesta provided that accretion took place less than 1.4 Myr after injection of ^{26}Al (Formisano et al., 2013).

It is also unclear how the impact heating model suggested by Wasson (2013b) would actually work from a collisional and dynamical modeling perspective. As recently reviewed by Marchi et al. (2013), typical impact velocities within the main belt are only

~5 km/s, too small to produce much heat. Numerical simulations combined with studies of impact melt found within terrestrial craters indicate the majority of impact melting takes place for velocities >10 km/s (Pierazzo et al., 1997). This probably explains why little impact melt has been identified within impact basins on Vesta (e.g., Schenk et al., 2012). Note that there are ways to get high velocity projectiles to strike Vesta, particularly in the primordial days of the solar system, but they may involve fairly elaborate processes and are likely limited to relatively small projectiles. The evidence for the impact heating scenario suggested by Wasson (2013b) is not obvious from either the HED data or Vesta images taken by the Dawn spacecraft.

While we favor a short-lived radiogenic heat source, the observations indicating early large-scale melting on the HED parent body are essentially independent of the mechanism involved. That Vesta experienced an early phase of global melting seems an inescapable consequence of a number of lines of evidence. These include the moderately and highly siderophile element depleted composition of the HEDs and the extremely homogeneous oxygen isotope composition of all the major HED lithologies.

4.3. The puzzling origin of diogenites

There remains considerable uncertainty about the geological relationships between the diogenites and eucrites (Barrat et al., 2008, 2010; Mittlefehldt et al., 2012; Shearer et al., 1997, 2010; Yamaguchi et al., 2011). Magma ocean models for the HED parent body generally envisage a layered structure, with eucrites underlain by diogenites (Righter and Drake, 1997; Schiller et al., 2011; Takeda, 1979). This simple relationship has been questioned on the basis of trace element data, which indicates that the parental magmas of some diogenites were contaminated by partial melts derived from fusion of preexisting eucritic crust (Barrat et al., 2010). In addition, there are a number of diogenites that retain compositionally zoned pyroxenes, suggesting that they crystallized at a high structural level and escaped the global metamorphism seen in the eucrites. Examples of these unequilibrated diogenites include Garland (Fowler et al., 1994), NWA 4215 (Barrat et al., 2006), Dho 700, A-881377 and Y-74097 (Yamaguchi et al., 2010, 2011). This evidence suggests that at least some diogenites formed later than the eucrites (Barrat et al., 2010). However, Mittlefehldt et al. (2012) have questioned this conclusion and suggested instead that the highly incompatible elements in diogenites were mobilized during impact mixing and that subsolidus equilibration can account for preferential redistribution of Eu^{2+} relative to Eu^{3+} (Mittlefehldt et al., 2012).

Diogenites display a diverse range of REE patterns suggesting that they formed from multiple parent magmas (Barrat et al., 2008; Fowler et al., 1995). Estimated FeO/MgO ratios for diogenite parental melts range from about 1.4 to 3.5 and overlap the values obtained for non-cumulate eucrites (Barrat et al., 2008). This evidence appears to contradict the generally accepted view that diogenites formed from parental melts more primitive than eucrites during the crystallization of a magma ocean (Barrat et al., 2008). This may indicate a complex evolution for diogenitic parental melts, possibly involving remelting of magma ocean cumulates (Barrat, 2004; Barrat et al., 2008). A recent model for the magmatic evolution of the HED parent body suggests that all of the major lithologies can be produced by 60–70% equilibrium crystallization of a magma ocean followed by extraction of melt into shallow magma chambers (Mandler and Elkins-Tanton, 2013). This model may provide an explanation for the seemingly ambiguous characteristics of diogenites in that they should be early formed based on the progressive crystallization of a magma ocean (Righter and Drake, 1997), and yet show trace element evidence for contamination by eucrites (Barrat et al., 2010). Thus, the majority of

diogenites present in our meteorite collections may have formed as late-stage cumulates within high-level plutons, whereas early-formed orthopyroxenites from the putative magma ocean may only rarely be sampled as meteorites. However, in detail the REE composition of diogenites remains a significant problem for any model involving progressive crystallization of a magma ocean (Barrat et al., 2010).

In addition to their REE diversity, diogenites display widely varying abundances of highly siderophile elements (HSE), with generally flat chondritic normalized patterns consistent with late accretion of primitive chondritic material (Dale et al., 2012; Day et al., 2012). This large range in HSE abundances has been interpreted in terms of a two stage process, with initial depletion taking place during core formation, followed by more localized addition to restricted “mantle domains” (Day et al., 2012). The HSE data for diogenites would therefore seem to favor a model for the formation of diogenites within localized plutons, rather than as cumulates from a magma ocean.

It is clear from the above that a simple stratified model for the relationship between the eucrites and diogenites is problematic. On balance, the evidence seems to favor relatively late emplacement of diogenite plutons into preexisting eucritic crust. The recent identification of olivine-rich lithologies in the walls of craters on Vesta suggests that cumulate materials may have been emplaced to high structural levels on the HED parent body (Ammannito et al., 2013) (assuming Vesta is the source of the HEDs, see Section 4.4). This again seems to suggest plutonic-style magmatism rather than global-scale processes. The complex relationship between eucrites and diogenites could therefore be interpreted as evidence against an early large-scale melting event on the HED parent body. However, as discussed in Section 4.2, there is also good evidence in the form of siderophile element and oxygen isotope data in favor of such an early global melting event. This paradox has some similarities to that seen in the case of the proposed lunar magma ocean (Warren, 1985). In the case of the Moon a distinct global layer of anorthosite is generally considered to have formed as a floatation cumulate and this was followed by a transition to serial magmatism with the emplacement of Mg-rich rocks (Warren, 1985). For the much smaller HED parent body the transition from a global to more local-scale magmatism would have been even more rapid than on the Moon. The uniform $\Delta^{17}\text{O}$ composition of all the major HED lithologies records the very earliest phase of magma evolution on the HED parent body. Once global homogenization had taken place oxygen isotope compositions would have evolved by normal mass-dependent fractionation processes, as is clearly seen in the case of the $\delta^{18}\text{O}$ differences between diogenites and eucrites (Fig. 1).

4.4. Oxygen isotope evidence for the source of the HEDs

In view of their uniform $\Delta^{17}\text{O}$ composition a single asteroidal source for all the main HED lithologies seems highly likely. A range of observations made by the Dawn spacecraft, including detailed visible/near-infrared spectroscopy and global compositional mapping by the GRaND instrument have strengthened the case that Vesta is the source of the HEDs (McSween et al., 2013; Russell et al., 2013). However, a very different conclusion was reached by Wasson (2013a) on the basis of spectroscopic data, orbital dynamics and isotopic constraints. He suggested that the HEDs are probably not from Vesta, but may be derived from the same asteroid as the IIIAB irons and main-group pallasites.

A common parent body for the HEDs, IIIABs and main-group pallasites would require that its $\Delta^{17}\text{O}$ values varied by ~0.07‰ (Wasson, 2013a). This is much smaller than the range of about 0.7‰ shown by the acapulcoites and lodranites, which probably come from a single partially melted asteroid (Greenwood et al.,

2012a, 2012b). Other groups such as the winonaites and brachinites also display a significant range of $\Delta^{17}\text{O}$ values (Greenwood et al., 2012a, 2012b). However, the major problem with Wasson's (2013a) proposal for a common parent body for HEDs and main-group pallasites is that it is highly unlikely that a single differentiated parent asteroid could retain isolated, highly homogenized zones with non-overlapping oxygen isotope compositions (Fig. 1). As demonstrated by the present study, the main HED lithologies display an extremely narrow range of $\Delta^{17}\text{O}$ values, $-0.246 \pm 0.014\text{‰}$ (2σ) for the diogenites and $-0.241 \pm 0.016\text{‰}$ (2σ) for the eucrites and cumulate eucrites. Analysis of olivine from 13 main-group pallasites by Greenwood et al. (2006) gave a narrow range of $\Delta^{17}\text{O}$ values: $-0.183 \pm 0.018\text{‰}$ (2σ) (Fig. 1). Increasing this dataset to 24 pallasites has not significantly altered this value i.e. $\Delta^{17}\text{O} = -0.187 \pm 0.016\text{‰}$ (2σ) ($n = 24$) (Greenwood et al., 2013). These results demonstrate that the mantle of the main-group pallasite parent body was isotopically homogeneous. As can clearly be seen from Fig. 1 there is no overlap between the $\Delta^{17}\text{O}$ values for HEDs and main-group pallasites. In the case of the acapulcoites and lodranites the samples do not cluster around different $\Delta^{17}\text{O}$ values, but show a complete range of values. It could be argued that eucrites with anomalous oxygen isotope compositions indicate that the HED parent body is in fact isotopically heterogeneous (Wiechert et al., 2004). However, as discussed in Section 4.1.2, the evidence suggests that these anomalous samples represent either material from distinct asteroids or late stage impact mixing events (Greenwood et al., 2013; Scott et al., 2009). As a consequence, a differentiated asteroid with an isotopically homogenized but distinct mantle and crust, as Wasson (2013a) suggested for the parent body of the HEDs and main-group pallasites, is highly implausible.

While accepting that most of the V-type asteroids in the Vesta family came from Vesta, Wasson (2013a) argued that a sizable fraction could have been derived from the destruction of another large differentiated asteroid. However, the spectral study of Moskovitz et al. (2010) suggests that such interlopers are rare. It is also unclear why the majority of the interlopers suggested by Wasson (2013a) would have similar proper inclinations to those of the core Vesta family. We argue that a more reasonable hypothesis is that most of the putative Wasson (2013a) interlopers are Vesta family members that can no longer be identified by asteroid proper element clustering algorithms. Consider that methods for identifying families have distinct limitations when (i) the ejection velocities are high, as they were from Vesta, and (ii) the families are old, giving time for family members to evolve across the main belt by the Yarkovsky effect. When the bodies have evolved far enough, the clustering algorithms can no longer pick out all possible family members among a crowded background.

It would seem unlikely that a limited population of interlopers could be the major source for the HEDs, which comprise roughly 6% of all witnessed falls (statistics from Meteoritical Bulletin Database; see also Burbine et al., 2002). Models of collisional and dynamical evolution suggest collisional cascades among asteroid families, combined with Yarkovsky thermal drift/resonances, provide most meteorites (Bottke et al., 2006b). Accordingly, most HEDs should naturally come from the Vesta family, the most prominent source of this kind of material in the asteroid belt. As discussed in Section 4.1.2, oxygen isotope and other evidence indicates that there are only a very few non-HED basaltic achondrites. It seems highly likely that nearly all HED meteorites were ultimately derived from asteroid 4 Vesta.

5. Conclusions

Oxygen isotope measurements of a suite of 22 diogenites indicate that they have a very homogeneous composition, displaying

a restricted range of $\Delta^{17}\text{O}$ values: $-0.246 \pm 0.014\text{‰}$ (2σ). These new analyses, together with our previously published results, do not support recent suggestions that the diogenites are isotopically heterogeneous and we see no evidence for distinct groups within the diogenites that might indicate multiple parent body sources. These results indicate that the diogenites form a single population consistent with a single parent body source. Our previously published analysis of eucrites and cumulate eucrites give very similar results to the diogenites, with $\Delta^{17}\text{O} = -0.241 \pm 0.016\text{‰}$ (2σ) and appear to confirm the generally held view that diogenites and eucrites are from the same parent asteroid.

The isotopic homogeneity displayed by diogenites, eucrites and cumulate eucrites, despite their geochemical diversity, provides strong evidence for an early global homogenization event on Vesta. The most likely process leading to oxygen isotope homogenization was large-scale melting, possibly resulting in the formation of a magma ocean.

The paradox, whereby diogenites show isotopic evidence in favor of global melting, but also geochemical features indicative of late stage interaction with eucritic crust, may reflect a rapid transition from global to serial magmatism on their parent body. The fact that all the lithologically varied HED units appear to have been derived from a single isotopically homogeneous source supports the proposal that they are derived from a single, large diverse asteroid, generally identified as being 4 Vesta. The recent suggestion that the HEDs are not from Vesta, but instead represent material from the same parent body as the main-group pallasites and the IIIAB irons is incompatible with our oxygen isotope data.

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