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Zinc isotopes in HEDs: Clues to the formation of 4-Vesta, and the unique composition of Pecora Escarpment 82502

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Abstract

The $\delta^{66}\text{Zn}$ (permil deviation of the $^{66}\text{Zn}/^{64}\text{Zn}$ ratio from a terrestrial standard) values for a suite of 20 non-Antarctic HED (howardite–eucrite–diogenite) meteorites and one mesosiderite, and for eight Antarctic eucrites and diogenites, were measured in order to determine the role of volatilization in the formation of their presumed parent body, the asteroid 4-Vesta. The 20 non-Antarctic HEDs had $\delta^{66}\text{Zn}$ values that ranged from -2.0‰ to $+1.67\text{‰}$, with a mean value of $-0.01 \pm 0.39\text{‰}$ (2 se); this range likely represents a small-scale heterogeneity due to brecciation induced by multiple impacts. The non-Antarctic eucrites ($\delta^{66}\text{Zn} = +0.00 \pm 0.58\text{‰}$ (2 se), $n = 12$) were isotopically the same as the diogenites ($\delta^{66}\text{Zn} = -0.31 \pm 0.80\text{‰}$ (2 se), $n = 4$), and the howardites ($\delta^{66}\text{Zn} = +0.26 \pm 0.37\text{‰}$ (2 se), $n = 4$). On average, non-Antarctic eucrite falls were isotopically heavier ($+0.50\text{‰}$) than non-Antarctic finds (-1.00‰). The Antarctic finds studied were all unbrecciated samples, and they were significantly heavier than the non-Antarctic samples with a $\delta^{66}\text{Zn}$ range of $+1.63\text{‰}$ to $+6.22\text{‰}$ for four eucrites (mean, $+4.32\text{‰}$) and $+0.94\text{‰}$ to $+1.60\text{‰}$ for three diogenites (mean $+1.23\text{‰}$), excluding one anomalous sample, while their Zn concentration is significantly lower than the brecciated samples. These data suggest that the unbrecciated eucrites probably represent the eucritic crust shortly after differentiation and cooling of the parent asteroid, at which time volatilization of lighter zinc isotopes led to an isotopically heavy crust. Early impact events caused the ejection of these unbrecciated meteorites, which were subsequently spared from brecciation caused by multiple additional impacts on the much larger Vesta. The range of $\delta^{66}\text{Zn}$ values and Zn concentration for the brecciated HEDs in this study supports a major contribution to the Vestan surface by chondritic impactors ($-1.30 < \delta^{66}\text{Zn} < +0.76\text{‰}$ for ordinary and carbonaceous chondrites). The anomalous eucrite PCA 82502 ($\delta^{66}\text{Zn} = -7.75\text{‰}$) is significantly isotopically lighter than the other HEDs and is the natural sample with the lightest Zn isotopic composition reported in the solar system to date. This meteorite most likely originated from a distinct parent body.
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1. INTRODUCTION

The HED meteorites (howardites, eucrites, and diogenites) comprise the largest group of achondrites, and are

generally agreed to have originated from asteroid 4 Vesta based on visible and near-infrared reflectance spectrographic similarities (e.g., McCord et al., 1970; Binzel and Xu, 1993; Burbine et al., 2001). With a few exceptions (Scott et al., 2009a), they share the same $\Delta^{17}\text{O}$ ratios that distinguish them from the Earth or the Moon (Clayton and Mayeda, 1996; Greenwood et al., 2005). Most eucrites are pigeonite-plagioclase basalts, most diogenites are

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orthopyroxenites, and howardites are mechanical mixtures of these (with some exceptions; see Warren et al. (2009)). Almost all of the HED meteorites are breccias, implying significant “gardening” occurred after their initial formation due to multiple impacts on the parent body. Mesosiderites are stony-iron meteorites with about equal parts metal (nickel–iron) and silicates that are similar in composition to HEDs. They have an oxygen isotope composition that is indistinguishable from the HEDs and may also have originated from Vesta (Greenwood et al., 2006).

Studies of major elements and rare earth elements in HED meteorites have led to different theories of formation and differentiation of 4 Vesta. In one model (Takeda, 1979), the asteroid is initially totally melted; then, differentiation led to a metallic core surrounded by a magma ocean. A fractional crystallization sequence then proceeded to form orthopyroxenites (diogenites), followed by increasing plagioclase content to form basalts (eucrites). Since the eucrites formed last in this model from the remaining melt, it is sometimes called the “residual liquid” model of eucrite petrogenesis (e.g., Warren, 1997). Alternatively, the original parent body formed and cooled, then underwent heating events that caused primary partial melts (Stolper, 1977). In this model, total melting would not be expected. Over the last 30 years a number of additional models have been proposed that are basically variants of these (e.g., Warren and Jerde, 1987; Hewins and Newsom, 1988; Righter and Drake, 1997; Ruzicka et al., 1997; Warren, 1997; Mittlefehldt and Lindstrom, 2003; Greenwood et al., 2005), however, consensus on a single model of HED petrogenesis has been elusive.

Recent petrological studies suggest that the magmatic history of Vesta was certainly much more complex than previously thought. Firstly, a magma ocean model cannot account for the diversity of the REE patterns displayed by the diogenites and their pyroxenes (e.g., Mittlefehldt, 1994; Shearer et al., 1997), and diogenites could have formed from melts produced by the remelting of magma ocean cumulates (Barrat, 2004; Barrat et al., 2008, 2009a). Secondly, the eucritic crust was probably remelted, producing new melts able to contaminate not only normal eucrites (e.g., Barrat et al., 2007; Yamaguchi et al., 2009) but also some of the parental melts of diogenites (Barrat et al., 2010). Finally, K-rich impact spherules in howardites indicate that the lithologies exposed on the surface of Vesta are not restricted to eucrites and diogenites, and point to some distinct K-rich areas (Barrat et al., 2009b).

Vesta shows spectroscopic evidence of differentiation by igneous processes (Binzel and Xu, 1993), which most likely led to a layered structure with a crust chiefly eucritic, an ultramafic mantle, and a metallic core (e.g., Righter and Drake, 1997). Most eucrites show evidence of metamorphism with reheating to >800 °C, as evidenced by altered pyroxene compositions from subsolidus diffusion of Mg, Fe and Ca (Takeda and Graham, 1991; Yamaguchi et al., 1996, 1997, 2009). The source of this additional heat may have been from large impacts (Nyquist et al., 1986), heating at depth after burial of surface basalts (Yamaguchi et al., 1996, 1997), or the differentiation into layers (Takeda, 1997). A large impact crater of 460 km diameter, 13 km depth with a large central peak, has been identified on Vesta

(Thomas et al., 1997) which may have extended beyond the crust into the mantle layer and ejected many Vestoids and HEDs (McSween et al., 2010). The age of this impact crater is controversial, with some evidence suggesting it occurred during the Late Heavy Bombardment period of 3.5–4.0 billion years ago (Scott et al., 2009b), and other evidence supporting an age of only 1 billion years (Asphaug, 1997). Ejecta from this large impact, possibly including samples of the deep asteroidal crust and mantle, may now be present on the surface of 4-Vesta.

Compared with chondritic meteorites, HEDs show large depletions in moderately volatile elements, Zn being one of the best examples. Zinc is present in very low concentrations ($[Zn] < 7$ ppm) in all three HED groups (e.g., Barrat et al., 2000, 2007; Kitts and Lodders, 1998) with most diogenites less than 1 ppm (Barrat et al., 2008); this is lower than the zinc level found on larger planetary bodies such as the Moon, the Earth, or Mars (2–20, 50 and 90 ppm, respectively; Lodders and Fegley, 1998; Wolf et al., 2009) and chondrite meteorites (40–300 ppm, Lodders and Fegley, 1998). The mechanism by which the moderately volatile elements were depleted from HEDs is still debated. Volatilization is known to fractionate isotopes, thus comparing the isotope compositions of volatile elements between HEDs and other meteorites may help to understand the physical and chemical conditions involved in the loss of volatile elements.

Zinc is a moderately volatile element with a 50% condensation temperature, $T_c(Zn)$, of ~ 730 K (Lodders, 2003) and seems to be even more volatile under conditions relevant to the metamorphism of ordinary chondrites (Schaefer and Fegley, 2010). Measurements of Zn isotopes in a variety of terrestrial magmatic materials show a remarkably homogeneous distribution, with $^{66}Zn/^{64}Zn$ ratios consistently within 0.2 permil of each other (Ben Othman et al., 2006). This suggests that within the Earth's mantle, Zn isotopes are well mixed and homogeneously distributed, and that igneous processes do not result in significant Zn isotopic fractionation (Ben Othman et al., 2006).

In this study, we used Zn isotopic measurements to investigate possible formation mechanisms of the HED parent body 4-Vesta. Previous studies have demonstrated the utility of Zn isotopes for this purpose. Zn isotopic determinations in chondrites and iron meteorites show significantly more variation than is found in terrestrial materials (Luck et al., 2005; Moynier et al., 2007; Barrat et al., 2012), suggesting volatilization processes and core/mantle segregation in their formation. On the Earth and on the Moon, volatilization from impact events is the primary cause of Zn isotopic fractionation (Moynier et al., 2006, 2009, 2010; Albarède et al., 2007; Herzog et al., 2009). We have previously used Zn isotope ratios to determine the role of impact-induced volatilization in the formation of tektites (Moynier et al., 2009) and ureilites (Moynier et al., 2010). Thus, the study of Zn isotopes in extraterrestrial samples can provide clues to their mechanisms of formation (Luck et al., 2005), especially as they relate to evaporation/condensation processes (Moynier et al., 2006). Here, we used zinc isotopic composition in HEDs to assess the role of volatilization processes in the formation of 4-Vesta.

Due to its very low abundance in HEDs, the analysis of zinc isotopic composition requires a highly sensitive technique. In this study, HED meteorites were analyzed for Zn isotopic composition using Multi Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS).

2. SAMPLES AND ANALYTICAL METHODS

2.1. Sample description

The Zn isotopic compositions of 43 samples from 28 HED meteorites, and one mesosiderite, were measured. There were 23 chips from 17 eucrites, six chips from four howardites, and eight chips from seven diogenites analyzed. In five cases, multiple chips were created from a single museum sample by fracturing it into two or more smaller chips, which were then processed separately (dissolution-chemical separation of Zn and mass-spectrometry analysis) on different dates. Among the eucrite samples, Pasamonte and PCA 82502 are unusual samples with $\Delta^{17}\text{O}$ plotting outside the HED range (Greenwood et al., 2009). In addition, to study the sample heterogeneity, three clasts and two matrix samples prepared from ‘large’ aliquots (>2 g each time, Barrat et al., 2003) of the eucrite Juvinas were analyzed.

Seventeen of the meteorites were falls, twelve were finds. Most of the eucrites were monomict breccias. The Antarctic finds (five eucrites and three diogenites) were all unbrecciated, as was one diogenite fall (Tatahouine). The sample descriptions are summarized in Table 1.

To better constrain the terrestrial isotopic composition of Zn, the isotopic composition of two terrestrial igneous geostandards GIT-IWG BE-N (a terrestrial basalt from Essy-la-Côte, France) and USGS G-2 (a terrestrial granite) were analyzed as well.

2.2. Methods

All sample processing was performed in a “clean room” in order to minimize any possible contamination. Each meteorite chip was 75–500 mg in order to extract enough zinc for analysis, the mass chosen was based on anticipated Zn concentrations from published studies. Fusion crust, if present, was gently removed; the chip was fractured into multiple small pieces, and then those with fusion crust were hand-picked and separated. Chips were cleansed in water in an ultrasonic bath, then crushed in an agate mortar into a homogenous powder. The powder was dissolved in HNO_3/HF in closed Teflon beakers at $\sim 120^\circ\text{C}$ for 2 days. A final step of dissolution in 6 N HCl was done in order to re-dissolve the fluorides formed by the HF. All reagents used were of the highest available purity.

The procedure described by Moynier et al. (2006) was used to extract and purify the zinc from the samples. The dissolved solute was evaporated under a heating lamp, and the residue was re-dissolved in 1.5 N HBr. Teflon columns were prepared for anion-exchange chromatography by loading with AG-1X8 (200–400 mesh), cleaning with 0.5 N HNO_3 , and then pre-loading with 1.5 N HBr. Each sample was loaded onto a column, and the Zn bound to

the mesh while the remaining non-Zn components passed through the column with additional 1.5 N HBr. The Zn was then recovered from the column with 0.5 N HNO_3 . The entire process was repeated twice more on smaller columns to further purify Zn from impurities. Column fractionation of Zn was avoided by near-complete (>99%) recovery of the Zn. The final Zn eluent was evaporated, then redissolved in 0.05 N HNO_3 for isotopic compositional analysis by MC-ICP-MS.

Zinc isotopic compositions were measured on a Nu Plasma High Resolution MC-ICP-MS at the Ecole Normale Supérieure de Lyon, France, or on a Thermo-Finnigan Neptune Plus MC-ICP-MS at Washington University, St. Louis, following the procedure described in Maréchal et al. (1999). Both instruments are high-resolution MC-ICP-MS and routinely provide similar quality Zn stable isotopic data. For both machines, the yield was found to be greater than 99% and the blank was ~ 10 ng. Isotope ratios are expressed as parts per 1000 deviations relative to a standard:

$$\delta^x\text{Zn}(\text{‰}) = \left(\frac{(^x\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^x\text{Zn}/^{64}\text{Zn})_{\text{standard}}} - 1 \right) \times 1000$$

with $x = 66$ or 68. The reference material used is the Zn “Lyon” standard JMC 3-0749 L (Maréchal et al. 1999). The “Lyon” standard is the most broadly used reference material to normalize Zn isotope data (reviewed in Albarède, 2004). At least two replicate analyses were performed for 80% of the samples; 3–6 replicates were performed for the more extreme samples such as PCA 82502. The replicate analyses of the same samples carried out during different analytical sessions define an external reproducibility (± 2 sd) of $\pm 0.09\text{‰}$ for $\delta^{66}\text{Zn}$ and $\pm 0.27\text{‰}$ for $\delta^{68}\text{Zn}$ (see Moynier et al. (2006) and Herzog et al. (2009) for extensive discussion of our analytical precision). With respect to the total amount of Zn in the samples, the blank of about 10 ng introduces an error of 0.10‰ or less, based on a “worst case” contaminant of $\delta^{66}\text{Zn} = -2.0\text{‰}$ added to the smallest Zn content sample (Zn = 290 ng) at a presumed +1.0‰ (thus the blank is 3.4‰ or less of the sample). We note that there are no known potential terrestrial contaminants with a $\delta^{66}\text{Zn}$ below zero, so this is a highly conservative estimate.

Elemental concentrations of Zn were calculated by comparing the voltage peak heights of ^{64}Zn with peak heights for known standards. In most cases the unknown concentrations were adjusted so as to be within $\pm 10\%$ of the standard concentrations. No systematic dependence of isotopic abundances on solution concentration was observed. Uncertainties in concentrations were about $\pm 10\%$.

3. RESULTS

The measurements of $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ for all of the samples are given in Table 1, and plotted in Fig. 1. All data plot on the mass-dependent fractionation line of slope 1.978 ($R^2 = 0.9993$) on the three-isotope plot. All of the non-Antarctic HED $\delta^{66}\text{Zn}$ values lie within $0 \pm 2\text{‰}$. The HED subgroup ranges overlap significantly: non-Antarctic

Table 1
Zinc isotope measurements for HED meteorites and terrestrial standards.

Class	Name	Split	Type	<i>f/f</i>	$\delta^{66}\text{Zn}$ (‰)	$\delta^{68}\text{Zn}$ (‰)	[Zn] (ppm)	Mass (mg)
<i>Eucrites</i>								
Falls	Béréba	MNHN 1297CPE	mm	Fall	1.67	3.40	1.30	242
	Jonzac	NMV A419	mm	Fall	0.33	0.74	1.40	460
	Juvinas	MNHN 40PE2	mm	Fall	0.06	0.17	2.50	300
	Matrix 1	MNHN	mm	Fall	0.30	0.72	2.30	~2000
	Matrix 2	MNHN	mm	Fall	0.37	0.86	0.70	~2000
	Clast 1	MNHN	mm	Fall	0.39	1.02	1.50	~2000
	Clast 2	MNHN	mm	Fall	0.57	1.22	2.90	~2000
	Clast 3	MNHN	mm	Fall	0.31	0.85	1.20	~2000
	<i>Mean – Juvinas</i>				0.33	0.81		
	Millbillillie	WAM 13357.3	mm	Fall	−0.79	−1.37	0.90	323
	Pasamonte chip 1	ASU 197 g	pm	Fall	0.05	0.14	6.70	813
	Pasamonte chip 2	ASU 197 g	pm	Fall	−0.81	−1.58	8.90	320
	Pasamonte chip 3	USNM 897	pm	Fall	1.35	2.57	2.10	975
	<i>Mean – Pasamonte</i>				0.20	0.38		
	Serra de Magé	MNHN 1560PE	cm	Fall	0.62	1.28	0.78	296
	Sioux County chip 1	NHM BM.1959,1029	mm	Fall	1.11	2.41	1.30	249
	Sioux County chip 2	NHM BM.1959,1029	mm	Fall	0.90	1.88	0.80	437
	Sioux County chip 3	ASU 198.3	mm	Fall	−0.73	−1.49	0.90	346
	<i>Mean – Sioux County</i>				0.43	0.93		
	Stannern chip 1	NMV	mm	Fall	1.42	2.90	1.00	334
	Stannern chip 2	MNHN 4027PE1	mm	Fall	0.95	2.05	7.80	290
	<i>Mean – Stannern</i>				1.19	2.48		
	<i>Mean – Eucrite falls (n = 8)</i>				0.50	1.08		
<i>Finds</i>								
Non-Antarctic	Bouvante	MNHN 3223PE	mm	Find	−1.76	−3.33	5.00	235
	Camel Donga	WAM 13715	mm	Find	−0.30	−0.26	0.90	356
	Palo Blanco Creek	UNM	mm	Find	−1.49	−2.70	2.30	396
	Pomozdino		mm	Find	−0.43	−0.65	4.50	72
	<i>Mean – Non-Antarctic Eucrite finds (n = 4)</i>				−1.00	−1.74		
Antarctic	PCA 82502	NASA, .97	unbr	Find	−7.75	−15.14	4.50	414
	GRA 98098 chip 1	NASA, .55	unbr	Find	5.84	11.75	0.46	530
	GRA 98098 chip 2	NASA, .55	unbr	Find	6.29	12.54	0.39	470
	<i>Mean – GRA 98098</i>				6.06	12.15	0.42	
	QUE 97014	NASA, .31	unbr	Find	1.63	3.33	0.69	557
	BTN 00300	NASA, .13	unbr	Find	3.32	7.12	0.11	575
	EET 90020	NASA, .51	unbr	Find	6.22	12.45	0.16	611
	<i>Mean – Antarctic Eucrite finds (n = 4)*</i>				4.31	8.76		
<i>Mean – All Eucrite finds (n = 8)*</i>				1.66	3.51			
<i>Mean – All non-Antarctic Eucrites (n = 12)*</i>				0.00	0.14			
<i>Mean – All Eucrites (n = 16)* ± 2 SE</i>				1.08	2.30			
				1.17	2.32			
<i>Howardites</i>								
	Kapoeta chip 1	NHM BM.1946,141	pm	Fall	−0.43	−0.68	1.90	169
	Kapoeta chip 2	NHM BM.1946,141	pm	Fall	0.38	0.77	8.00	546
	<i>Mean – Kapoeta</i>				−0.03	0.05		
	LeTeilleul	MNHN 711PE	pm	Fall	0.09	0.21	3.00	218
	Pavlovka chip 1	MNHN 2698PE	pm	Fall	0.22	0.63	3.00	261
	Pavlovka chip 2	MNHN 2698PE	pm	Fall	1.38	3.04	4.50	77
	<i>Mean – Pavlovka</i>				0.80	1.84		
	Petersburg		pm	Fall	0.16	0.38	1.20	511
	<i>Mean – All Howardites (n = 4) ± 2 SE</i>				0.26	0.62		
					0.37	0.82		

(continued on next page)

Table 1 (continued)

Class	Name	Split	Type	<i>flf</i>	$\delta^{66}\text{Zn}$ (‰)	$\delta^{68}\text{Zn}$ (‰)	[Zn] (ppm)	Mass (mg)	
<i>Diogenites</i>									
Falls	Aioun el Atrouss chip 1	FMNH Me2778#3	pm	Fall	−2.00	−3.81	0.80	396	
	Aioun el Atrouss chip 2	ASU 1058f	pm	Fall	0.36	0.75	3.10	824	
	<i>Mean – Aioun el Atrouss</i>					−0.82	−1.53		
	Johnstown	AMNH	mm	Fall	0.58	1.17	0.70	491	
	Shalka	NMV	mm	Fall	0.15	0.31	1.50	529	
	Tatahouine	FMNH Me2651#10	unbr	Fall	−1.13	−1.94	0.90	839	
<i>Mean – Diogenite falls (n = 4)</i>					−0.31	−0.50			
Antarctic (an) (oliv)	ALHA 77256	NASA, .167	unbr	Find	1.15	2.34	0.81	586	
	GRO 95555	NASA, .43	unbr	Find	1.60	3.32	0.29	524	
	MIL 07001	NASA, .29	unbr	Find	0.94	1.91	0.57	590	
	<i>Mean – Antarctic Diogenite finds (n = 3)</i>					1.23	2.52		
<i>Mean – All Diogenites (n = 7)</i>					0.35	0.80			
$\pm 2\text{ SE}$					0.77	1.49			
<i>HEDs</i>	<i>Mean – All HEDs (n = 27)*</i>				0.77	1.66			
	$\pm 2\text{ SE}$				0.72	1.44			
	<i>Mean – non-Antarctic HEDs (n = 20)</i>				−0.01	0.11			
	$\pm 2\text{ SE}$				0.39	0.75			
<i>Mean – Antarctic HEDs* (n = 7)</i>				2.99	6.09				
$\pm 2\text{ SE}$				1.73	3.45				
<i>Mesosiderite</i>	Estherville	UNM		Fall	−1.66	−2.97	0.80	405	
<i>Geostandards</i>	GIT-IWG BE-N		Basalt		0.32	0.79		100	
	USGS G-2		Granite		0.30	0.57		101	

$\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ measurements in per mil (‰). Zn concentrations in ppm.

Samples were generously provided by the following collections: Meteorite Working Group, NASA, Houston (8); Museum National D'Histoire Naturelle, Paris (MNHN, seven samples including the powders prepared by Barrat); Arizona State University (ASU, 3); Naturhistorisches Museum, Vienna (NMV, 3); Natural History Museum, London (NHM) (BM, 2); Field Museum of Natural History, Chicago (FMNH, 2); Western Australian Museum, Perth (WAM, 2); University of New Mexico (UNM, 2); Smithsonian Institution, Washington D.C. (USNM, 1); American Museum of Natural History, New York (AMNH, 1).

* PCA 82502 excluded from Euclite and HED means.

euclites from -1.76‰ to $+1.67\text{‰}$, with a mean of $\delta^{66}\text{Zn} = 0.00 \pm 0.58\text{‰}$ (2 se); howardites from -0.43‰ to $+1.38\text{‰}$, with a mean of $\delta^{66}\text{Zn} = +0.26 \pm 0.62\text{‰}$ (2 se); non-Antarctic diogenites from -2.00‰ to $+0.58\text{‰}$, with a mean of $\delta^{66}\text{Zn} = -0.31 \pm 0.80\text{‰}$ (2 se). The mean $\delta^{66}\text{Zn}$ for all of the non-Antarctic HEDs studied is $-0.01 \pm 0.39\text{‰}$ (2 se). The Antarctic values are significantly heavier, with one notable exception (PCA 82502, discussed below): the Antarctic euclites (excluding PCA 82502) have $\delta^{66}\text{Zn}$ from $+1.63\text{‰}$ to $+6.22\text{‰}$, with a mean of $4.31 \pm 2.23\text{‰}$ (2 se), while the Antarctic diogenites have $\delta^{66}\text{Zn}$ from $+0.94\text{‰}$ to $+1.60\text{‰}$, with a mean of $1.23 \pm 0.39\text{‰}$ (2 se). The three separated clasts and two separated matrix samples of Juvinas show some limited isotopic variability with $0.30 < \delta^{66}\text{Zn} < 0.57$. The mesosiderite Estherville is isotopically light with $\delta^{66}\text{Zn} = -1.66 \pm 0.09\text{‰}$. Fig. 1 also gives the results for $\delta^{68}\text{Zn}$, which are consistent with the $\delta^{66}\text{Zn}$ values as the results of mass-dependent fractionation.

The two terrestrial geostandards analyzed in the present study, the basalt BE-N ($\delta^{66}\text{Zn} = 0.32$) and the granite G-2 ($\delta^{66}\text{Zn} = 0.30$) show typical terrestrial isotopic composition ($\delta^{66}\text{Zn} = 0.20\text{--}0.60$) reported by Albarède (2004), Ben Othman et al. (2006), and Cloquet et al. (2008).

In Fig. 2, the $\delta^{66}\text{Zn}$ ranges for the HEDs in this study and literature values for other groups of meteorites, terrestrial samples and lunar samples are shown for comparison. The non-Antarctic HED mean is similar and the range only slightly broader than corresponding values for ordinary and carbonaceous chondrites. The unbrecciated Antarctic HEDs are heavier and range from $\delta^{66}\text{Zn} = +0.94\text{‰}$ to $+6.22\text{‰}$. By contrast, the range for terrestrial igneous rocks is quite narrow, with $\delta^{66}\text{Zn} = +0.2\text{‰}$ to $+0.6\text{‰}$ (Ben Othman et al., 2006; Cloquet et al., 2008, and this study); while the range for enstatite meteorites is very broad, from -7.08‰ for aubrites to $+7.35\text{‰}$ for EL chondrites (Paniello et al., 2009; Moynier et al., 2011). Nevertheless, with $\delta^{66}\text{Zn} = -7.75\text{‰}$, PCA 82502 lies outside this range as the most extreme Zn fractionation reported to date.

Fig. 3 shows the $\delta^{66}\text{Zn}$ values as a function of zinc concentration. In general there is no clear relationship among these samples, although the plot does highlight the very low zinc concentrations in most of the samples. Considering only the Antarctic meteorites, there is a definite trend of higher $\delta^{66}\text{Zn}$ with lower concentration ($R^2 = 0.8271$). This would be consistent with mass-dependent evaporation with preferential loss of lighter isotopes.

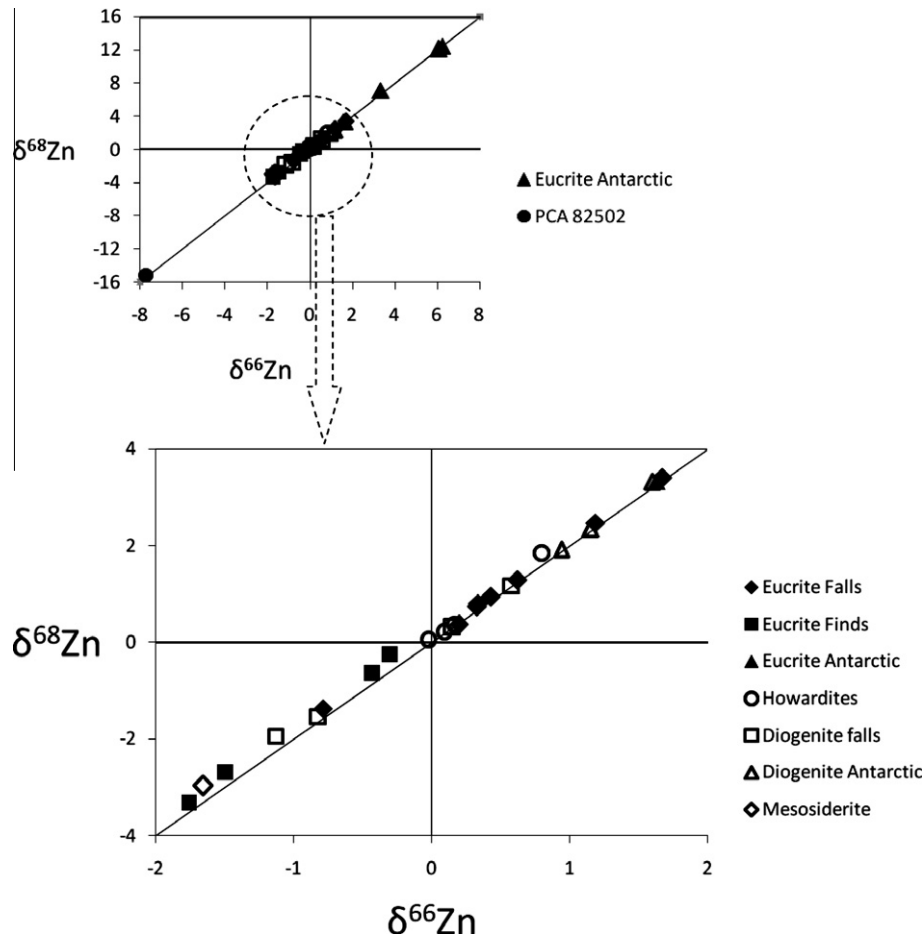


Fig. 1. Three-isotope plot of Zn isotopic measurements in HED meteorites and one mesosiderite. With the exceptions of PCA 82502 (more negative) and the other Antarctic eucrites (more positive), all $\delta^{66}\text{Zn}$ values fall between $0 \pm 2\text{‰}$. All data plot on the mass-dependent fractionation line of slope 1.978.

4. DISCUSSION

4.1. Isotopic variation within an individual meteorite

Some of the samples showed significant Zn isotopic heterogeneity within the same small chip from the meteorite. For example, two analyses on different fragments of the chip of howardite Kapoeta gave $\delta^{66}\text{Zn}$ values of -0.43‰ and $+0.38\text{‰}$. Two analyses on different fragments of the eucrite Pasamonte chip from ASU gave $\delta^{66}\text{Zn}$ values of -0.81‰ and $+0.05\text{‰}$. These variations occur in fragments of the rock that are physically separated by only a few millimeters. Variations were also seen in different chips from the same meteorite. Chips obtained from two different museums gave significantly different values for the eucrites Pasamonte ($+1.35$ (New Mexico) vs. $+0.05\text{‰}$ and -0.81‰ (ASU)) and Sioux County (-0.73 (ASU) vs. $+1.0\text{‰}$ (NHM)), and for the diogenite Aïoun el Atrouss (-2.0 (FMNH) vs. $+0.36\text{‰}$ (ASU)). It is not known how far apart these chips were on the original meteorite, but it was likely on the order of centimeters based on the sizes of the meteorites at the time of recovery.

This small-scale heterogeneity is best explained by the brecciation process present in almost all of these samples. Some of the samples are polymict and contain multiple lithologies; further, the single-lithology monomict samples may or may not represent the bulk. The chips prepared for analysis contain variable amounts of matrix, clast, and inclusion contaminants; thus, small-scale variability should be expected in these measurements.

Less small-scale variability would be expected if larger samples were analyzed, since the homogenized powder essentially gives the average of the total mass. This concept was tested using larger (~ 2 g) samples from the monomict eucrite fall Juvinas. Two matrix samples had the same $\delta^{66}\text{Zn}$, within error (0.30 and 0.37), while three large clasts showed small heterogeneity (0.39, 0.57 and 0.31). This resembles a chondritic Zn isotopic composition (see below).

Zinc isotopic heterogeneity has been previously reported in chondrites and in iron meteorites by Luck et al. (2005) and by Ghidan and Loss (2011). Ghosh and McSween (1998) proposed a model for Vesta of a melted center with an unmelted outer shell which would be expected to retain some isotopic heterogeneity. This idea was further sup-

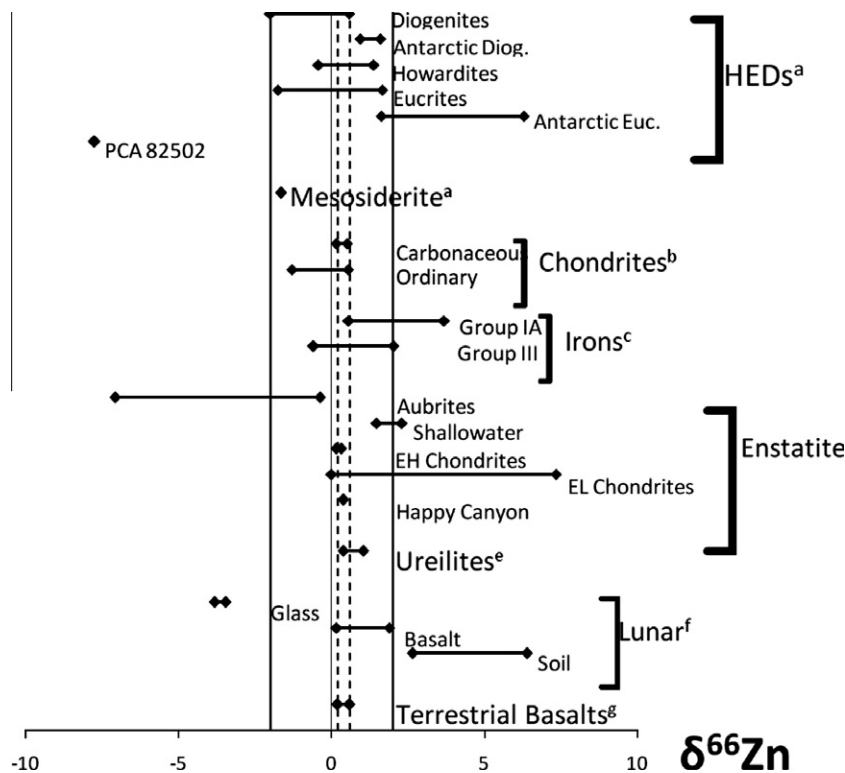


Fig. 2. $\delta^{66}\text{Zn}$ ranges for different group of meteorites, lunar samples and terrestrial igneous rocks. Vertical broken lines show the range for terrestrial basalts, $+0.2\text{‰}$ to $+0.6\text{‰}$; solid lines represent the heterogeneity range of non-Antarctic HEDs, $0 \pm 2\text{‰}$. References: a – this work; b – Luck et al., 2005; Moynier et al., 2007; c – Luck et al., 2005; d – Paniello et al., 2009; Moynier et al., 2010; e – Moynier et al., 2010; f – Moynier et al., 2006; Herzog et al., 2009; g – Ben Othman et al., 2003, 2006; Cloquet et al., 2008; this study.

ported by Wiechert et al. (2004), who reported heterogeneous oxygen isotope measurements in HEDs consistent with a very rapid early history of large-scale, incomplete mixing on Vesta. The Zn isotopic heterogeneity found in our study fits with both of these models if the Zn was initially isotopically heterogeneous in Vesta or if some isotopic fractionation occurred early in Vesta history.

The low zinc concentration in these rocks (about 1 ppm for most HEDs) also contributes to the measured heterogeneity. Very small inclusions rich in light or heavy isotopes of zinc could significantly alter the isotopic composition of these small chips. For example, carbonaceous chondrite xenoliths have been reported in Kapoeta (Wilkening, 1973) and Pasamonte (Metzler et al., 1995) and could alter the measured Zn ratios; these may have been introduced by an impactor. CM- and CR- like clasts, ranging in size from 25 μm to 5 mm, have been reported in HEDs by Buchanan et al. (2009); their wide distribution in the breccias suggested efficient energetic mixing of impactors as the most likely source. Since the HEDs are almost all monomict or polymict breccias, there is also a possibility that the measured fractionation is influenced by the isotopic makeup of the matrix, which contains higher levels of contaminant debris than the clast minerals, rather than the primary minerals themselves.

By contrast, terrestrial basalts from a variety of magmatic settings show a very narrow range of $+0.2 < \delta^{66}\text{Zn} < +0.60$ (Ben Othman et al., 2003, 2006; Albarède, 2004; Cloquet et al., 2008; Herzog et al., 2009; this

study) which suggest that Zn isotopes are homogeneously well distributed within the Earth's mantle, and that igneous processes do not lead to subsequent Zn isotopic fractionation. This may be related to the higher zinc concentrations in terrestrial igneous rocks ($[\text{Zn}] = 50\text{--}100$ ppm; Lodders and Fegley, 1998), or a greater homogenization of kilogram-sized terrestrial samples used as standards, but it may also indicate a significant difference in the formation history of the two planetary bodies. Earth is substantially larger than Vesta, and would have required a much longer cooling time, with a corresponding greater degree of convection and equilibration than Vesta. Thus, Earth would also be expected to have greater isotopic homogeneity than Vesta, as described above for Zn isotopes.

4.2. Unbrecciated Antarctic samples & weathering

Of the nearly 600 eucrites currently recognised with official names, there are 30 meteorites (about 5%) that are classified as unbrecciated eucrites, and all of these are Antarctic finds. Our $\delta^{66}\text{Zn}$ measurements in five of these meteorites were striking; four were isotopically quite heavy (mean, $+4.31\text{‰}$), while one was anomalously light (PCA 82502, discussed below). These unbrecciated specimens are most likely samples of the original, early Vestan crust, which were expelled by early impacts and thus spared from further impacts that would have led to their brecciation. The three unbrecciated Antarctic diogenites studied were also isotopically hea-

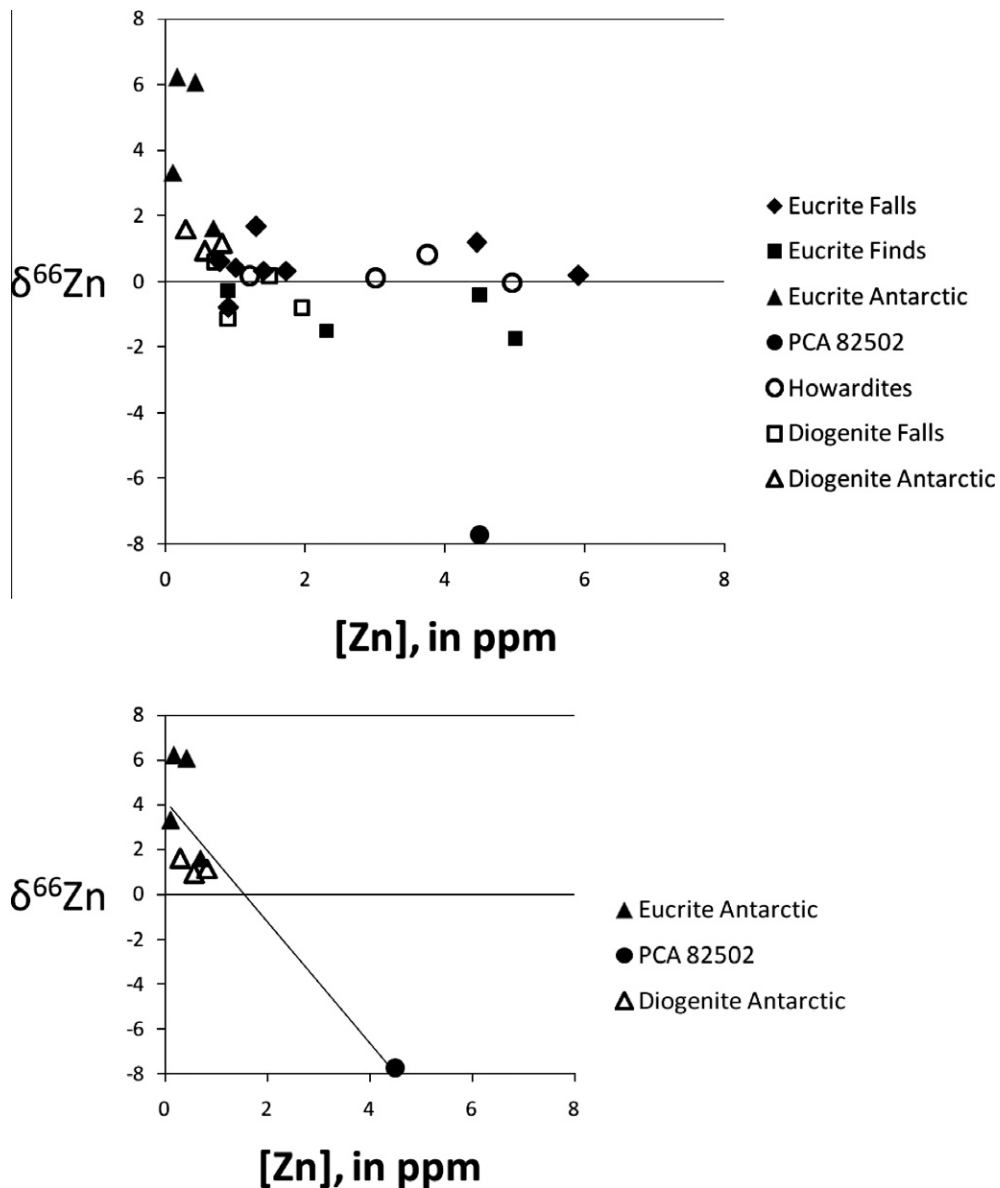


Fig. 3. $\delta^{66}\text{Zn}$ values as a function of Zn concentration. Overall, no correlation was found (upper plot); but a loose correlation ($R^2 = 0.8271$) was seen among the Antarctic meteorite samples (lower plot).

vier than the other diogenites, but to a lesser degree. These likely formed deeper in the crust or upper mantle, where volatilization of Zn would occur to a lesser extent, making them isotopically heavy but not as extreme as the eucrites.

The role of weathering on the measured Zn fractionation is unclear, but is likely limited. Biswas et al. (1980) studied trace elements in four Antarctic meteorites, and found that there was limited contamination or leaching of trace elements at the periphery of the meteorites, but interior samples gave reasonably normal values for their respective subgroups. Kallemeyn et al. (1993) compared chondrite Antarctic finds with falls, and found “concentration ranges and median values of two chalcophile elements, Se and Zn, are nearly identical between the Antarctic H chondrites and H falls.” Wang et al. (1992) studied a large suite of chondrites, HEDs and lunar meteorites, and found that

although REE composition may have been altered in some eucrites, there was no evidence for labile trace element transport into or out of eucrites of weathering grade A to B (our five eucrites include four A and one B; our three diogenites are all A/B). Carbonaceous chondrites and lunar meteorites were also essentially unaltered. Wang and Lipschutz (1995) also found no weathering effects in Zn and other trace elements for Antarctic ureilites. Mittlefehldt and Lindstrom (1991) found significant REE depletion in a group of abnormal Antarctic eucrites, but trace elements such as Zn were not reported.

We note that there are no known terrestrial materials with the extreme fractionations seen in these Antarctic meteorites (either very heavy, like four in this study, or very light, like PCA 82502), so this degree of Zn fractionation cannot be explained by local contamination. We conclude that weather-

ing effects in our Antarctic meteorites, if any, are likely small ($<1\%$) and thus cannot possibly explain the large differences in Zn fractionation seen between the unbrecciated Antarctic samples and the brecciated falls and finds.

4.3. Falls vs. finds

There was a small difference in $\delta^{66}\text{Zn}$ values based on the mechanism of recovery of the meteorite. For the eucrites, the $\delta^{66}\text{Zn}$ for the eight observed falls averaged $+0.50 \pm 0.51\%$ (2 se), while the four non-Antarctic finds averaged $-1.00 \pm 1.01\%$. This finding may simply be a result of sampling, as all of the HEDs seem to be scattered between $\delta^{66}\text{Zn} = 0 \pm 2\%$. This observation could also suggest that the terrestrial non-Antarctic weathering process preferentially removes heavy isotopes from the meteorite. This direction of isotopic fractionation during weathering was also reported by Luck et al. (2005) for Zn isotopes in undifferentiated ordinary chondrites: an H3.7 find was 0.40% lighter (for $\delta^{66}\text{Zn}$) than an H3.8 fall, while an L3.6 find was 1.27% lighter than an L3.6 fall. All of the howardites and diogenites in the present study were falls.

4.4. Chondritic origin for Vesta and the origin of the elemental depletion of HEDs

The range of $\delta^{66}\text{Zn}$ observed in the three large clasts and two matrix samples from Juvinas ($0.30\text{--}0.57\%$) and the average value close to zero (-0.01 ± 0.39 (2 se) for all non-Antarctic HED samples) suggest a chondritic Zn isotopic composition for Vesta. Individual fragments of brecciated HEDs exhibit a small scale isotopic heterogeneity. The isotopic variation measured in lunar soils (Moynier et al., 2006) suggests that the heterogeneity observed in brecciated eucrites is the result of the brecciation processes. Zinc isotopes are redistributed at the surface of 4-Vesta, presumably by evaporative processes. Under this scenario, the volatilized isotopically light zinc may have left the molten body's surface, then remained in a primordial atmosphere and was later recondensed back into the asteroid, initially at the surface. The result would be a heterogeneous Vesta surface with some isotopically light and isotopically heavy regions. Subsequent impacts would pulverize these rocks to varying degrees, and result in brecciation such as seen in the meteorites that reach the Earth. The depletion of moderately volatile elements such as Zn would have to have occurred prior to this process.

The average Zn fractionation for this group of HED meteorites was approximately zero, similar to ordinary chondrites (Luck et al., 2005; Moynier et al., 2007; Ghidani and Loss, 2011). Considering only the eucrite falls, the average $\delta^{66}\text{Zn}$ value of $+0.50 \pm 0.51\%$ was identical to the CI chondrites reported by Luck et al. (2005), who found mean $\delta^{66}\text{Zn} = +0.49\%$ and $+0.47\%$ for Orgueil and Ivuna, respectively. In addition, large clasts and matrix samples from Juvinas show a fairly homogeneous Zn isotopic composition of $0.33 \pm 0.13\%$, similar to chondritic values.

Thus, Vesta may have originally accreted from chondritic material. However, the typical chondrite Zn abundance is about 50 ppm (e.g., Luck et al., 2005), while the

range of Zn in HEDs is about 1–7 ppm, so the HEDs must have lost 86–98% of their Zn without any isotopic fractionation. The unbrecciated samples allow us to propose an explanation for these findings. The data fit with a model in which Vesta originally accreted from material with a chondritic Zn content; Vesta then lost by evaporation most ($>90\%$) of its volatiles (e.g. Zn) early in its history as it slowly cooled. This left a surface comprised of unbrecciated, isotopically heavy eucritic material, with a layer of diogenites below that was also heavy, but less so. Early impacts ejected the unbrecciated meteorites that were found in this study to be enriched in heavy Zn isotopes, before they could become brecciated. Additional impacts, likely from largely chondritic material, led to the brecciation of the surface as well as the addition of Zn with a chondritic isotopic composition. This hypothesis is consistent with Scott et al. (2009b), who note that unbrecciated eucrites show no shock features, unlike most brecciated ones.

A Rayleigh evaporation model can be used to further test this hypothesis, using the equation

$$\delta^{66}\text{Zn} = (\delta^{66}\text{Zn}_0 + 1000)f^{(\alpha-1)} - 10^3 \quad (1)$$

where $f = [\text{Zn}]/[\text{Zn}]_0$ and $\alpha = (64/66)^{0.5}$ based on the masses of the species. Starting with chondritic values from Luck et al. (2005) of $[\text{Zn}]_0 = 50$ ppm and $\delta^{66}\text{Zn}_0 = +0.50\%$, using (1), we find that the expected Zn fractionation for pure Rayleigh evaporation to a final $[\text{Zn}]$ of 1 ppm gives $\delta^{66}\text{Zn} = +62.1\%$. The measured $\delta^{66}\text{Zn}$ values reported in this study are all substantially lower than this, implying that significant mixing must have occurred after evaporation. This supports the model for evaporative volatile loss proposed above.

A comparison may also be made with the surface of the Moon. Like Vesta, the lunar surface has been largely depleted of its Zn, with $[\text{Zn}]$ of 5–20 ppm in most samples. The lunar basalts show Zn fractionation that is largely chondritic, while the soil, which has been substantially gardened by impacts, is isotopically heavy (Moynier et al., 2006; Herzog et al., 2009) (Fig. 2). Micrometeorite vaporization and sputtering were proposed as mechanisms by which the regolith might become isotopically heavier; but evaporation of light isotopes and Zn contributions from chondritic impactors, as proposed for Vesta herein, may also have played a role on the Moon.

Schönbächler et al. (2008) found a similar depletion without fractionation of another moderately volatile element, cadmium, in three eucrites, Béréba, Bouvante, and Juvinas. The cadmium isotopic composition of these eucrites was chondritic, within error ($\sim 0.4\%$), and the concentration was depleted by a factor of ~ 600 to the ~ 1 ppb level compared to CI chondrites. Wombacher et al. (2008) had similar results for $^{114}\text{Cd}/^{110}\text{Cd}$ ratios in two monomict eucritic breccias. They also concluded that the primary volatile element depletion of the inner solar system did not involve kinetic Rayleigh evaporation or condensation. Moynier et al. (2011) also reported Zn depletion without fractionation in enstatite chondrites and aubrites, again concluding that the findings were not due to evaporative/condensation processes. It is possible that Vesta's original depletion in Zn may have also been non-evaporative, but the heavy unbrecciated Antarctic samples

support a mass-dependent fractionation process such as volatilization.

If we assume that 4-Vesta accreted from chondritic material, then most of the Zn was subsequently removed or stored in phases not sampled by HEDs, with no associated isotopic fractionation, early in 4-Vesta history. One possibility includes the sequestration of Zn into spinel, as suggested by Chikami et al. (1997), which would have happened at high temperature with little or no associated isotopic fractionation and is consistent with the depletion of Cu, Zn, and Cd in these meteorites. Another proposed phase is the sulfides (troilite), but studies have found little or no troilite in the HEDs, and little or no Zn in the troilite that is found (Nishimura and Sandell, 1964; Chikami et al., 1997). Another alternative would be that the chondritic material that formed Vesta lost most of its Zn in a non-fractionating process prior to or during accretion. These speculations regarding zinc-containing phases cannot be resolved with the data collected in this study.

4.5. PCA 82502

The Antarctic eucrite Pecora Escarpment (PCA) 82502 was extremely light in Zn isotopes compared with the other HEDs, with $\delta^{66}\text{Zn}$ of -7.75‰ , a value that represents the most extreme Zn fractionation in the solar system reported to date. It is an unbrecciated eucrite (Grossman, 1994; Borgard and Garrison, 2003), although Bermingham et al. (2008) describe it as consisting of rounded basaltic clasts surrounded by a fine-grained matrix. These authors suggest this meteorite is unequibrated, and probably erupted as a surface flow. Bermingham et al. (2008) report that PCA 82502 has a light REE-depleted pattern with a positive europium anomaly, as well as other incompatible trace element depletions, and they suggest that this meteorite (and three others in their study) should be considered a “new variety of non-cumulate basaltic eucrite.” It has a weathering grade of “A,” and its initial write-up indicated that essentially no weathering was observed. This suggests that the extreme Zn isotopic fractionation measured was not significantly affected by its Antarctic exposure.

PCA 82502 is unusual in other ways. Jovanovic and Reed (1988) found that it had a higher Hg equilibration temperature than the other eucrites tested, and proposed that it could be a rapidly chilled magma representing the original crust that has not undergone impact melting and burial. Greenwood et al. (2009) noted that PCA 82502 has a $\Delta^{17}\text{O}$ value enough outside the expected range that its origin on Vesta can be regarded as uncertain (along with Pasamonte and four others). Herpers et al. (1995) found this meteorite to have an extremely low ^{10}Be activity, implying, at minimum, a “complex exposure history.” These peculiarities, and especially the extremely negative Zn isotopic fractionation, lead us to conclude that PCA 82502 most likely originated from a different parent body, and not from 4-Vesta.

5. CONCLUSION

The isotopic composition of 20 non-Antarctic HEDs show an average $\delta^{66}\text{Zn} = -0.01 \pm 0.39\text{‰}$ (2 se), with a

range of about $0 \pm 2\text{‰}$. This isotopic variation among and within HED meteorites is much larger than anything observed in terrestrial igneous rocks from various magmatic settings and suggest that the HED parent body (4 Vesta) retained an initial heterogeneity that has been lost on Earth, or acquired heterogeneity later from impact contributions. This is probably due to a weaker and much shorter geological activity on Vesta than on Earth. The unbrecciated Antarctic HEDs are isotopically heavy, suggesting that Vesta may have lost most of its zinc (and other volatiles) early in its accretion history, and impacts led to the creation of isotopically heavy Vestoids. Additional impacts led to impact gardening and brecciation, with major contributions to the surface zinc delivered by chondritic impactors.

The unbrecciated eucrite PCA 82502 is a unique sample which has the lightest Zn isotopic composition measured so far in any solar system materials ($\delta^{66}\text{Zn} = -7.75\text{‰}$). This dramatic enrichment in light isotopes of PCA 82502 together with its unusual oxygen isotopic composition suggest that this sample has a very different history than the other HED meteorites. PCA 82502 is most likely derived from a completely different parent body.

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