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Calcium Isotope Evolution During Differentiation of Vesta and Calcium Isotopic Heterogeneities in the Inner Solar System

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Key Points:

- Eucrites possess isotopically light Ca than diogenites; the Ca isotope modeling shows they are co-genetic
- Earth, Mars, and Vesta do not share a common Ca isotope reservoir, reflecting isotopic heterogeneities in the inner solar system
- The Ca stable isotopes of the planets/asteroids do not overlap those of chondrules, which does not support a chondrule-rich model for planet accretion

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract We employed MC-ICP-MS to measure the mass-dependent Ca isotope compositions of Vesta-related meteorites. Eucrites and diogenites show distinct Ca isotope compositions, which is caused by crystallization of isotopically heavy orthopyroxene. The Ca isotope data support a model where the two lithologies are linked, where the diogenites, mainly composed of orthopyroxene crystallized from an eucritic melt. As normal eucrites are the main Ca reservoir on Vesta, their $\delta^{44/40}$Ca values (per mil ^{44}Ca/^{40}Ca ratios relative to NIST 915a) best represents that of bulk silicate Vesta (0.83 ± 0.04‰). This value is different from those of bulk Earth (0.94 ± 0.05‰) and Mars (1.04 ± 0.07‰), suggesting that there exists notable Ca isotope heterogeneity between inner solar system bodies. The $\delta^{44/40}$Ca difference between chondrules and these planets does not support the pebble accretion model as the main mechanism for planetary growth.

Plain Language Summary Calcium is a major, refractory element in solar system, and its mass-dependent isotope fractionation effect is a robust proxy for probing planetary magmatic evolution and tracing the genetic relationships between solar system materials. We report high-precision Ca isotope data for the howardite-eucrite-diogenite and mesosiderite meteorites, which potentially derive from the asteroid 4 Vesta, to better understand the origin and differentiation of Vesta. Eucrites and diogenites have different mass-dependent Ca isotope compositions, which is caused by orthopyroxene crystallization from a magma ocean. We have modeled the Ca isotope evolution of this magma ocean and find that eucrites and diogenites can have formed from this melt. Eucrites show similar Ca stable isotope compositions to howardites and mesosiderites, consistent with a mixing model of eucrites and diogenites for howardites and the silicate portion of mesosiderites originating from Vesta. The Ca-rich eucrites can best represent the Ca isotope composition of bulk Vesta. It shows Earth, Mars, and Vesta do not share a common Ca isotope composition, suggesting their potentially different precursor material. All these planets and asteroids possess different Ca isotope composition from the chondrules formed in the inner solar system, which does not support a chondrule-rich model for accretion of terrestrial planets.

1. Introduction

Asteroid 4 Vesta is the second largest differentiated body in the asteroid belt (e.g., Russell et al., 2012), and is believed to have experienced large-scale melting and magma ocean processes (Greenwood et al., 2005; Mittlefehldt, 2015) during its history. Such magmatic events are the key junctures for shaping the chemical reservoirs and volatile inventory of Vesta and also other terrestrial planets (Greenwood et al., 2005), but in the case of Vesta, these are still ambiguous and lack more geochemical constraints. Vesta formed and differentiated very early, within the first ~3 Ma after solar system formation (Schiller et al., 2011; Trinquier et al., 2008), and subsequently differentiated into a metallic core and silicate mantle plus crust, similar to other planets like Earth and Mars (Mittlefehldt, 2015; Russell et al., 2012). Hence, understanding the differentiation processes of Vesta not only important for understanding Vesta itself, but also sheds light on the formation and differentiation of planetesimals in early solar system in general.

Based on the findings of the Dawn Mission and other spectral observations, the howardite-eucrite-diogenite (HED) meteorite clan is believed to derive from Vesta (Binzel & Xu, 1993; McCord et al., 1970; Russell

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et al., 2012), so the HEDs serve as potentially direct samples of the silicate portions of Vesta. Eucrites are mostly basaltic in composition, though geochemically distinct from terrestrial mid-ocean ridge basalts (MORB), and their mineralogy is dominated by clinopyroxene (e.g., pigeonite) and plagioclase. Eucrites are believed to represent the composition of Vesta's crust (Mayne et al., 2009). However, a small number of eucrites (e.g., Pasamonte and Ibitira) have anomalous petrological, chemical, and mass-independent O isotope compositions (Δ^{17}O values) compared to most HEDs of which the origin remains poorly understood (Scott et al., 2009). Diogenites are broadly orthopyroxene-rich lithologies, with some olivine-rich variants, that are conventionally viewed as cumulate rocks crystallized from a Vestan magma ocean or during magma intrusion events on Vesta, and howardites are impact-brecciated mixtures of eucrites and diogenites (Mittlefehldt, 2015). However, the petrological relationship between eurcrites and diogenites remains enigmatic, and two opposite views are generally considered. Early studies argue that eucrites and diogenites are cogenetic and formed during the crystallization of a global-scale magma ocean (Righter & Drake, 1997; Ruzicka et al., 1997; Warren, 1997), while an alternative model explains diogenites as originating from melts that are different from eucrites (Barrat et al., 2008; Shearer et al., 1997; Stolper, 1977; Yamaguchi et al., 2011), and possibly crystallized in the Vestan crust (Barrat et al., 2010). This debate was tested by an improved model in Mandler and Elkins-Tanton (2013), who used major element constraints to propose that eucrites and diogenites can be produced from one parental melt via a two-step magma evolution. However, this model is challenged by inconsistent trace elements, for example, rare earth elements (REEs), especially Dy/Yb (Barrat & Yamaguchi, 2014). In addition to HEDs, stony-iron mesosiderite meteorites are also thought to be related to Vesta because their silicate portions show petrographic and O isotopic similarities with HEDs (Greenwood et al., 2006; Mittlefehldt et al., 1979). Zircons ages from mesosiderites suggest they formed from a hit-and-run collision on Vesta at ∼4,525.4 Ma, which that caused the thick crust observed by NASA's Dawn mission and explains the missing olivine in HEDs (Haba et al., 2019), but this hypothesis needs more evidence.

Calcium (Ca) is a major element in solar system materials (e.g., ∼1 wt.% in chondrites), and large mass-dependent Ca isotope fractionations have been observed on Earth as a result of magmatic processes (Antonelli et al., 2019; Chen et al., 2020, 2019; Dai et al., 2020; Eriksen & Jacobsen, 2022; Fu et al., 2022; S. Huang et al., 2010; Kang et al., 2017; Moynier et al., 2022; Valdes et al., 2014; Wang et al., 2019; H. Zhu et al., 2021, 2018). In terrestrial mantle peridotites, equilibrium Ca isotope fractionation causes orthopyroxene (OPX) to have an isotopically heavier Ca isotope composition than clinopyroxene (CPX), which results from the differences of Ca–O bonds and Ca coordination numbers, for example, 2.50 Å and 8 for CPX and 2.15 Å and 6 for OPX (Feng et al., 2014; S. Huang et al., 2010; Smyth & Bish, 1988). This fractionation behavior makes Ca isotopes a robust proxy for probing planetary magmatic differentiation and the genesis of igneous rocks, not only on Earth (Antonelli et al., 2021; Chen et al., 2020, 2019; Dai et al., 2020; Eriksen & Jacobsen, 2022; Kang et al., 2017; Zhang et al., 2018; H. Zhu et al., 2018) but also other differentiated bodies in the Solar System such as the Moon (F. Huang et al., 2019; Klaver et al., 2021; Wu et al., 2020) and Mars (Magna et al., 2015).

Ca is a refractory lithophile element which means that its isotope composition is likely insensitive to other planetary processes, such as metal crystallization, core formation, and volatile depletion, which means Ca stable isotopes do not fractionate during these processes. Hence, Ca isotopes are useful as a tracer for testing the genetic relationships between normal eucrites, anomalous eucrites, howardites and the silicate portions of mesosiderites, and the chondritic precursor material for Vesta. Another application of Ca isotopes as a "tracer" is testing the precursor materials that formed Earth. Amsellem et al. (2017) observed that Earth has similar mass-dependent Ca isotope compositions as chondrules, with $\delta^{44/40}$Ca values ranging from 1.00‰ to 1.21‰ ($\delta^{44/40}$Ca is the deviation of mass-dependent ^{44}Ca/^{40}Ca relative to NIST SRM 915a), in Vigarano-type (CV) chondrites, and concluded their Ca isotope similarities support the pebble-accretion model (Johansen et al., 2021), that is, chondrules may contribute to the growth of terrestrial planets. However, due to the nucleosynthetic isotope signatures, including Cr, Ti, Ni, and Ca (Dauphas et al., 2014; Steele et al., 2012; Trinquier et al., 2007, 2009), Earth and CV chondrites accreted very far from each other, in the inner and outer solar system respectively. Also, a recently revised estimation of the Ca isotope composition ($\delta^{44/40}$Ca = 0.94 ± 0.05‰) of bulk silicate Earth (BSE; Kang et al., 2017) does not match that of CV chondrules, which makes this issue more ambiguous. Comparing the Ca isotope composition of chondrules with those of other differentiated planets/asteroids in the solar system may be useful.

Some of the previous $\delta^{44/40}$Ca data are measured by thermal ionization mass spectrometer (TIMS) using double spike techniques, which usually measures the signal of ^{40}Ca. Due to the ^{40}K decay (half-life of ∼1.25 Ga), the ingrowth of the daughter nuclide ^{40}Ca can shift the mass-dependent Ca isotope fractionation effect and result in inaccurate data, especially for some early formed meteorites. Employing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), we present high-precision and high-accuracy Ca isotope compositions for nine eucrites (including one anomalous eucrite), four diogenites, two howardites, and two mesosiderites. These new data help to constrain not only the origin and differentiation of Vesta and the related meteorites, but also the precursor materials of Vesta and other terrestrial planets.

2. Results

Detailed sample information, analytical methods, and data quality validation can be found in the Supporting Information. Note that REEs could have potential matrix effect on Ca isotope measurements on MC-ICP-MS (Sun et al., 2021). To test this issue, we also measured the Ca isotope data for two REE-rich standards GSP-2 and COQ-1, with La/Ca ratios of ∼0.0105 and ∼0.0015 (before column chemistry), and our data of the two samples are well consistent with those in Lewis et al. (2022) and Sun et al. (2021). As for the HED samples, their La/Ca ratios are usually less than 0.00005 (Table 2 and Table S4), so the matrix effect of REEs cannot be a problem for our data.

Eucrites and diogenites have variable and anti-correlated Ca contents (ranging from 5,000 to 80,000 μg/g) and Mg# (0.38–0.76) that are further correlated with the $\delta^{44/40}$Ca values. Eucrites show isotopically light $\delta^{44/40}$Ca values with a mean 0.83 ± 0.04 ‰, including Pasamonte (2SD, $n = 9$). Diogenites, have variable $\delta^{44/40}$Ca ranging from 1.01 ± 0.05 ‰ to 1.16 ± 0.03 ‰ (Table 1 and Figure 1). The two howardites have similar $\delta^{44/40}$Ca to the eucrites (0.86 ± 0.08 and 0.87 ± 0.07, 2SD) whilst the two mesosiderites, with $\delta^{44/40}$Ca values of 0.87 ± 0.00 ‰ and 0.79 ± 0.02 ‰ also fall within the $\delta^{44/40}$Ca range of eucrites. Elemental content data are shown in Table 2 and Table S4.

3. Discussion

3.1. Ca Isotope Difference Between Diogenites and Eucrites and Implications for Their Petrological Relationships

The difference in Ca isotopes between eucrite and diogenite meteorites is unlikely to be caused by terrestrial weathering because fall and find meteorites in a same group/type do not show systematic Ca isotope differences (Amsellem et al., 2017; S. Huang & Jacobsen, 2017; Klaver et al., 2021; Magna et al., 2015; Valdes et al., 2014; Wu et al., 2020). Rather, the variation in Ca contents between eucrites and diogenites results from their different mineralogy. Most of the diogenites are monomineralic orthopyroxene cumulates with low CaO contents (<2.5 wt.%), while eucrites are more Ca-rich basaltic rocks containing orthopyroxene, pigeonite, high-Ca pyroxenes, and plagioclase phenocrysts (Mittlefehldt, 2015). The $\delta^{44/40}$Ca variation among eucrites and diogenites and their correlation with Ca content and Mg# is likely caused by magmatic processes (Figure 1). Given the preference of orthopyroxene for heavy Ca isotopes (Feng et al., 2014; S. Huang et al., 2010), the high $\delta^{44/40}$Ca of the diogenites can result from equilibrium crystallization of orthopyroxene that is Ca-poor and Mg-rich.

To test the petrological relationship between eucrites and diogenites, that is, whether they are co-genetic, we model the Ca isotope and major element implications (Mg# and Ca contents) of this process using a simple orthopyroxene fractional crystallization model (Figure 1), based on the experimentally determined liquid line of descent of Ashcroft and Wood (2015). The bulk $\delta^{44/40}$Ca of the parental Vestan magma ocean in this model is assumed to be ordinary chondrites (OCs), with $\delta^{44/40}\text{Ca} = 0.92 \pm 0.11$‰ (S. Huang & Jacobsen, 2017; Valdes et al., 2014). The details of the parameters and methods are given in the Supporting Information. As shown in Figure 1, this model adequately explains the difference in $\delta^{44/40}$Ca between the cumulate diogenites and derivative eucritic melt as an equilibrium signature. As orthopyroxene has a low Ca content, its crystallization has little leverage on the Ca budget of the melt. Hence, $\delta^{44/40}$Ca of the melt only decreases by 0.01‰ even after removal of 40% orthopyroxene, which is consistent with the general homogeneity in $\delta^{44/40}$Ca between eucrites with highly variable CaO contents (7.1–12.8 wt.%). This Ca isotope model also has significance on the petrogenesis of eucrites and diogenites. Formation of diogenites mostly result from the crystallization of OPX in the eucritic melt, and eucrites and diogenites can be co-genetic (Mandler & Elkins-Tanton, 2013; Righter & Drake, 1997; Ruzicka et al., 1997; Warren, 1997).

However, our Ca isotope model cannot reproduce the Ca isotope composition of the two diogenites, NWA 7831 and Dhofar 700, as their $\delta^{44/40}$Ca is resolvably lower than the modeled composition of orthopyroxene cumulates.

Table 1
Ca Isotope Data for Howardite-Eucrite-Diogenite and Mesosiderite Meteorites and Reference Materials

Name	Type	Fall/ find	Mass (mg)	CaO (wt.%)	Mg# (%)	$\Delta^{44/42}Ca_{NIST915a}$ (‰)	2SD	$\delta^{43/42}Ca_{NIST915a}$ (‰)	2SD	$\delta^{44/40}Ca_{NIST915a}$ (‰)	2SD	2SE	N
Bou Kra 004	Eucrite-mmict	Find	30.11	10.4	38%	0.40	0.05	0.18	0.02	**0.82**	0.08	0.05	3
Pasamonte	Eucrite-pmict	Fall	~20	12.8	38%	0.42	0.05	0.18	0.02	**0.85**	0.08	0.05	3
NWA 769	Eucrite-mmict	Find	30.47	10.7	38%	0.40	0.01	0.19	0.03	**0.83**	0.02	0.01	3
NWA 8048	Eucrite	Find	30.3	11.1	42%	0.39	0.04	0.18	0.03	**0.80**	0.06	0.04	3
NWA 7263	Eucrite	Find	30.3	7.1	49%	0.42	0.02	0.20	0.04	**0.85**	0.03	0.02	3
NWA 10962	Eucrite-unbr	Find	30.91	10.0	39%	0.40	0.01	0.19	0.04	**0.81**	0.02	0.01	3
NWA 8554	Eucrite-mmict	Find	30.12	10.1	41%	0.42	0.04	0.19	0.02	**0.85**	0.06	0.04	3
Tirhert	Eucrite-unbr	Fall	30.34	9.0	40%	0.41	0.02	0.19	0.01	**0.84**	0.04	0.02	3
NWA 10515	Eucrite-unbr	Find	30.65	9.7	40%	0.42	0.03	0.19	0.02	**0.85**	0.05	0.03	3
NWA 5480	Diogenite	Find	29.68	1.1	74%	0.56	0.03	0.29	0.04	**1.16**	0.06	0.03	3
NWA 7831	Diogenite	Find	29.88	1.9	71%	0.50	0.04	0.25	0.05	**1.03**	0.06	0.04	3
Repeat	Diogenite	Find	30.84	2.0	71%	0.48	0.03	0.23	0.04	**0.98**	0.04	0.02	3
Dhofar 700	Diogenite	Find	30.45	2.4	68%	0.53	0.01	0.25	0.05	**1.08**	0.02	0.01	3
Tatahouine	Diogenite	Fall	30.17	0.8	76%	0.56	0.05	0.28	0.03	**1.14**	0.09	0.05	3
NWA 11003	Howardite	Find	45.4			0.42	0.05	0.19	0.08	**0.86**	0.08	0.05	3
NWA 8712	Howardite	Find	36.29			0.42	0.04	0.20	0.02	**0.87**	0.07	0.04	3
Youxi	Mesosiderite-C	Find	~300			0.42	0.03	0.19	0.04	**0.87**	0.06	0.03	3
Repeat	Mesosiderite-C	Find				0.43	0.04	0.19	0.02	**0.87**	0.06	0.03	3
NWA 1182-silicate rich	Mesosiderite-C	Find				0.39	0.01	0.19	0.04	**0.79**	0.02	0.01	3
NIST SRM 915b						0.36	0.06	0.16	0.11	**0.73**	0.09	0.05	3
Sea Water Ave.						0.91	0.03	0.45	0.04	**1.87**	0.07		23
BHVO-2 Ave.						0.38	0.04	0.18	0.05	**0.78**	0.08		23
BCR-2						0.41	0.02	0.17	0.06	**0.84**	0.04	0.02	3
GSP-2						0.30	0.04	0.11	0.05	**0.61**	0.07	0.03	6
Repeat						0.33	0.03	0.17	0.02	**0.68**	0.06	0.02	8
COQ-1						0.35	0.03	0.12	0.05	**0.71**	0.08	0.03	8
Repeat						0.36	0.06	0.17	0.06	**0.72**	0.12	0.04	8

Note. The individual $\delta^{44/40}$Ca data for Sea Water and BHVO-2 are reported in Table S3 in Supporting Information S1. GSP-2 and COQ-1 are rich in REEs, and their Ca isotope data are tested for the REE matrix effect of Ca isotope measurements on MC-ICP-MS (Sun et al., 2021).

This inconsistency could reflect the two diogenites represent mixtures between orthopyroxene and the residual melt. Alternatively, some diogenites may crystallize from the different melts, due to their diversity of heavy REEs (Barrat & Yamaguchi, 2014; Barrat et al., 2008). However, note that, this argument about REEs is based on an assumption that HED parent body has chondritic REE composition, which might not be true, because a REE-depleted reservoir has not been found in HED sample collections, considering eucrites are largely rich (seven to ten times) in REEs relative to chondrites (Consolmagno et al., 2015).

3.2. Genetic Relationships Between HEDs and Mesosiderites

The anomalous eucrite, Pasamonte ($\delta^{44/40}$Ca = 0.85 ± 0.05‰) has the same Ca isotope composition as other eucrites, which is consistent with their similar mass-independent ^{54}Cr/^{52}Cr (Trinquier et al., 2007). Note that Ibitira, another anomalous eucrite (Wilkening & Anders, 1975), also has the same mass-independent ^{50}Ti/^{47}Ti as normal eucrites (Trinquier et al., 2009). The anomalous eucrites, that is, Pasamonte and Ibitira, should have similar metal isotope compositions as normal eucrites (Trinquier et al., 2009). However, their different mass-independent ^{17}O/^{16}O (Mittlefehldt, 2015; Scott et al., 2009) could be evidence that these anomalous eucrites

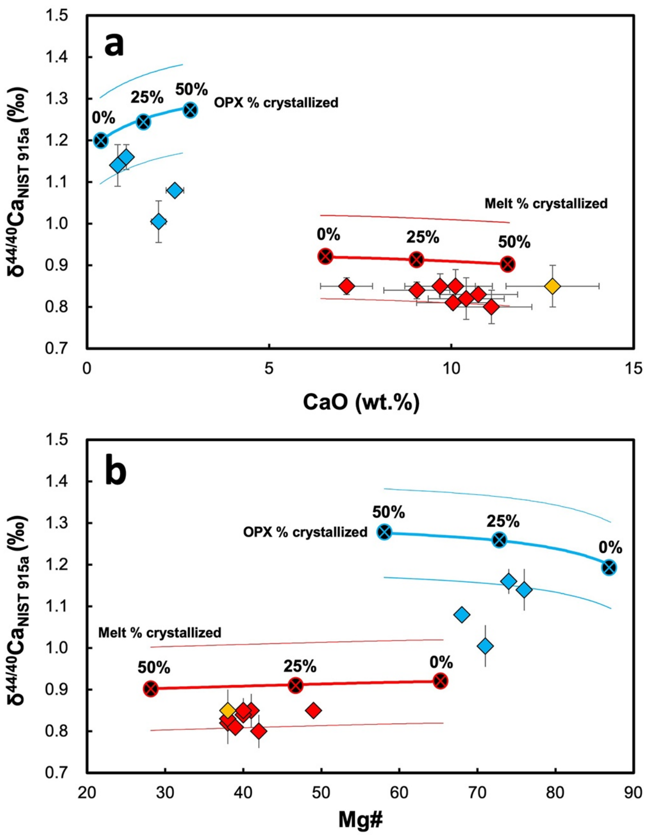

Figure 1. Calcium isotope composition of eucrites and diogenites. The red diamonds represent normal eucrites; anomalous eucrite Pasamonte is shown in orange; the blue diamonds for diogenites. The uncertainty for CaO content is estimated as 10% (RSD). The bold lines are the Ca isotope evolution model for orthopyroxene crystallization, taking ordinary chondrites ($\delta^{44/40}$Ca = 0.92 ± 0.11‰) as the initial composition of melt (i.e., bulk Vesta composition); the thin lines at two sides represent the 2SD uncertainty; the black circles marked in blue and red represent percentage for orthopyroxene and melt crystallization respectively. See Supporting Information for details on the model.

come from the Vestoids, that is, smaller asteroids around Vesta (Burbine et al., 2001), and experienced some secondary alteration (e.g., fluid-assisted metasomatic processes) that changed their O isotope compositions (Shisseh et al., 2023) but not their metal isotope compositions.

Similar $\delta^{44/40}$Ca values between howardites and eucrites attest to howardites being physical mixtures of eucrites and diogenites (Mittlefehldt, 2015). The mean Ca contents and $\delta^{44/40}$Ca of eucrites and diogenites are ∼10 wt.% and ∼2 wt.%, and ∼0.83‰ and ∼1.10‰, respectively, so the product of mixing (mass for mass) would be dominated by the isotopic signature of eucrites. For mesosiderites, the metal phase is Ca-free, so the Ca isotope composition of the two mesosiderites are representative of their silicate portions. Both Youxi (0.87 ± 0.004‰) and NWA 1182 (0.79 ± 0.01‰) have $\delta^{44/40}$Ca values falling into the range of that of eucrites (0.83 ± 0.04‰, 2SD), supporting the idea that the silicate proportions of mesosiderites could have similar precursors as Vesta (Haba et al., 2019; Mittlefehldt, 2015). This is also consistent with similar mass-independent ^{54}Cr/^{52}Cr and ^{50}Ti/^{47}Ti between mesosiderites and HEDs, considering that Cr and Ti are also lithophile elements at Vesta's conditions (Trinquier et al., 2007, 2009).

3.3. Calcium Stable Isotope Composition of Bulk Vesta and Ca Isotopic Heterogeneities in the Inner Solar System Bodies

Since Ca is non-siderophile and does not exist in the core (Rubin, 2011), the Ca isotope composition of bulk silicate Vesta should be mostly representative of that of bulk Vesta. Since no mantle rocks of Vesta are in our meteorite collection, eucrites and diogenites are the only direct samples from the silicate proportions of Vesta. Diogenites consisting mostly of orthopyroxene and minor olivine are cumulates and do not represent the average composition of the Vestan mantle (Lunning et al., 2015). Also, the CaO contents in diogenites (0.8 wt.%–2.4 wt.%) are relative low, relatively to that of bulk silicate Vesta, for example, ∼2.5 wt.%, estimated by cosmochemical models (Ruzicka et al., 1997; Wänke & Dreibus, 1980). Hence, the diogenites with isotopically heavy Ca nay be difficult to link the Ca isotope composition of bulk Vesta. Alternatively, the Ca-rich basaltic eucrites (with 7 wt.%–13 wt.% CaO) represent a most important Ca reservoir of Vesta.

In Figure 2, we compared the basalts from different planets in the inner solar system, including for example, normal mid-ocean ridge basalts (N-MORB) from Earth (Eriksen & Jacobsen, 2022; H. Zhu et al., 2018), lunar basalts (Klaver et al., 2021; Valdes et al., 2014; Wu et al., 2020), shergottites from Mars (Magna et al., 2015), and eucrites from Vesta. The $\delta^{44/40}$Ca value for N-MORB (0.84 ± 0.12‰; 2SD, N = 28), lunar basalts (0.86 ± 0.13‰; 2SD, N = 22), eucrites (0.83 ± 0.04‰; 2SD, N = 8; excluding Pasamonte) and shergottites (0.95 ± 0.22‰; 2SD, N = 14) have nearly identical Ca isotope compositions. Note that the $\delta^{44/40}$Ca data for Apollo lunar basalts measured by collision-cell-based MC-ICP-MS using the double spike technique are more homogeneous: 0.85 ± 0.06‰ (2SD, N = 13) (Klaver et al., 2021). However, basalts generally do not represent the Ca isotope composition of the bulk planetary body. For example, the bulk Earth $\delta^{44/40}$Ca value (∼0.94‰) is around ∼0.1‰ higher than the average N-MORB, which is caused by low-degree partial melting with clinopyroxene retaining a significant fraction of Ca in the residue (Eriksen & Jacobsen, 2022; Kang et al., 2017; Klaver et al., 2021; Soderman et al., 2022). Similarly, mare basalts are low-degree partial melts of a highly heterogeneous lunar mantle, but their $\delta^{44/40}$Ca is consistent with a bulk (silicate) Moon that is isotopically heavier than lunar basalts and similar to bulk (silicate) Earth (e.g., Klaver et al., 2021; Wu et al., 2020). Also considering the relatively large Ca isotope variation and its 2SD uncertainty (e.g., >0.10‰) of basalts of a same planet/asteroid, we cannot directly compare their basalts for Ca isotope comparison between different planets.

The distinct petrogenesis of eucrites means that, unlike terrestrial MORB or lunar basalts, eucrites can be used to gauge the Ca isotope composition of bulk silicate Vesta. The major element composition of eucrites is consistent

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Table 2
Elemental Contents of Eucrites and Diogenites in This Study

Sample	Type	Mg#	La/Ca	Li	Be	Na	Mg	Al	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	La
NWA 769	Eucrite-mmict	0.38	0.00004	8.96	0.31	3639	36,302	66,494	305	664	76,764	32	4068	65.5	1916.3	4183	138,714	3.10
Bou Kra 004	Eucrite-mmict	0.38	0.00004	9.27	0.26	3383	35,924	66,64	328	661	74,370	33	4860	70.1	2045.9	3672	136,827	3.34
NWA8048	Eucrite	0.42	0.00004	9.18	0.25	3329	44,367	63,168	328	613	79,340	29	3917	69.7	1978.2	4055	139,849	2.81
NWA 7263	Eucrite	0.49	0.00002	6.48	0.14	1937	69,194	36,452	191	398	50,902	30	2880	75.9	2520.9	4814	165,532	1.21
NWA 10962	Eucrite-unbr	0.39	0.00002	6.54	0.22	3101	40,369	66,652	201	424	71,798	30	3944	75.1	2140.3	4322	145,930	1.20
NWA 8554	Eucrite-mmict	0.41	0.00005	8.59	0.33	3935	42,485	64,251	290	830	72,286	29	4108	71.5	2216.1	4036	138,121	3.41
Tirhert	Eucrite-unbr	0.40	0.00004	6.83	0.17	2787	43,641	62,303	181	381	64,671	28	1990	75.9	1968.6	4422	147,426	2.50
NWA 10515	Eucrite-unbr	0.40	0.00003	8.22	0.23	2931	41,626	63,223	212	542	69,247	30	3433	67.6	1783.0	4317	143,606	2.05
Tatahouine	Diogenite	0.76	0.00000	1.24	0.01	102	168,364	3069	129	134	5989	14	446	112.5	4689.4	3810	119,031	0.01
NWA 5480	Diogenite	0.74	0.00000	2.79	0.00	123	155,013	2529	113	138	7662	13	365	100.3	3568.9	4019	122,834	0.03
NWA 7831	Diogenite	0.71	0.00001	2.18	0.02	152	140,815	5649	113	193	13,791	20	725	125.6	4462.5	4446	134,323	0.13
NWA 7831	Diogenite	0.71	0.00001	2.25	0.03	168	142,708	5749	116	205	14,260	21	745	132.9	4870.0	4544	136,726	0.14
Dhofar 700	Diogenite	0.68	0.00000	1.70	0.01	151	128,533	5894	127	152	17,205	26	403	152.3	4346.4	5088	140,690	0.04
BHVO-2	Basalt	0.54	0.00018	4.34	1.13	16,168	43,363	70,688	1181	4608	80,627	32	16,190	314.5	278.3	1319	85,446	14.79
BHVO-2	Basalt	0.54	0.00018	4.89	1.01	16,498	43,714	72,048	1166	4471	81,345	32	16,344	316.7	276.9	1338	86,691	14.90
BHVO-2	Basalt	0.53	0.00018	4.25	1.08	15,864	42,620	69,671	1172	4360	80,317	32	16,390	320.2	275.9	1330	86,717	14.62
BHVO-2	Basalt	0.54	0.00019	4.70	1.08	16,341	43,330	71,082	1167	4499	80,711	32	16,268	317.3	278.5	1332	86,210	14.98
BHVO-2	Basalt	0.54	0.00019	4.41	1.04	16,650	43,960	72,598	1155	4617	81,639	32	16,358	317.6	277.7	1348	86,582	15.55
BHVO-2	Basalt	0.54	0.00019	4.24	1.09	16,304	43,689	72,263	1174	4366	80,776	32	16,414	318.2	277.7	1335	86,429	15.33
BCR-2	Basalt	0.34	0.00050	9.50	2.23	23,595	22,244	72,478	1555	15,201	52,042	34	13,692	420.4	14.9	1584	97,576	26.23
BCR-2	Basalt	0.34	0.00051	9.46	2.21	23,253	21,727	72,008	1547	15,143	50,877	34	13,538	417.7	15.0	1564	96,345	25.83
BCR-2	Basalt	0.33	0.00051	8.56	2.20	21,951	20,320	66,579	1505	14,170	49,982	33	13,196	408.9	15.1	1531	94,730	25.37
BCR-2	Basalt	0.34	0.00050	9.71	2.15	22,962	21,478	70,726	1494	14,788	50,596	34	13,520	414.1	15.1	1551	95,875	25.25
BCR-2	Basalt	0.34	0.00049	9.13	2.04	23,512	21,715	72,326	1500	15,552	51,219	33	13,576	415.7	14.8	1558	96,626	25.13
BCR-2	Basalt	0.34	0.00049	8.78	2.19	23,273	21,851	71,653	1539	15,021	50,395	33	13,440	415.4	14.9	1554	96,255	24.83

Note. We did not measure the elemental contents of Pasamonte, since it is a well-studied eucrite. The Ca content and Mg# of Pasamonte are cited from Barrat et al. (2000). The repeated measurements for BHVO-2, BCR-2, and NWA 7831 are well consistent, and the external uncertainty of these elemental content data are estimated as 10% (2σ). We also measured other content data for other elements, for example, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Ce, Lu, Hf, Ta, Pb, Th, U and REEs, which can be found in Table S4.

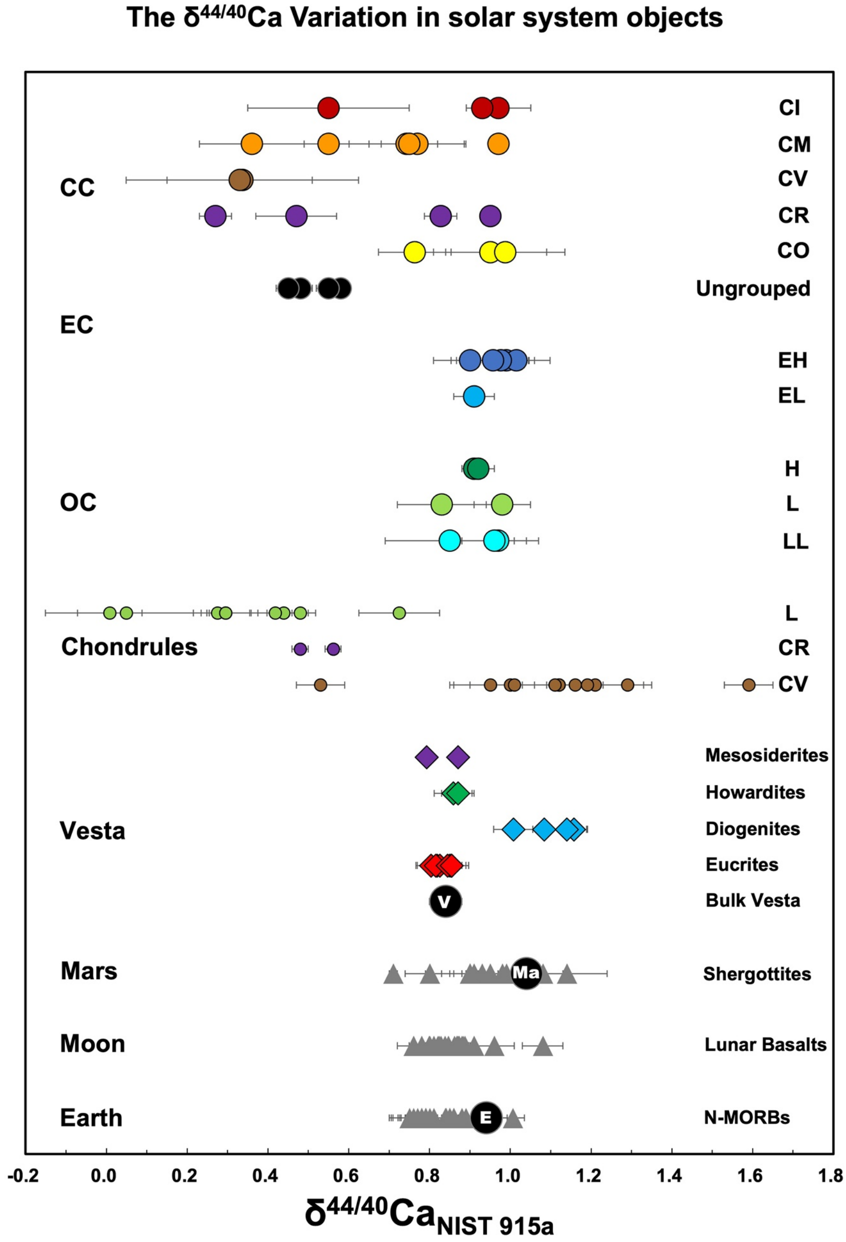

Figure 2. Calcium isotope panorama for solar system materials, including Vesta related meteorites, chondrites (big circles), chondrules (small circles), basaltic rocks (gray triangles) from Earth, Moon, and Mars in comparison with the new data for howardite-eucrite-diogenite meteorites from this study. All the data resources can be found in Table S2 in Supporting Information S1. Abbreviations: CC, carbonaceous chondrites, OC, ordinary chondrites, EC, enstatite chondrites, TL, Tagish Lake (an ungrouped CC), V, Vesta, Ma, Mars, and E, Earth. The gray triangles represent the $\delta^{44/40}$Ca of basalt samples from Earth (N-MORBs), Moon (lunar basalts), and Mars (Shergottites), and the big black circles means Ca isotope compositions of bulk planets: Earth, 0.94 ± 0.05‰ (Kang et al., 2017); Mars, 1.04 ± 0.09‰ (Magna et al., 2015); and Vesta, 0.84 ± 0.04‰ (this study). The Ca isotope heterogeneities for the inner solar system bodies indicate their distinct precursor material. All the information for the reference data can be found in *Data Availability Statement*.

with fractional crystallization of orthopyroxene from a high-degree parental melt (Shearer et al., 1997). Subsequent evolution of this melt through fractional crystallization of orthopyroxene gave rise to the eucrites and diogenites. Calcium-poor, orthopyroxene-rich diogenites are in Ca isotope equilibrium with a eucritic melt (Figure 1). Our modeling shows that fractional crystallization of isotopically heavy orthopyroxene does not effectively alter $\delta^{44/40}$Ca of the residual melt (Figure 1). The Ca content of orthopyroxene is so low that, even after 50% orthopyroxene removal, $\delta^{44/40}$Ca of the residual melt has decreased by <0.03‰. From this, it follows that $\delta^{44/40}$Ca of the eucrites, which represent the residual melt after 25%–50% orthopyroxene crystallization, is similar to their parental melt well withing the analytical resolution. As this parental melt is contains >99% of Ca on Vesta, with the remaining <1% hosted in deep olivine cumulates and the core, we argue that $\delta^{44/40}$Ca of bulk Vesta is best estimated by the normal eucrites, that is, 0.83 ± 0.04‰ (2SD, $N = 8$; excluding Pasamonte).

A mass-balance calculation for the Ca isotope reservoirs in Vesta will be helpful to validate this hypothesis. Vesta has a thick crust (Consolmagno et al., 2015; Russell et al., 2012) that can be up to 80 km as thick as the Vestan mantle (Clenet et al., 2014), so the Vestan crust has a higher volume than the mantle by 7 times: $V_{\mathrm{crust}} = \pi \times (160^3 - 80^3)$; $V_{\mathrm{mantle}} = \pi \times 80^3$. Although the eucritc Vestan crust is intruded by diogenites, like the howadite, its Ca isotope composition should also be eucretic. Considering the much larger volume of the Vestan crust, although the Ca isotope composition of the olivine-rich mantle is unknown, we can predict the Ca isotope composition of bulk silicate Vesta can be represented by eucrites.

Previous studies have given the $\delta^{44/40}$Ca values of bulk Earth and Mars, 0.94 ± 0.05‰ (Kang et al., 2017) and 1.04 ± 0.09‰ (Magna et al., 2015), respectively (Figure 2). As for Moon, lack of the mantle derived rocks limits the accurate estimation of its bulk $\delta^{44/40}$Ca value, so we do not discuss it in this study. Although the uncertainty for the $\delta^{44/40}$Ca value for Mars is relatively large, it can be seen Vesta has clearly different $\delta^{44/40}$Ca value from Earth and Mars. Hence, the three inner solar system bodies, that is, Earth, Mars, and Vesta may have different mass-dependent Ca isotope compositions. The nucleosynthetic anomaly of ^{48}Ca isotope (expressed as ^{48}Ca/^{44}Ca ratios) is also a robust fingerprint to test the kinships between solar system materials (Dauphas et al., 2014; Moynier et al., 2010; Schiller et al., 2018, 2015; K. Zhu et al., 2023). In fact, Earth, Mars, and Vesta have different mass-independent ^{48}Ca/^{44}Ca signatures (Dauphas et al., 2014; Schiller et al., 2018), consistent with their mass-dependent Ca isotope difference. However, $\delta^{44/40}$Ca and the mass-independent ^{48}Ca/^{44}Ca compositions of Earth, Mars, and Vesta do not correlate with each other, possibly because the different origins of the two Ca isotope fractionation mechanisms, that is, mass-dependent isotope fractionation and nucleosynthesis.

Volatile depletion is a key stage during planetary differentiation (Allègre et al., 2001), which could fractionate isotopes (e.g., Paniello, Day, & Moynier, 2012), even for some more refractory elements, for example, Si (Pringle et al., 2014), Ca and Ti (Zhang et al., 2014). Compared to Earth and Mars, Vesta has lower Rb/Sr and K/U, suggesting it is more depleted in volatile elements (Davis, 2006), and this volatile depletion of Vesta has been traced by Zn (Paniello et al., 2012), K (Tian et al., 2019) and Cr stable isotope measurements (K. Zhu et al., 2019). Kinetic isotope fractionation during element evaporation would enrich the heavy isotopes in the residue, which is not consistent with the isotopically lighter Ca of Vesta relative to those of Earth and Mars, so the Ca isotope difference is not likely caused by Ca evaporation during volatile loss. Since no other planetary processes are likely to fractionate Ca isotopes, their isotope difference can reflect their different precursor materials, and furthermore suggest Ca isotopic heterogeneities in the inner solar system. Earth, Moon, and Vesta accreted at different regions in the inner solar system and thus their Ca isotope difference suggests that their precursor materials experienced different condensation histories.

3.4. Ca Isotopes Test the Chondrule-Rich Accretion Model for Terrestrial Planets

Bulk chondrites and chondritic components are potential candidates for the planetary precursors (Allègre et al., 1995; Johansen et al., 2021). Ordinary chondrites (OCs) and enstatite chondrites (ECs) have a non-carbonaceous (NC) isotope anomaly signature, and thus constitute inner solar system material (Dauphas et al., 2014; Schiller et al., 2018; Steele et al., 2011; Trinquier et al., 2007, 2009). It is consistent that the inner-solar system bodies, including Earth, Mars, and Vesta, have similar $\delta^{44/40}$Ca values as the NC chondrites, including OCs (OCs; 0.92 ± 0.11‰; 2SD, $N = 7$), and ECs (0.96 ± 0.08‰; 2SD, $N = 6$), instead of those of carbonaceous chondrites (CCs) with $\delta^{44/40}$Ca values ranging from ~0.2‰ to ~1.0‰ (Amsellem et al., 2017; S. Huang & Jacobsen, 2017; Schiller et al., 2018; Valdes et al., 2014).

Amsellem et al. (2017) first found that chondrules in CV chondrites, with average $\delta^{44/40}$Ca values of 1.10 ± 0.10‰, mimic those of the BSE with $\delta^{44/40}$Ca = 1.05 ± 0.04 (S. Huang et al., 2010), and bulk silicate Mars, $\delta^{44/40}$Ca = 1.04 ± 0.09‰ (Magna et al., 2015). Also considering chondrules in carbonaceous chondrites including CV, Ornans-type (CO) and Renazzo-type (CR) groups have similar volatile element (e.g., Mn, K, Ga, and Zn) contents and Si/Mg ratios as terrestrial primitive mantle, the authors argue that chondrules may contribute most (>90%) of the precursor materials to accretion of Earth and maybe other terrestrial planets

(Amsellem et al., 2017). However, the mass-dependent Ca isotope composition of BSE has been revised to $\delta^{44/40}$Ca = 0.94 ± 0.05‰, through investigating the fertile spinel and garnet peridotites that experienced little or no melting and metasomatism (Kang et al., 2017). This updated $\delta^{44/40}$Ca data of BSE only overlaps the edge of the average $\delta^{44/40}$Ca value CV chondrules (1.11 ± 0.14‰; 2SE, $N = 12$; Amsellem et al., 2017; Bermingham et al., 2018). In fact, this comparison is not valid, because the nucleosynthetic anomalies of multiple metal isotopes, for example, Ca (Dauphas et al., 2014), Ni (Steele et al., 2012), Cr (Trinquier et al., 2007), Ti (Trinquier et al., 2009), Mo (Budde et al., 2019), suggests that CV chondrites accreted in the outer solar system.

OCs have closer nucleosynthetic isotope compositions to the inner solar system bodies (Budde et al., 2019; Dauphas et al., 2014; Steele et al., 2012; Trinquier et al., 2007, 2009), so comparison of Ca isotopes between OC chondrules (Schiller et al., 2018) and Earth, Mars and Vesta should be more reasonable to test the chondrule-rich model. The $\delta^{44/40}$Ca values for OC chondrules vary from ~0.05‰ to ~0.72‰ (Figure 2) that are obviously lower than those of Earth, Vesta, and Mars. Hence, from mass-dependent Ca isotope perspective, it does not support the pebble accretion model, which predicts that chondrules may contribute to the accretion of terrestrial planets (Johansen et al., 2021), although some OC chondrules have overlapping mass-independent ^{48}Ca/^{44}Ca compositions as Vesta (Schiller et al., 2018). As for Earth, ECs have similar mass-independent isotope compositions as Earth for multiple elements (Dauphas, 2017), and are considered as the possible precursor materials for Earth. Therefore, the $\delta^{44/40}$Ca data for EC chondrules will be useful to discuss the chondrule-Earth model (e.g., K. Zhu et al., 2020).

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data used in this study have been deposited at https://doi.org/10.5281/zenodo.7551580. All the supporting data can be found in the cited references (Amsellem et al., 2017; Bermingham et al., 2018; Chen et al., 2020; S. Huang & Jacobsen, 2017; Kang et al., 2017; Klaver et al., 2021; Magna et al., 2015; Moynier et al., 2022; Schiller et al., 2018; Soderman et al., 2022; Valdes et al., 2014; Wu et al., 2020).
Data and sources: chondrites (Amsellem et al., 2017; S. Huang & Jacobsen, 2017; Moynier et al., 2022; Schiller et al., 2018; Valdes et al., 2014), chondrules (Amsellem et al., 2017; Bermingham et al., 2018; Schiller et al., 2018), Shergottites (Magna et al., 2015), Lunar basalts (Klaver et al., 2021; Schiller et al., 2018; Valdes et al., 2014; Wu et al., 2020), N-MORBs (Chen et al., 2020; Soderman et al., 2022). All the data were transformed to $\delta^{44/40}$Ca values relative to NIST 915a.

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