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Planetary accretion and core formation inferred from Ni isotopes in enstatite meteorites

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Abstract

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Nickel is a siderophile and near-refractory element, making its isotopes a potential tool for tracing planetary accretion and differentiation. However, the origin of the Ni stable isotope difference between bulk silicate Earth (BSE) and chondrites remains enigmatic. To address this problem, we report high precision Ni stable isotope data of enstatite chondrites and achondrites that possess similar mass independent O and Ni isotope compositions like the Earth-Moon system. Bulk enstatite chondrites have $\delta^{60/58}$ Ni values of 0.24 ± 0.08 ‰ (2 s.d., n = 13). Enstatite achondrites, including main-group aubrites, Shallowater and Itqiy, show relatively large $\delta^{60/58}$ Ni variations, ranging from 0.03 ± 0.02 ‰ to 0.57 ± 0.04 ‰. This could reflect fractionations

between sulfide and metal phases, as is evidenced by correlation between their S/Ni ratios and $\delta^{60/58}$ Ni values. In enstatite achondrites, Ni is mainly hosted in metal and to a lesser extent in sulfides, so $\delta^{60/58}$ Ni values in enstatite achondrites may represent the Ni isotopic values of the cores of their parent bodies. The overlapping $\delta^{60/58}$ Ni values between bulk enstatite achondrites and enstatite chondrites indicate limited Ni stable isotope fractionation during core formation processes on reduced, sulfur-rich parent bodies. The Ni stable isotope gap between chondrites and the BSE could be possibly explained by chondrule-rich accretion model.

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Introduction

Core formation is one of the first planetary differentiation processes that can be reconstructed by using the stable isotope composition of siderophile elements. Nickel (Ni) is one such siderophile element; it is also a major element (>1 wt. %) in chondrites, nearly refractory (T_{c50} % of 1363 K), and occurs as Ni⁰ and Ni²⁺ in planetary materials (Wood *et al.*, 2019). These properties suggest that Ni stable isotopes probably were not, or only little, fractionated by volatilisation and silicate differentiation processes (Klaver *et al.*, 2020; Wang *et al.*, 2021; Zhu *et al.*, 2022). Core formations in the Earth and other differentiated planets/asteroids can be traced by comparing the bulk Ni stable isotope compositions (represented by chondritic Ni isotope compositions) and Ni isotope compositions in the silicate portion.

Previous studies have investigated the Ni stable isotope composition (expressed as $\delta^{60/58}$ Ni, the mass dependent deviation of 60 Ni/ 58 Ni ratios of samples relative to the ratio of NIST SRM 986, given in per mille) of chondrites with an average $\delta^{60/58}$ Ni value of 0.23 ± 0.14 ‰ (2 s.d.) and of the bulk silicate Earth (BSE) with an average $\delta^{60/58}$ Ni value of 0.10 ± 0.07 ‰ (2 s.d.) (Cameron *et al.*, 2009; Gall *et al.*, 2017; Klaver *et al.*, 2020; Wang *et al.*, 2021; Zhu *et al.*, 2022). Klaver *et al.* (2020) were the first to resolve a difference of Ni stable isotope compositions between the chondrites and BSE ($\Delta^{60/58}$ Ni_{Chondrites-BSE} ≈ 0.13 ‰), which is, however,

impossible to explain by single stage terrestrial core formation. Evidences include 1) Ni isotope similarity between chondrites and mantle of ureilite parent body (Zhu et al., 2022), 2) ab initio calculations (Guignard et al., 2020; Wang et al., 2021), and 3) high pressure experiments (Lazar et al., 2012; Guignard et al., 2020) which show that metal-silicate partitioning of Ni during core segregation at high temperatures and pressures would not induce measurable Ni stable isotope fractionation in Earth's mantle. Two scenarios were considered for this issue: 1) chondrites cannot represent bulk Earth while chondrules are potential precursor material of Earth (Zhu et al., 2022), and 2) Wang et al. (2021) proposed a different model in which the object (Theia) that hit the Earth during the Moon-forming impact was Mercury-like, i.e. highly reduced, and its mantle may have been rich in sulfide with isotopically light Ni. According to this hypothesis, the impactor mantle merged into the Proto-Earth's mantle and decreased the chondritic $\delta^{60/58}$ Ni value of the proto-Earth's mantle to the modern BSE value.

Enstatite achondrites, which include aubrites (most of them are brecciated; Table 1; Keil, 2010), come from the silicate portions of multiple differentiated asteroids that have similar isotope compositions as the Earth-Moon system (Clayton *et al.*, 1984; Zhu *et al.*, 2021). Depletion in highly siderophile elements (HSEs), supports the idea that their parent body (or bodies) have a core (van Acken *et al.*, 2012a). Therefore, comparing the Ni isotope signatures between enstatite achondrites and enstatite

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								N						
Meteorite	Fall/ Find	Type	Petrology	Mass (mg)	Mg#	S content (%)	Uncertainty	content (ppm)	S/Ni	8 ^{60/58} Ni (%)	2 s.d.	2 s.e.	и	References, notes
Enstatite chondrites														
GRO 95517	Find	EH3		7.8		4.0	0.2			0.28	0.03	0.02	0	
QingZhen	Fall	EH3		5.5		4.1	I			0.27	0.04	0.03	Ч	
SAH 97096	Find	EH3		33.2		4.4	0.5			0.26	0.06	0.04	2	
Kota-Kota	Find	EH3								0.20	0.03	0.01	8	Klaver et al. (2020)
Kota-Kota	Find	EH3								0.26	0.04			Wang et al. (2021)
Kota-Kota	Find	EH3								0.21	0.04			Wang et al. (2021)
Kota-Kota Avg.						3.6	0.1			0.22	0.06			
Indarch	Fall	EH4								0.29	0.05	0.04	0	
Indarch	Fall	EH4								0.27	0.09	0.03	6	Gall et al. (2017)
Indarch	Fall	EH4								0.19	0.03	0.01	8	Klaver et al. (2020)
Indarch Avg.						3.6	0.8			0.22	0.09			
Abee	Fall	EH4								0.19	0.05			Cameron <i>et al.</i> (2009)
Abee	Fall	EH4								0.25	0.02	0.01	IJ	Klaver et al. (2020)
Abee Avg.						4.5	0.9			0.22	0.09			
St. Mark's	Fall	EH5				3.3	0.9			0.18	0.02	0.01	15	Klaver et al. (2020)
MAC 88184	Find	EL3		4.6		2.2	0.1			0.21	0.08	0.05	5	
MAC 02837	Find	EL3		6.5		2.8	0.2			0.35	0.03	0.02	З	
Khairpur	Fall	EL6								0.29	0.08	0.03	6	Gall et al. (2017)
Khairpur	Fall	EL6								0.21	0.02	0.01	11	Klaver et al. (2020)
Khairpur Avg.						3.3	I			0.25	0.09			
Atlanta	Find	EL6				2.3	I			0.21	0.03	0.01	8	Klaver et al. (2020)
Hvittis	Fall	EL6				2.4	0.3			0.22	0.02	0.01	4	Klaver et al. (2020)
Yilmia	Find	EL6						i	-	0.21	0.02	0.01	8	Klaver et al. (2020)
Indarch acid leachates														
magnetic	Fall	EH4								0.27	0.03	0.02	0	
non-magnetic sulfides	Fall	EH4								0.25	0.07	0.04	ю	
non-magnetic sulfides	Fall	EH4								0.18	0.04	0.02	4	
non-magnetic silicates	Fall	EH4								0.27	0.05	0.04	0	
S content data are from Defouilloy <i>et al.</i> (2016). All the bulk enstatite chondrites show average δ^{6058} Ni values of 0.24 ± 0.08 % (2 s.d., $n = 13$), and the δ^{6058} Ni variation should not be caused by the S contents	oy et al. (20	16). All the t	oulk enstatite chondrites	show average 8	6 ^{0/58} Ni valu	es of 0.24 ± 0.08	‰₀ (2 s.d., <i>n</i> = 13), a	nd the $\delta^{60/58}$]	Vi variation	should not	be caused	by the S coi	ntents.	

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Table 1 Ni stable isotopic compositions of enstatite meteorites.

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Table 1	

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Meteorite	Fall/ Find	Type	Petrology	Mass (mg)	Mg#	S content (%)	Uncertainty	Ni content (ppm)	S/Ni	δ ^{60/58} Ni (%)	2 s.d.	2 s.e.	и	References, notes
Enstatite achondrites Norton County Bishopville Bustee Larmed Cumberland Falls ALH 84007 LAR 04316 Khor Temiki ALHA 78113 Peña Blanca Spring Aubres Pesyanoe Shallow Water Itqiy	Fall Fall Fall Fall Fall Fall Fall Fall	Aubrite Aubrite Aubrite Aubrite Aubrite Aubrite Aubrite Aubrite Aubrite Aubrite Aubrite EH7	Aubrite Fragmental breccia Aubrite Fragmental breccia Aubrite Regolith breccia Aubrite Fragmental breccia Aubrite Regolith breccia Aubrite Regolith breccia Aubrite Non-brecciated EH7 Non-brecciated	~5000 318 293 500 50.7 50.7 69.59 69.59 69.59 69.59 409 30.92 ~50	98.1 97.4 97.8 97.2 98.5 98.8 98.9 98.9 98.9 98.5 98.5 98.5	0.6 1.0 0.1 1.5 0.3 0.0	0.1 0.0 1.0 	127 50 253 240 539 241 635 40 11485 13010	86.7 36.7 108.8 22.8 4.5 0.0	0.57 0.34 0.14 0.13 0.05 0.05 0.05 0.05 0.12 0.18 0.18 0.18 0.18	0.06 0.06 0.06 0.03 0.03 0.03 0.03 0.03	0.04 0.04 0.04 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01	0 0 0 0 0 0 4 0 0 4 4 0 0 4	Mostly silicate
Standards BHVO-2 BHVO-2 BCR-1 NOD-P Allende	Fall	CV3								0.03 0.04 0.26 0.33 0.35	0.02 0.03 0.05 0.06 0.04	0.01 0.02 0.03 0.03 0.03	4 6 6 4 6	

⁸Ni variation should not be caused by the S contents. ⁸Ni values of 0.24 ± 0.08 ‰ (2 s.d., n = 13), and the δ^{60} S content data are from Defouilloy *et al.* (2016). All the bulk enstatite chondrites show average δ^{60}



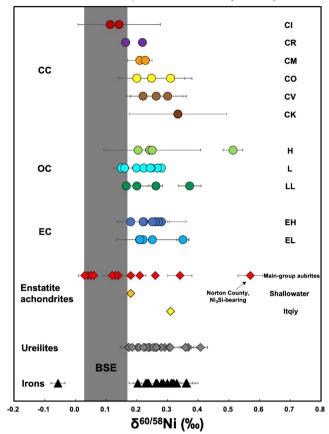


Figure 1 Ni stable isotope composition of solar system materials (Table S-1). Circles and triangles are chondrites and iron meteorites, respectively (Cameron *et al.*, 2009; Steele *et al.*, 2012; Gall *et al.*, 2017; Klaver *et al.*, 2020; Wang *et al.*, 2021), while diamonds are enstatite achondrites and ureilites (Zhu *et al.*, 2022). The uncertainty is mostly at 2 s.e. level, or 2 s.d. level when the 2 s.e. is not available in literature or there are averaged values of multiple data. The grey bar represents the Ni isotope composition of bulk silicate Earth (0.10 ± 0.07 ‰; Klaver *et al.*, 2020; Wang *et al.*, 2021). Enstatite achondrites (diamonds), representing their core composition for Ni, have $\delta^{60/58}$ Ni values (0.14 ± 0.18 ‰, 2 s.d.; excluding Norton County) overlapping with ECs, suggesting the core formation does not effectively fractionate Ni isotopes.

chondrites (i.e. the potential precursors of enstatite achondrites), is important to understand the Ni isotope fractionation during core formation and the Ni isotope gap between chondrites and BSE (Klaver et al., 2020; Wang et al., 2021; Zhu et al., 2022). Enstatite achondrites are highly reduced (IW-2 to IW-6) like Mercury and rich in sulfide (Mittlefehldt et al., 1998), so their Ni isotope compositions can also be used to constrain the role of metal-sulfide fractionation. On the other hand, the number of Ni isotope data of enstatite chondrites, are limited, and the Ni isotope variation in chondrites is poorly understood. Thus, we determined the Ni stable isotope compositions of both enstatite chondrites (ECs), including the leaching components, and enstatite achondrites for 1) surveying the Ni stable isotope reservoir of ECs, 2) understanding core formation in highly reduced differentiated asteroids, and 3) understanding the possible origin of the Ni stable isotope difference between the Earth and chondrites.

Results

The sample information, elemental and Ni stable isotope data are shown in Table 1. Additional sample information, leaching

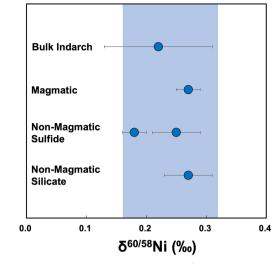


Figure 2 Ni stable isotope compositions of acid leaching phases of Indarch [EH4]. The light blue bar represents the average $\delta^{60/58}$ Ni value of bulk ECs. Sulfide phases show similar $\delta^{60/58}$ Ni values as bulk and other phases, suggesting the sulfide in chondrites does not cause any Ni isotope variation.

and analytical methods (using the double spike technique) are provided in detail in the Supplementary Information. Bulk enstatite chondrites show variable $\delta^{60/58}$ Ni values ranging from 0.18 ‰ to 0.35 ‰ with an average value of 0.24 ± 0.08 ‰ (2 s.d.) or ± 0.02 ‰ (2 s.e., n = 13; Table 1, Fig. 1; including data from the literature). The Ni isotopic variation is independent of the EH or EL grouping, meteorite fall or find and petrological (E3–E6) types. Bulk and leachates (including leachates of the magnetic sulfide-bearing fraction) of magnetically separated phase mixtures of Indarch (EH4) show similar Ni stable isotope compositions (Fig. 2), and no correlation has been found between S contents and $\delta^{60/58}$ Ni values for bulk enstatite chondrites (Fig. 3c).

In contrast, Ni stable isotope compositions of enstatite achondrites vary more, ranging from -0.03 ± 0.03 ‰ (Pesyanoe) to 0.57 ± 0.06 ‰ (Norton County). $\delta^{60/58}$ Ni values of enstatite achondrites do not correlate with Ni contents nor with Mg#, *i.e.* the molar Mg/(Mg + Fe) ratio (Fig. 3a,b), while their $\delta^{60/58}$ Ni values broadly correlate with the S contents and S/Ni ratio (excluding Norton County; Fig. 3c,d). The mean $\delta^{60/58}$ Ni values of enstatite achondrites (0.19 ± 0.28 ‰, 2 s.d., n = 14) overlap with ECs and BSE. Samples from the three enstatite achondrite parent bodies, *i.e.* main-group aubrites, Shallowater and Itqiy (Zhu *et al.*, 2021) have overlapping Ni isotope compositions.

Discussion

Ni stable isotope composition of enstatite chondrites. No systematic Ni stable isotope variation exists between meteorite falls and finds, suggesting that terrestrial weathering had no, or just a limited, effect on modifying the Ni stable isotope compositions. The $\delta^{60/58}$ Ni similarity of Indarch components suggests that Ni stable isotopes may not be fractionated to a measurable degree during nebular and parent body heating processes at this sampling scale, and nor also during the leaching processes (*e.g.*, intermediate leaching phases might adsorb Ni which could induce kinetic isotope fractionation processes). Also considering the lack of correlation between S contents and Ni isotopes for ECs (Fig. 3c), it is difficult to envision that sulfides in chondrites may cause the $\delta^{60/58}$ Ni variation in chondrites (Wang *et al.*, 2021;

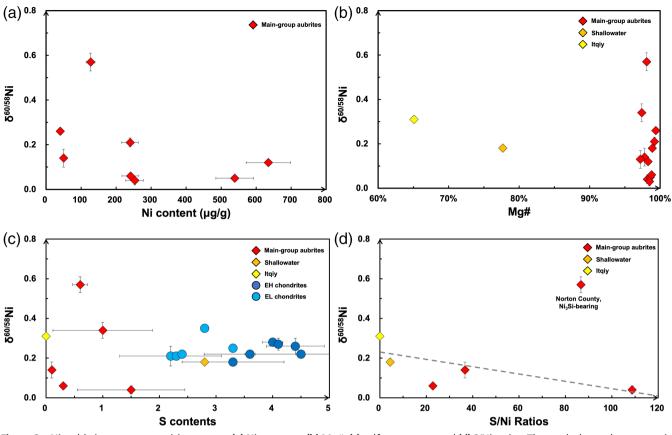


Figure 3 Ni stable isotope compositions versus (a) Ni contents, (b) Mg#, (c) sulfur contents and (d) S/Ni ratios. The symbols are the same as in Figure 1. EC Ni isotope data are from this study and literature (Cameron et al., 2009; Gall et al., 2017; Klaver et al., 2020; Wang et al., 2021), while S content data are from Defouilloy et al. (2016). Lack of correlation between Ni isotopes and Ni contents and Mg# (a, b) indicates Ni isotope variation in enstatite achondrites is not caused by silicate differentiation. We also do not find a co-variation between S contents and Ni isotopes in ECs (c), suggesting sulfide does not control the Ni isotope variation in chondrites. A broad correlation between S/Ni ratio and Ni isotopes for enstatite achondrites is consistent with a mixing between sulfide and metal (d).

Fig. 1). Considering that Ca-Al-rich inclusions (CAIs) are extremely rare in ECs and have rather low Ni contents, CAIs are unlikely to contribute to the Ni stable isotope variation in ECs. Some coarse grained CAIs have extremely heavy $\delta^{60/58}$ Ni compositions (Render et al., 2018); this implies that the limited $\hat{\delta}^{60/58}$ Ni variation among the ECs, and resolvable but small isotopic variation in other chondrites, could reflect heterogeneities and non-representative sampling of chondrules, matrix and refractory inclusions. Compared to the more equilibrated type 4–6 ECs (with $\delta^{60/58}$ Ni = 0.21 ± 0.04 ‰, 2 s.d., n = 6), the unequilibrated ECs of type 3 possess more variable (larger 2 s.d. uncertainties) $\delta^{60/58}$ Ni values (0.28 ± 0.12 ‰, 2 s.d., n = 6). This hints that parent body metamorphism equilibrates stable Ni isotopic compositions and thus yields more homogeneous bulk compositions. The average $\delta^{60/58}$ Ni composition of ECs is 0.24 ± 0.08 ‰ (2 s.d., n = 13), very similar to the mean of ordinary chondrites (OCs; $\delta^{60/58}$ Ni = 0.25 ± 0.18 ‰, 2 s.d., *n* =16) and carbonaceous chondrites (CCs; $\delta^{60/58}$ Ni = 0.23 ± 0.12 ‰, 2 s.d., n = 13). This implies a relatively homogeneous $\delta^{60/58}$ Ni of 0.24 ± 0.14 ‰ (2 s.d., n = 43) of diverse nebular reservoirs and this average composition can be used as a baseline for tracing planetary differentiation, despite the potential for small Ni isotope differences on the typical sampling scale.

Mineralogical control on $\delta^{60/58}$ Ni variations in enstatite achondrites. Enstatite achondrites show variable $\delta^{60/58}$ Ni values ranging from $-0.03 \pm 0.03 \%$ to $0.57 \pm 0.06 \%$; note, Norton County shows the heaviest $\delta^{60/58}$ Ni value among all the enstatite achondrites, which could be caused by the presence of the Ni-rich mineral carletonmooreite (Ni₃Si) (Garvie et al., 2021). The impact of this phase on the Ni isotope composition of bulk Norton County is unknown, however. Lack of correlation between Ni contents and Mg# (Fig. 3b) suggests this variation is not controlled by a simple differentiation and partitioning process involving silicates. This is also consistent in that the enstatite contains little Ni, typically less than the detection limit of electron microprobe analyses (Watters and Prinz, 1979). The Ni budget in enstatite achondrites is dominated by Fe-Ni metal and sulfide (e.g., troilite) with Ni contents of 4-80 wt. % and 0.03-0.9 wt. %, respectively (Casanova et al., 1993; van Acken *et al.*, 2012b). Hence, the $\delta^{60/58}$ Ni variation in aubrites may be caused by heterogeneities in the fractions of these minerals, since Ni should have different valance states in metal (Ni⁰) and sulfide, phosphides, and other non-metal phases (Ni²⁺). It is known that magmatic sulfides in terrestrial komatiites can possess isotopically light $\delta^{60/58}$ Ni values down to approximately -1 ‰ (Hiebert et al., 2022), however, these rocks formed at very different fO2 compared to the highly reduced enstatite achondrites. The $\delta^{60/58}$ Ni variations in ureilites may also be controlled by isotopically light sulfide, relative to metal (Zhu et al., 2022). In the present data set on enstatite achondrites, a relationship between sulfides and the variation in $\delta^{60/58}$ Ni is supported by the correlation between Ni/S ratios and $\delta^{60/58}$ Ni (except for Norton County; Fig. 3d). $\delta^{60/58}$ Ni variations in enstatite achondrites are both isotopically lighter and heavier compared to chondrites. From these observations we conclude that the variable $\delta^{60/58}$ Ni values for the main-group aubrites reflects the mixing of sulfides (light) and metal (heavy) in these

rocks, and the metal-sulfide fractionation factor can also be roughly estimated as $\Delta^{60/58} \text{Ni}_{metal-sulfide}$ \thickapprox 0.3 ‰ by the $\delta^{60/58} \text{Ni}$ variation amongst enstatite aubrites. This is in accord with the variable $\delta^{60/58} Ni$ values of ureilites and interpretation of metalsulfide mixing (Zhu et al., 2022). It is also comparable to the $\delta^{60/58}$ Ni variation in iron meteorites (Fig. 3d, Table S-1), which potentially reflect asteroidal core crystallisation (e.g., Ni et al., 2020). Magmatic sulfides in enstatite achondrites have a different petrogenesis compared to sulfides in chondrites which do not show light $\delta^{60/58}$ Ni values. The sulfide minerals in enstatite achondrites are diverse; besides troilite, other Ni-rich minerals may contribute to their bulk Ni isotope compositions, e.g., schreibersite [(Fe,Ni)₃P], djerfisherite [(K,Na)₆(Cu,Fe,Ni)₂₅S₂₆Cl], lawrencite [(Fe,Ni)Cl₂] (Weisberg and Kimura, 2012). In the next section we discuss the origin of the assemblage of Ni-bearing phases in enstatite achondrites and their significance for the difference of $\delta^{60/58}$ Ni between chondrites and the bulk silicate Earth.

 $\delta^{60/58}$ Ni compositions of enstatite achondrites and core formation of their parent bodies. Since Ni is very abundant in Fe-Ni metal, the measured $\delta^{60/58}$ Ni values of the aubrites (except the acid leaching residue of Larned) should dominantly reflect the composition of the metal in the aubrites. Lack of appreciable fractionation in the trace element signature of the metal suggests that the latter may have been trapped during incomplete metalsilicate segregation in their parent body (Casanova et al., 1993). Van Acken et al. (2012b) proposed that the aubrite parent body (ies) experienced a complicated history, including break up and re-accretion by impact, which may have involved trapping of minor metal and sulfide from the cores of their parent bodies. Assuming the metal and sulfide in aubrites represent re-accreted core material, the Ni stable isotope composition of aubrites could be representative of the bulk isotopic composition of the core of the main-group aubrite parent body, *i.e.* $\delta^{60/58}$ Ni = 0.14 ± 0.19 ‰ (2 s.d., n = 11; except for Norton County). This large $\delta^{60/58}$ Ni variation of main -group aubrites and large uncertainty of the esti-mated core $\delta^{60/58}$ Ni composition may reflect heterogeneous sulfide distribution in the core. On the other hand, the acid leaching residue of Larned mostly represents the composition of the silicate portion, and thus the mantle after core formation, of the main-group aubrite parent body. The $\delta^{60/58}$ Ni value of the silicate portion of Larned, 0.13 ± 0.04 ‰ (2 s.e.), could suggest that both the core and mantle of the aubrite parent body have $\delta^{60/58}$ Ni values overlapping those of ECs (0.24 ± 0.08 ‰) and the average of all the chondrites $(0.24 \pm 0.14 \text{ }\%)$. This suggests limited Ni isotope fraction during the segregation of sulfur-rich cores of the main-group aubrite parent body, i.e. S can be present as an FeS phase in the core (e.g., Wood et al., 2014). Shallowater and Itqiy contain more metal and show higher Ni contents relative to main-group aubrites (Keil et al., 1989; Patzer et al., 2001), so their bulk $\hat{\delta}^{60/58}$ Ni values may also reflect the isotopic composition of the core of their parent bodies. The $\delta^{60/58}$ Ni values, $0.18 \pm$ 0.02 % for Shallowater and 0.31 ± 0.01 % for Itqiy, fall into the average of chondrites too, which is consistent with the conclusion that metal-sulfide segregation processes at highly reduced conditions possibly do not effectively fractionate Ni isotopes. This interpretation of the aubrite data is also supported by the overlapping Ni stable isotope compositions of rocks derived from the mantle of the ureilite parent body and chondrites (Zhu et al., 2022). The mantle of the ureilite parent body also underwent segregation of sulfide melt into its core (Warren et al., 2006). However, this interpretation should be further tested, since 1) metal-sulfidesilicate segregation in aubrite parent bodies may have been incomplete (Casanova *et al.*, 1993), and 2) the $\delta^{60/58}$ Ni variation range for the aubrites is relatively large.

Earth might be built from chondrules, not bulk chondrites. Since core formation cannot be caused by a Ni isotopic gap between chondrites and Earth (Klaver *et al.*, 2020), other possible scenarios include 1) pebble accretion (Zhu *et al.*, 2022), 2) a highly reduced Moon-forming impactor (Wang *et al.*, 2021), and 3) nebular fractionation (Morbidelli *et al.*, 2020). Bulk chondrites are not the only candidates for the precursor material for Earth; instead, chondrules can be the main accretion material for Earth and other terrestrial planets (Johansen *et al.*, 2015), which could be tested by measuring Ni isotope compositions of chondrules, especially chondrules from ECs with Earth-like isotopic signatures (Zhu *et al.*, 2020).

Wang *et al.* (2021) proposed a different model in which the object (Theia) that hit the Earth during the Moon-forming impact was like Mercury, *i.e.* highly reduced, with its mantle rich in sulfur and isotopically light Ni. The Ni isotope data of enstatite achondrites cannot be used to directly test this model because enstatite achondrites are mainly composed of sulfide minerals (Keil, 2010), rather than S^{2–} in silicates (*e.g.*, in the Mercury mantle). This model could be more readily tested by measuring Ni stable isotope compositions of lunar samples and experimental samples of sulfur-rich metal-silicate segregation. Alternatively, this Ni stable isotope fractionation could have occurred during condensation and evaporation at the nebular stage, predating the accretion of the terrestrial planets (Morbidelli *et al.*, 2020).

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Editor: Helen Williams

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2306.



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References

- CAMERON, V., VANCE, D., ARCHER, C., HOUSE, C.H. (2009) A biomarker based on the stable isotopes of nickel. *Proceedings of the National Academy of Sciences* 106, 10944–10948. https://doi.org/10.1073/pnas.0900726106
- CASANOVA, I., KEIL, K., NEWSOM, H.E. (1993) Composition of metal in aubrites: Constraints on core formation. *Geochimica et Cosmochimica Acta* 57, 675– 682. https://doi.org/10.1016/0016-7037(93)90377-9
- CLAYTON, R.N., MAYEDA, T.K., RUBIN, A.E. (1984) Oxygen isotopic compositions of enstatite chondrites and aubrites. *Journal of Geophysical Research: Solid Earth* 89, C245–C249. https://doi.org/10.1029/JB089iS01p0C245

- DEFOUILLOY, C., CARTIGNY, P., ASSAYAG, N., MOYNIER, F., BARRAT, J.-A. (2016) Highprecision sulfur isotope composition of enstatite meteorites and implications of the formation and evolution of their parent bodies. *Geochimica et Cosmochimica Acta* 172, 393–409. https://doi.org/10.1016/j.gca.2015.10. 009
- GALL, L., WILLIAMS, H.M., HALLIDAY, A.N., KERR, A.C. (2017) Nickel isotopic composition of the mantle. *Geochimica et Cosmochimica Acta* 199, 196–209. https://doi.org/10.1016/j.gca.2016.11.016
- GARVIE, L.A.J., MA, C., RAY, S., DOMANIK, K., WIITMANN, A., WADHWA, M. (2021) Carletonmooreite, Ni₃Si, a new silicide from the Norton County aubrite meteorite. *American Mineralogist* 106, 1828–1834. https://doi.org/10. 2138/am-2021-7645
- GUIGNARD, J., QUITTÉ, G., MÉHEUT, M., TOPLIS, M.J., POITRASSON, F., CONNETABLE, D., ROSKOSZ, M. (2020) Nickel isotope fractionation during metal-silicate differentiation of planetesimals: Experimental petrology and *ab initio* calculations. *Geochimica et Cosmochimica Acta* 269, 238–256. https://doi.org/10. 1016/j.gca.2019.10.028
- HIEBERT, R.S., BEKKER, A., HOULÉ, M.G., ROUXEL, O.J. (2022) Nickel isotope fractionation in komatiites and associated sulfides in the hart deposit, Late Archean Abitibi Greenstone Belt, Canada. *Chemical Geology* 603, 120912. https://doi. org/10.1016/j.chemgeo.2022.120912
- JOHANSEN, A., LOW, M.-M.M., LACERDA, P., BIZZARRO, M. (2015) Growth of asteroids, planetary embryos, and Kuiper belt objects by chondrule accretion. *Science Advances* 1, e1500109. https://doi.org/10.1126/sciadv.1500109
- KEIL, K. (2010) Enstatite achondrite meteorites (aubrites) and the histories of their asteroidal parent bodies. *Geochemistry* 70, 295–317. https://doi.org/10. 1016/j.chemer.2010.02.002
- KEIL, K., NTAFLOS, T., TAYLOR, G.J., BREARLEY, A.J., NEWSOM, H.E., ROMIG JR., A.D. (1989) The Shallowater aubrite: Evidence for origin by planetesimal impacts. *Geochimica et Cosmochimica Acta* 53, 3291–3307. https://doi.org/ 10.1016/0016-7037(89)90108-7
- KLAVER, M., IONOV, D.A., TAKAZAWA, E., ELLIOTT, T. (2020) The non-chondritic Ni isotope composition of Earth's mantle. *Geochimica et Cosmochimica Acta* 268, 405–421. https://doi.org/10.1016/j.gca.2019.10.017
- LAZAR, C., YOUNG, E.D., MANNING, C.E. (2012) Experimental determination of equilibrium nickel isotope fractionation between metal and silicate from 500 °C to 950 °C. *Geochimica et Cosmochimica Acta* 86, 276–295. https://doi.org/10. 1016/j.gca.2012.02.024
- MITTLEFEHLDT, D.W., MCCOY, T.J., GOODRICH, C.A., KRACHER, A. (1998) Nonchondritic meteorites from asteroidal bodies. In: PAPIKE, J.J. (Ed.) Reviews in Mineralogy 36: Planetary Materials. De Gruyter, Berlin, 1–195. https:// doi.org/10.1515/9781501508806-019
- MORBIDELLI, A., LIBOUREL, G., PALME, H., JACOBSON, S.A., RUBIE, D.C. (2020) Subsolar Al/Si and Mg/Si ratios of non-carbonaceous chondrites reveal planetesimal formation during early condensation in the protoplanetary disk. *Earth and Planetary Science Letters* 538, 116220. https://doi.org/10.1016/j.epsl.2020. 116220
- NI, P., CHABOT, N.L., RYAN, C.J., SHAHAR, A. (2020) Heavy iron isotope composition of iron meteorites explained by core crystallization. *Nature Geoscience* 13, 611–615. https://doi.org/10.1038/s41561-020-0617-y
- PATZER, A., HILL, D.H., BOYNTON, W.V. (2001) Itqiy: A metal-rich enstatite meteorite with achondritic texture. *Meteoritics and Planetary Science* 36, 1495–1505. https://doi.org/10.1111/j.1945-5100.2001.tb01841.x
- RENDER, J., BRENNECKA, G.A., WANG, S.-J., WASYLENKI, L.E., KLEINE, T. (2018) A Distinct Nucleosynthetic Heritage for Early Solar System Solids Recorded by Ni Isotope Signatures. *The Astrophysical Journal* 862, 26. https://doi.org/10.3847/1538-4357/aacb7e
- STEELE, R.C.J., COATH, C.D., REGELOUS, M., RUSSELL, S., ELLIOTT, T. (2012) Neutronpoor nickel isotope anomalies in meteorites. *The Astrophysical Journal* 758, 59. https://doi.org/10.1088/0004-637X/758/1/59
- VAN ACKEN, D., BRANDON, A.D., LAPEN, T.J. (2012a) Highly siderophile element and osmium isotope evidence for postcore formation magmatic and impact processes on the aubrite parent body. *Meteoritics and Planetary Science* 47, 1606–1623. https://doi.org/10.1111/j.1945-5100.2012.01425.x
- VAN ACKEN, D., HUMAYUN, M., BRANDON, A.D., PESLIER, A.H. (2012b) Siderophile trace elements in metals and sulfides in enstatite achondrites record planetary differentiation in an enstatite chondritic parent body. *Geochimica et Cosmochimica Acta* 83, 272–291. https://doi.org/10.1016/j.gca.2011.12.025
- WANG, S.-J., WANG, W., ZHU, J.-M., WU, Z., LIU, J., HAN, G., TENG, F.-Z., HUANG, S., WU, H., WANG, Y., WU, G., LI, W. (2021) Nickel isotopic evidence for latestage accretion of Mercury-like differentiated planetary embryos. *Nature Communications* 12, 294. https://doi.org/10.1038/s41467-020-20525-1
- WARREN, P.H., ULFF-MØLLER, F., HUBER, H., KALLEMEYN, G.W. (2006) Siderophile geochemistry of ureilites: A record of early stages of planetesimal core

formation. Geochimica et Cosmochimica Acta 70, 2104–2126. https://doi.org/10.1016/j.gca.2005.12.026

- WATTERS, T.R., PRINZ, M. (1979) Aubrites: Their origin and relationship to enstatite chondrites. Proceedings of the 10th Lunar and Planetary Science Conference, 19–23 March 1979, Houston, Texas, 1073–1093. https://articles.adsabs. harvard.edu/pdf/1979LPSC...10.1073W
- WEISBERG, M.K., KIMURA, M. (2012) The unequilibrated enstatite chondrites. Geochemistry 72, 101–115. https://doi.org/10.1016/j.chemer.2012.04.003
- WOOD, B.J., KISEEVA, E.S., MIROLO, F.J. (2014) Accretion and core formation: The effects of sulfur on metal-silicate partition coefficients. *Geochimica et Cosmochimica Acta* 145, 248–267. https://doi.org/10.1016/j.gca.2014.09.002
- WOOD, B.J., SMYTHE, D.J., HARRISON, T. (2019) The condensation temperatures of the elements: A reappraisal. *American Mineralogist* 104, 844–856. https://doi. org/10.2138/am-2019-6852CCBY
- ZHU, K., MOYNIER, F., SCHILLER, M., BIZZARRO, M. (2020) Dating and Tracing the Origin of Enstatite Chondrite Chondrules with Cr Isotopes. *The Astrophysical Journal Letters* 894, L26. https://doi.org/10.3847/2041-8213/ ab8dca
- ZHU, K., MOYNIER, F., SCHILLER, M., BECKER, H., BARRAT, J.A., BIZZARRO, M. (2021) Tracing the origin and core formation of the enstatite achondrite parent bodies using Cr isotopes. *Geochimica et Cosmochimica Acta* 308, 256–272. https://doi.org/10.1016/j.gca.2021.05.053
- ZHU, K., BARRAT, J.-A., YAMAGUCHI, A., ROUXEL, O., GERMAIN, Y., LANGLADE, J., MOYNIER, F. (2022) Nickel and Chromium Stable Isotopic Composition of Ureilites: Implications for the Earth's Core Formation and Differentiation of the Ureilite Parent Body. *Geophysical Research Letters* 49, e2021GL095557. https://doi.org/10.1029/2021GL095557