Nickel isotopic evidence for late-stage accretion of Mercury-like differentiated planetary embryos

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Earth’s habitability is closely tied to its late-stage accretion, during which impactors delivered the majority of life-essential volatiles. However, the nature of these final building blocks remains poorly constrained. Nickel (Ni) can be a useful tracer in characterizing this accretion as most Ni in the bulk silicate Earth (BSE) comes from the late-stage impactors. Here, we apply Ni stable isotope analysis to a large number of meteorites and terrestrial rocks, and find that the BSE has a lighter Ni isotopic composition compared to chondrites. Using first-principles calculations based on density functional theory, we show that core-mantle differentiation cannot produce the observed light Ni isotopic composition of the BSE. Rather, the sub-chondritic Ni isotopic signature was established during Earth’s late-stage accretion, probably through the Moon-forming giant impact. We propose that a highly reduced sulfide-rich, Mercury-like body, whose mantle is characterized by light Ni isotopic composition, collided with and merged into the proto-Earth during the Moon-forming giant impact, producing the sub-chondritic Ni isotopic signature of the BSE, while delivering sulfur and probably other volatiles to the Earth.

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The Earth experienced a protracted accretion history over several tens up to 100 million years, which proceeded by the collision of numerous planetesimals and planetary embryos. A fundamental assumption was that the Earth’s building blocks as a whole were compositionally similar to undifferentiated chondritic meteorites. Researchers have looked among different classes of chondrites for the closest representative of the accreting materials that formed Earth. However, emerging evidence points to a mismatch in many crucial elemental and isotopic ratios between chondritic meteorites and the accessible Earth, arguing for the possible accretion of additional materials that are chemically and isotopically different from extant meteorite collections. Constraining the nature of these building blocks of Earth is important, because they not only provide fundamental information on terrestrial planet formation, but also help understand how the Earth evolved into its current habitable status.

The late accretion stages, including the Moon-forming giant impact and the late veneer event, likely account for only <10% of Earth’s total mass, but they represent a critical step for Earth to build its life-essential volatile budgets. Dynamical models of Earth’s growth suggest that the late accretion stages were highly heterogeneous, consisting of a mixture of materials from two genetically distinct reservoirs in the Solar nebula. One end-member may originate from the inner Solar system and contain a reduced, non-carbonaceous component that is probably ‘missing’ in known meteorites. The other may be oxidized, carbonaceous chondrite-like material from the outer Solar system. When these materials were added to Earth is still debated. The carbonaceous chondrite-like materials are commonly thought to be the source of major volatiles in Earth. Recent high pressure-temperature experiments on metal alloy-silicate partitioning of volatiles (e.g., carbon, sulfur, and nitrogen), however, suggest that Earth’s volatile abundance patterns could have been largely established by impact of a sulfur-rich, differentiated planetary body with minimal contributions from carbonaceous chondrite-like materials. Due to the lack of proper meteorite proxies, the nature of late-stage impactors remains poorly known.

Nickel isotopic compositions of meteorites and terrestrial rocks may hold important clues. Nickel in the bulk silicate Earth (BSE) was mostly derived from late-stage impactors, as that from earlier stages was largely segregated into the core due to its moderately siderophile nature. Models predict that ~95% of Ni in the BSE was derived from the last ~35% of mass that accreted to Earth. Nickel is non-volatile and partitions compatibly into the mantle dominant phase – olivine – following accretion, so that the BSE can potentially capture the Ni isotopic signature of late-stage accreting materials.

Nickel isotopic variations in meteorites have been well documented as shown in Fig. 1. Mass-independent nucleosynthetic Ni isotope anomalies arise from the heterogeneous distribution of presolar matters in the Solar protoplanetary disk, and thus trace the provenance of Earth’s building blocks. The nucleosynthetic anomalies are present in carbonaceous and ordinary chondrites, with enstatite chondrites largely within error of the BSE. Iron meteorites display similar anomalies, together with different groups of chondrites, forming a dichotomy between carbonaceous and non-carbonaceous meteorites as found in many other isotope systems (e.g., Mo, Cr, Ru, Ti). Mass-dependent isotopic variations stem from physico-chemical processes in the Solar nebula and on the planetary parent bodies. Nickel isotopic compositions of enstatite, ordinary, and most carbonaceous chondrites exhibit a common value, expressed as \( \delta^{60/58}\text{Ni} \) (the \( 60\text{Ni}/58\text{Ni} \) ratio in parts per thousand, relative to the SRM986 standard; \( \delta^{60/58}\text{Ni} = \left( \frac{60\text{Ni}_{\text{sample}}}{60\text{Ni}_{\text{SRM986}}} - 1 \right) \times 10^6 \)) and \( \delta^{62/58}\text{Ni} \) (\( 62\text{Ni}/58\text{Ni} \) ratio in parts per thousand, relative to the SRM986 standard; \( \delta^{62/58}\text{Ni} = \left( \frac{62\text{Ni}_{\text{sample}}}{62\text{Ni}_{\text{SRM986}}} - 1 \right) \times 1000 \)), with an average of \( +0.23 \pm 0.11\% \) (2 SD, \( n = 34 \)).

Fig. 1 A summary of mass-independent and mass-dependent Ni isotopic variations in meteorites. The \( \epsilon^{62/58}\text{Ni} = \left( \frac{62\text{Ni}_{\text{sample}}}{62\text{Ni}_{\text{SRM986}}} / \frac{60\text{Ni}_{\text{sample}}}{60\text{Ni}_{\text{SRM986}}} - 1 \right) \times 10^6 \) after internal normalization to \( 60\text{Ni}/58\text{Ni} \), are from literature. The carbonaceous chondrites (CC), enstatite chondrites (EC), and ordinary chondrites (OC) have average \( \delta^{60}\text{Ni} \) values of \( 0.23 \pm 0.14\% \) (2 SD), \( 0.22 \pm 0.02\% \) (2 SD) and \( 0.24 \pm 0.02\% \) (2 SD), respectively. A roughly negative correlation between \( \delta^{60}\text{Ni} \) and sulfur abundance is observed in carbonaceous chondrites (upper panel), which may be caused by the presence of various abundances of sulfides with \( \delta^{60}\text{Ni} \) values as low as \( -1\% \). The gray areas represent the dichotomy between carbonaceous and non-carbonaceous meteorites. The sulfur abundances are from ref. 71. Meteorite data from this study and literature are presented in Supplementary Table 2. Error bars represent 2 SD.

The Ni isotopic composition of present BSE is poorly constrained. An earlier report of a few ultramafic rocks yielded \( \delta^{60/58}\text{Ni} \) values indistinguishable from the chondritic average, and they concluded that the BSE has a chondritic Ni isotopic composition. This conclusion is questioned in a recent study combining new and reported peridotite samples, which suggested that the BSE has a \( \delta^{60}\text{Ni} \) lower than the chondrite average, a difference that was attributed to Earth’s core formation and mantle differentiation.

Here, we show that the BSE has a sub-chondritic Ni isotopic composition by applying Ni isotope analysis to meteorites and terrestrial rocks. Our first-principles calculations further suggest that the light Ni isotopic signature of the BSE is not a result of...
Results and discussion

Non-chondritic Ni isotopic composition of the bulk silicate Earth

Our new high-precision, inter-laboratory analyses on 60 terrestrial silicate rocks demonstrate that the present BSE is unambiguously sub-chondritic. Fertile peridotites, whose major element compositions are closest to the Primitive Mantle (e.g., Mg<sup>2+</sup> = 89.6 ± 1.0; Al<sub>2</sub>O<sub>3</sub> = 3.52 ± 0.60 wt.%)<sup>44</sup>, have δ<sup>60/58</sup>Ni values clustering tightly around +0.10 ± 0.07‰ (2 SD; n = 13, Fig. 2 and Supplementary Fig. 2). Peridotites overprinted by mantle metasomatism have Ni isotopic compositions shifted towards either heavier or lighter, but only to a limited degree (Supplementary Note 1). The melting products of mantle have similar or lighter Ni isotopic compositions compared to peridotites (Fig. 2). Komatiites formed by high-degree mantle melting (>45%) record an isotopic signature similar to fertile peridotites (+0.13 ± 0.09‰, 2 SD; n = 15; Fig. 2). Oceanic basalts (OIBs and MORBs), which are produced by relatively low-degree melting (<25%), have Ni isotopic compositions slightly lighter than peridotites (Fig. 2; Student’s t-test; p < 0.001), with an average δ<sup>60/58</sup>Ni value of 0.03 ± 0.16‰ (2 SD, n = 15). Eclogites, formed from metamorphism of basalts, display a similar average δ<sup>60/58</sup>Ni value of 0.02 ± 0.06‰ (2 SD, n = 7; Fig. 2). Whether the difference between oceanic basalts and peridotites implies possible Ni isotope fractionation during partial melting or results from the limited dataset of oceanic basalts deserves further investigations. Nevertheless, the present BSE, as best represented by fertile peridotites reported in this study and literature<sup>46</sup>, has δ<sup>60/58</sup>Ni of +0.11 ± 0.06‰, lower than the chondritic average, +0.23 ± 0.11‰ (Student’s t-test, p = 0.001; Supplementary Note 1).

First-principles calculations on Ni isotope fractionation during core formation

The sub-chondritic Ni isotopic composition of the BSE could have resulted from two possible processes: isotope fractionation associated with Earth’s differentiation, or the accretion of non-chondritic materials.

The former hypothesis is examined using first-principles calculations on Ni isotope fractionation factors (10<sup>3</sup>ln α<sub>Ni</sub> of δ<sup>60/58</sup>Ni) among Earth’s major Ni-bearing phases: olivine, wadsleyite, ringwoodite, bridgmanite, and Fe–Ni alloy. Limited differences in 10<sup>3</sup>lnα are found between olivine and wadsleyite/ringwoodite in the mantle transition zone and bridgmanite in the lower mantle (e.g., 10<sup>3</sup>lnα < 0.05% at 1500 K and <0.03% at 2000 K; Fig. 3a), which excludes the possibility of a hidden reservoir enriched in heavy Ni isotopes in the mantle. This lends credence to the use of accessible mantle and mantle-derived samples as representative of the present BSE Ni isotopic signature. Nickel isotope fractionation between Fe–Ni alloys and silicates (e.g., bridgmanite) under core-formation conditions is also negligible (P = 25–130 GPa; Fig. 3b and Supplementary Note 2). Notably, incorporation of sulfur into the Fe–Ni alloy slightly reduces the force constant of Ni, leading to the enrichment of light Ni isotopes in Fe–Ni alloys relative to the silicates (Fig. 3b).

To directly assess the equilibrium Ni isotope fractionation between silicate and metallic melts during core–mantle differentiation, we performed first-principles molecular dynamical simulations on melt phases of Fe<sub>92</sub>Ni<sub>5</sub>S<sub>3</sub> and Mg<sub>50</sub>NiSi<sub>32</sub>O<sub>96</sub> based on the density functional theory. The 10<sup>3</sup>lnα between Fe<sub>92</sub>Ni<sub>5</sub>S<sub>3</sub> and Mg<sub>50</sub>NiSi<sub>32</sub>O<sub>96</sub> melts is ~0.011‰ at ~38 GPa and 3500 K (Fig. 3b; Supplementary Note 2), further confirming the conclusion based on crystals that core–mantle differentiation does not significantly fractionate Ni isotopes.

Two experimental studies investigated equilibrium Ni isotope fractionation between metal and silicate mineral or melt at low pressures (<1.3 GPa) and temperatures (<1623 K)<sup>35,46</sup>. Both studies predict limited Ni isotope fractionation under core-formation temperatures (<0.01% in terms of δ<sup>60/58</sup>Ni at T > 3000 K), a result that is consistent with our first-principles calculations at higher pressures, implying negligible pressure effect on silicate–metal Ni isotope fractionation. If the bulk Earth (BE) has a chondritic Ni isotopic composition, mass balance calculations using high-pressure metal–silicate Ni elemental partition coefficients<sup>47</sup> and isotope fractionation factors obtained from our first-principles calculation demonstrate that core–mantle differentiation cannot explain the sub-chondritic Ni isotopic composition of the BSE (Fig. 3c).

Other possible events including evaporative loss, collision erosion, and core–mantle chemical diffusion can also be discounted as causes for the sub-chondritic Ni isotopic signature of BSE<sup>40</sup>. Evaporative loss of Ni is unlikely given the relatively refractory nature of Ni. In addition, kinetic isotope fractionation associated with evaporation would lead to a heavy BSE Ni isotopic composition, opposite to observations (Fig. 2). Collisional erosion during Earth’s formation preferentially removed early formed basaltic crust<sup>48</sup>. The terrestrial oceanic basalts have an average δ<sup>60/58</sup>Ni (0.03 ± 0.16‰; 2 SD) slightly lower than the BSE value, and thus collisional erosion cannot explain the
sub-chondritic Ni isotopic composition of BSE. The presence of a Ni chemical gradient between Earth’s core and mantle may induce diffusive isotope fractionation, due to the faster diffusivity of light isotopes relative to heavy ones. A one-dimensional diffusion model shows that core–mantle chemical diffusion produces ~0.1% variation in the silicate part but is restricted to the lowermost two kilometers of the mantle on a time scale of 10 million years (Supplementary Note 3).

The nature of late-stage accreting materials and its implications. Therefore, the Earth’s mantle must have accreted sub-chondritic materials during its growth. In the early stages, metal and silicate melts equilibrate completely in the magma ocean49, so that the proto-BSE likely has a low Ni concentration and a chondritic Ni isotopic composition. Because of the moderately siderophile nature of Ni23 and a possible disequilibrium scenario for the late-stage accretion49,50, the BSE’s sub-chondritic Ni isotopic signature was likely established in the late stages. The late veneer following the main growth stage added the last <0.5% of mass to Earth and contributed <5% of the Ni budget of the BSE18. Hence, it is unlikely to be the event that produced the sub-chondritic Ni isotopic composition of BSE. To account for the observed Ni isotopic value of the present BSE, the late-veneer material accreted to the BSE would have to have had extremely low $\delta^{60/58}$Ni of around ~2.5‰ (Supplementary Fig. 8), a value that has not been found in any natural rocks, and would be inconsistent with the Ni isotopic composition of an average carbonaceous chondrite-like material for the late veneer17,19,24,25.

The last significant stage of Earth’s accretion was the Moon-forming giant impact, contributing >20% of Ni budget of the BSE49. The Ni isotopic composition of the BSE could have been strongly influenced by the Moon-forming impactor18,23. Assuming a chondritic Ni isotopic composition for the proto-BSE as discussed above, mass balance calculation suggests that materials accreted to the proto-BSE have $\delta^{60/58}$Ni values as low as ~0.35‰ (Supplementary Fig. 8). Accordingly, the Moon-forming impactor is unlikely to have a composition represented by chondrites.

Instead, we hypothesize that the sub-chondritic Ni isotopic composition of the BSE resulted from the impact and accretion of the sulfide-rich mantle of a highly reduced, differentiated planetary body. It has long been recognized that accretion of planetary embryos that were already differentiated into cores and mantles contributed significantly to the growth of Earth51–53. The Moon-forming impactor has been suggested to be a sulfur-rich, differentiated planetary body15,16,27; but uncertainties remain as to whether it is a highly reduced, Mercury-like impactor23,24,27, or a relatively more oxidized body20,21,26. Mercury is the most reduced planet in the inner Solar system and has an abnormally high abundance of sulfides in its mantle34–36, whereas oxidized planetary embryos have sulfur segregated into their cores57. This is because sulfur is highly siderophile at high oxygen fugacity (FO2) and partitions into the metallic core, but becomes lithophile and enters into the silicate melt as sulfide species under low FO2 (e.g., five units below the iron-wüstite buffer; IW-5)58,59. Magmatic sulfides are the only major Ni-bearing phases that are isotopically much lighter than silicates ($\delta^{60/58}$Ni_sulfide down to ~1‰)41. Rocks with high sulfide/silicate ratios have light Ni isotopic compositions, which is most evident in magmatic Ni-sulfide deposits where the bulk $\delta^{60/58}$Ni values are negatively correlated with the sulfur content41,42. Therefore, when small planetary embryos (the proto-impactor) were formed in a sulfur-rich early Solar nebula and differentiated into core and mantle under highly reduced environment similar to the Mercury (mean IW-5.4)58, the mantle would be sulfur-rich and have a light Ni isotopic composition (Fig. 4). By contrast, in the large proto-Earth, core–mantle differentiation proceeded under much higher pressure and likely more oxidizing condition (>IW-3; Fig. 4)60, in which sulfur behaves as a siderophile element61,62, leading to a sulfur-poor mantle. In this case, limited silicate–metal Ni isotope fractionation is expected (see discussion above), and thus the proto-Earth mantle likely has a chondritic Ni isotopic

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**Fig. 3 Equilibrium fractionation factors from first-principles calculations and the modeled Ni isotope fractionation during core–mantle differentiation.**

a. Equilibrium fractionation factors (103 lnfi) between olivine, wadsleyite, ringwoodite, and bridgmanite. b. Equilibrium fractionation factors between Fe–Ni (S) alloy and bridgmanite, and between FeNiS melt (Fe92Ni5S3) and silicate melt (Mg30NiSi32O96). c. $\delta^{60/58}$Ni vs. distribution coefficient of Ni between metal and silicate ($D^{\text{Ni}_{\text{metal-silicate}}}$). If the bulk Earth (BE) has a chondritic Ni isotopic composition, the BSE $\delta^{60}$Ni after core formation can be evaluated using the Rayleigh fractionation equation:

$$\delta^{60}_{\text{Ni}} = \delta^{60}_{\text{Ni}}^{\text{BSE}} = \Delta \delta^{60/58}_{\text{Ni}}^{\text{metal-silicate}} \times \text{f}_{\text{BSE}}$$

where $\text{f}_{\text{BSE}}$ is the fraction of Ni in the BSE. $\delta^{60}_{\text{Ni}}$ can be calculated using the mass balance model:

$$\delta^{60}_{\text{Ni}}^{\text{BSE}} = \frac{M_{\text{metal}}}{M_{\text{metal}} + D \times M_{\text{core}}} \times \delta^{60/58}_{\text{Ni}}^{\text{sulfide}}$$

The masses of the mantle and the core are 0.675 and 0.325, respectively. Given that the $D^{\text{Ni}_{\text{metal-silicate}}}$ is likely <45,27, core segregation induced Ni isotope difference between metal and silicate cannot account for the light Ni isotopic composition of the BSE. of olivine, wadsleyite, rw ringwoodite, bdg bridgmanite, FeNi Fe-Ni alloy, FeNiS S bearing Fe-Ni alloy or melt.
The absence of pressure results in the formation of a planet-wide, more oxidizing magma ocean with high solubility of sulfur\(^{60}\). The impactor’s mantle likely had a sub-chondritic Ni isotopic composition due to the enrichment of sulfides. Differentiation on the large, proto-Earth partitioned sulfur dominantly into the core because sulfur is more siderophile at relatively high O\(_2\) and pressure\(^{58,59,61,62}\). The impactor’s mantle likely had a sub-chondritic Ni isotopic composition due to the enrichment of sulfides. The proposed late-stage accretion of the Earth from the matrices was achieved using a three-stage, cation exchange chromatography procedure using Bio-Rad 200–400 mesh Ag 50W-X8 resin. Briefly, the first column applies mixture of 20% 10 M HCl and 80% acetone to separate Ni from Fe, Mn, and Cr. The second column uses 15% 10 M HCl and 85% acetic acid to separate Ni from elements such as Mg, Al, Ca, and Ti, and the last column further purifies Ni using 0.9 M HNO\(_3\) to remove Na and K. The Ni isotopic ratios were measured using Nu Plasma II MC-ICPMS at Indiana University.

**Methods**

_Nickel isotope analyses._ We undertook an inter-laboratory comparison of geological reference materials using different analytical protocols in two labs: Indiana University (IU) and China University of Geosciences, Beijing (CUGB). Despite different double spike solutions and different column chemistry methods, the results of standards from two labs agree with each other within analytical uncertainty (Supplementary Table 1). A comparison of our data with published values is shown in Supplementary Fig. 1.

**First-principles calculations.** Ab initio calculations were performed using the software “Quantum Espresso”\(^{65}\), which is based on the density functional theory (DFT), plane wave, and pseudopotentials. The generalized gradient approximation (GGA) was adopted to describe the exchange-correlation functional. The pseudopotential for magnesium and nickel was generated using von Barth and Car’s methods\(^{66}\) with a cutoff radius of 2.5 Bohr. The electron configurations of Ni are 3s\(^2\)3p\(^0\), 3s\(^1\)3p\(^1\), 3s\(^0\)3p\(^2\), 3s\(^1\)3p\(^1\)3d\(^0\), 3s\(^0\)3p\(^2\)3d\(^1\) with decreasing weights of 1.5, 0.6, 0.3, 0.3, and 0.2, respectively. The pseudopotentials for nickel, silicon, and oxygen were generated in the method of Trouiller and Martins\(^{67}\). The cutoff radius is 1.47 Bohr with the electron configuration of 2s\(^2\)2p\(^4\) for oxygen and 1.47 Bohr with the electron configuration of 3s\(^3\)3p\(^3\)3d\(^0\) for silicon. The cutoff radius for nickel is 2.1 Bohr with the electron configuration of 3s\(^2\)3p\(^4\)3d\(^0\)\(^8\) for oxygen and 1.47 Bohr with the electron configuration of 3s\(^3\)3p\(^3\)3d\(^0\)\(^8\) for silicon. The cutoff radius for nickel is 2.1 Bohr with the electron configuration of 4s\(^2\)3d\(^8\)4p\(^4\)\(^8\)\(^8\) for oxygen and 1.47 Bohr with the electron configuration of 4s\(^2\)3d\(^8\)4p\(^4\)\(^8\) for nickel. The pseudopotential for Fe was generated using the Vanderbilt method\(^{68}\) with a valence configuration of 3s\(^3\)3p\(^3\)3d\(^4\)4p\(^5\)\(^8\) and a cutoff radius of 2.0 Bohr for Fe.

We first optimized all crystal structures of Ni-bearing minerals using the variable cell shape molecular dynamics method\(^{69}\) with different \(k\) points per cell depending on the sizes of unit cells (Supplementary Table 7). The energy cutoff for plane wave and charge density are set to 70 Ry and 700 Ry, respectively. The residual forces converge within 10\(^{-4}\) Ry/Bohr. After the relaxed structures were obtained, we then calculated vibrational frequencies using the finite displacement method as implemented in the open-source code PHONOPY\(^{99}\). Consequently, the reduced partition function ratios \(\beta = 600\text{Ni}/\text{Ni}^{2+}\) for all phases can be calculated from the equation:

\[
\beta_{\text{Ni}} = \frac{1}{\beta} = \frac{1}{\beta_{\text{Ni}^{2+}}} = \frac{1}{\beta_{\text{Ni}^{2+}}} = \frac{1}{\beta_{\text{Ni}^{2+}}} = \frac{1}{\beta_{\text{Ni}^{2+}}}
\]

In order to directly estimate the equilibrium Ni isotope fractionation between silicate and metallic melts, we conducted first-principles molecular dynamics (FPMD) simulations on Mg\(_x\)Ni\(_{1-x}\)Si\(_3\)O\(_8\) and Fe\(_x\)Ni\(_{1-x}\)Si\(_3\) melts based on the DFT using the Vienna ab initio simulation package (VASP). The GGA was adopted for the exchange-correlation functional and the projector-augmented-wave (PAW) pseudopotentials were used. The energy cutoff for the plane wave was 600 eV. The Brillouin zone summations over the electronic states were performed at gamma

**Fig. 4 Cartoon showing the merger of a highly reduced, Mercury-like planetary body with the relatively more oxidizing proto-Earth, and schematic evolution of Ni isotopic composition of the BSE.** The small, proto-impactor from the highly reduced innermost region of the Solar system differentiated into a core, a sulfur-rich mantle, and likely a sulfide layer at the mantle-core boundary, because sulfur behaves more lithophile at low O\(_2\) and pressure\(^{58,59,61,62}\). The impactor’s mantle likely had a sub-chondritic Ni isotopic composition due to the enrichment of sulfides. Therefore, the mantle of the proto-Earth had a Ni isotopic composition close to the chondritic value. The impactor’s mantle likely had a sub-chondritic Ni isotopic composition due to the enrichment of sulfides. The Moon-forming giant impact would have completely melted the Earth, forming a planet-wide, more oxidizing magma ocean, producing a planet-wide, more oxidizing terrestrial magma ocean, and produced the sub-chondritic Ni isotopic composition for the Earth’s mantle. The Mooneforming giant impact would have completely melted the Earth, forming a planet-wide, more oxidizing magma ocean, and produced the sub-chondritic Ni isotopic composition for the Earth’s mantle. The late veneer following the main growth stage added carbonaceous chondrite-like materials to the Earth with limited effects on the Ni isotopic systematics of the BSE as discussed in the text.

During the Moon-forming impact, the impactor’s core merged directly into the proto-Earth’s core due to its limited emulsification, while the remaining parts of the impactor were incorporated into the Earth’s mantle\(^{49,50}\). The Mercury-like impactor’s sulfur-rich mantle would have been completely dissolved in the planet-wide, more oxidizing terrestrial magma ocean\(^{63}\), and produced the sub-chondritic Ni isotopic signature of Earth’s mantle (Fig. 4).

Our findings imply that, instead of an outer Solar system origin\(^{20,21}\), the Moon-forming impactor may represent a ‘missing’ Earth’s building component originated from a highly reduced reservoir in the inner Solar system. This is in accordance with variations in nucleosynthetic Ni isotopic anomalies in enstatite chondrites that are consistent with an inner Solar system provenance for the Moon-forming impactor\(^{23}\), the sub-chondritic mass-dependent Ni isotopic composition of the BSE further points towards a sulfide-rich, Mercury-like impactor, likely from closer to the Sun. This is in accordance with variations in nucleosynthetic Ni isotopic anomalies of other elements in meteorites, suggesting that the Earth possesses the most \(s\)-process enriched materials from the inner Solar system\(^{11,22,24,64}\). A recent study found sulfur enriched runebium (Ru) isotopic signatures in Earth-like rocks, supporting the idea that the pre-late veneer Earth incorporated building materials from the innermost region of the Solar system, most likely through the Moon-forming giant impact\(^{24}\). The impactor might be sulfur-rich, such that the highly siderophile Ru was partially retained in the mantle without being completely extracted to the core. Later addition of a carbonaceous chondrite-like late veneer with sulfur-rich Ru deficits from the outer Solar system ultimately built up the modern mantle Ru isotopic composition\(^{34}\). The proposed late-stage accretion of the highly reduced, Mercury-like planetary body may not only explain the broad geochemical similarity between Earth and Moon\(^{27}\), but also account for the volatile abundance patterns in the BSE\(^{18}\). Our study highlights the importance of inner planets, e.g., Mercury and Venus, in searching for the Earth’s ‘missing’ building blocks that are not present in extant meteorite collections. Future studies on achondrites from the inner Solar system and samples from Venus and Mercury as well as experimental work will shed more light on these issues.
point. The FPMD simulations were performed in the NVT thermodynamic ensemble with a fixed temperature of 3000 K and the Nose thermostat was used. The time step was set to 1 fs, and the total running time is up to 60 ps. The initial liquid configurations were prepared by conducting simulations on the structures at 6000 K. The cell parameter of the cubic box is 11.15 Å for Mg$_30$Ni$_2$Si$_32$O$_{96}$ silicate melt and 10.05 Å for Fe$_{32}$Ni$_5$S$_{32}$ melt. The simulated statistical pressures of Mg$_30$Ni$_2$Si$_32$O$_{96}$ and Fe$_{32}$Ni$_5$S$_{32}$ are 37.6 GPa and 38.5 GPa at 3000 K (Supplementary Fig. 5), respectively. After equilibration, we extracted 66 snapshots from the FPMD trajectory every 200 steps and only optimized the atomic positions of Ni with fixed cubic boxes. This strategy makes the Ni atoms in each snapshot are at the local equilibrium positions. Then we estimated the force constant matrix of Ni atoms in all snapshots using the small displacement method based on the harmonic approximation. The force constants <F> of the Ni atom in Mg$_30$Ni$_2$Si$_32$O$_{96}$ and Fe$_{32}$Ni$_5$S$_{32}$ melts are the cumulative averages in the time domain. According to the high-temperature approximation of the Urey equation, it can be written as: 
\[
\beta = \frac{1}{T} - \frac{1}{T_0} + \frac{2}{\gamma} \cdot \frac{C}{\gamma - 1} \sqrt{\frac{C_0}{C}}
\]

where $m_l$ and $m_h$ are the masses of light and heavy isotopes, respectively. The equilibrium Ni isotope fractionation between Mg$_30$Ni$_2$Si$_32$O$_{96}$ and Fe$_{32}$Ni$_5$S$_{32}$ melts can be derived from the <F>-difference between these two melts. The resulting <F>-of Ni in Mg$_30$Ni$_2$Si$_32$O$_{96}$ and Fe$_{32}$Ni$_5$S$_{32}$ melts at ~38 GPa are $272.1 \pm 7.5$ and $214.4 \pm 2.8$ N/m (Supplementary Fig. 6), respectively. Therefore, the $10^5$ln <F> between Mg$_30$Ni$_2$Si$_32$O$_{96}$ and Fe$_{32}$Ni$_5$S$_{32}$ melts is 0.016 $\pm$ 0.003 % at 3000 K and 0.011 $\pm$ 0.002 % at 3500 K.

### Data availability
All data in this study are included in the supplementary information files and are available from the corresponding author.

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Author contributions
S.J.W. and W.Z.W. contributed equally to this work. S.J.W. conceived and designed the project, interpreted the data, and drafted the manuscript. W.Z.W. performed the theoretical simulations. J.M.Z and S.J.W performed the experimental data analyses. Z.Q.W., J.G.L., G.L.H., F.Z.T., S.C.H., H.J.W., Y.J.W., G.L.W., and W.H.L. participated in the discussion of the experimental results. All the authors contributed to the overall scientific interpretation and edited the manuscript.

Competing interests
The authors declare no competing interests.

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