

The isotopic nature of the Earth's accreting material through time

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The Earth formed by accretion of Moon- to Mars-size embryos coming from various heliocentric distances. The isotopic nature of these bodies is unknown. However, taking meteorites as a guide, most models assume that the Earth must have formed from a heterogeneous assortment of embryos with distinct isotopic compositions^{1–3}. High-precision measurements, however, show that the Earth, the Moon and enstatite meteorites have almost indistinguishable isotopic compositions^{4–10}. Models have been proposed that reconcile the Earth–Moon similarity with the inferred heterogeneous nature of Earth-forming material, but these models either require specific geometries for the Moon-forming impact^{11,12} or can explain only one aspect of the Earth–Moon similarity (that is, ¹⁷O)^{1–3}. Here I show that elements with distinct affinities for metal can be used to decipher the isotopic nature of the Earth's accreting material through time. I find that the mantle signatures of lithophile O, Ca, Ti and Nd, moderately siderophile Cr, Ni and Mo, and highly siderophile Ru record different stages of the Earth's accretion; yet all those elements point to material that was isotopically most similar to enstatite meteorites. This isotopic similarity indicates that the material accreted by the Earth always comprised a large fraction of enstatite-type impactors (about half were E-type in the first 60 per cent of the accretion and all of the impactors were E-type after that). Accordingly, the giant impactor that formed the Moon probably had an isotopic composition similar to that of the Earth, hence relaxing the constraints on models of lunar formation. Enstatite meteorites and the Earth were formed from the same isotopic reservoir but they diverged in their chemical evolution owing to subsequent fractionation by nebular and planetary processes¹³.

Except for elements affected by nuclear transmutations, the isotopic compositions of most elements in terrestrial specimens are related by the chemical law of mass-dependent fractionation. Measurements of meteorites originating from Mars, Vesta and other unspecified asteroids have revealed that extraterrestrial matter was characterized by the presence of isotopic anomalies (that is, departure from mass-dependent fractionation) arising from the heterogeneous distribution of presolar matter at the planetary scale, or unusual photochemical processes¹⁰. Those anomalies have proved extremely valuable in establishing genetic ties between planetary bodies and evaluating possible building blocks to the terrestrial planets.

The picture that is emerging from numerous studies over the past several years is that the terrestrial mantle is isotopically identical or very similar to a group of highly reduced meteorites known as enstatite meteorites that comprise EH and EL chondrites, and aubrites^{8–10} (Extended Data Fig. 1). It is still unclear whether this similarity means that the Earth accreted from a homogeneous isotopic reservoir very similar to enstatite meteorites, or whether it means that the Earth accreted from diverse embryos whose mixture coincidentally matched the composition of enstatite meteorites.

This is a difficult question to tackle observationally because melting and differentiation in the Earth have erased most records of its accretion. I show here that isotopic anomalies in $\Delta^{17}\text{O}$, $\epsilon^{48}\text{Ca}$, $\epsilon^{50}\text{Ti}$, $\epsilon^{54}\text{Cr}$,

$\epsilon^{64}\text{Ni}$, $\epsilon^{92}\text{Mo}$, $\epsilon^{100}\text{Ru}$, and $\mu^{142}\text{Nd}$ can provide insight into the nature of the Earth's accreting material through time. This follows from the consideration that all elements present in the Earth's mantle today were not all delivered at the same time, depending on their affinity with metal versus silicate during core formation. To illustrate this concept, I focus on two endmembers: lithophile and highly siderophile elements. On the one hand, lithophile elements that have little affinity for metal in natural settings, such as O, Ca, Ti and Nd, stayed in the mantle when they were delivered by impacts. Their isotopic compositions therefore reflect the average of all materials accreted by the Earth throughout its history. On the other hand, highly siderophile elements such as Ru were efficiently scavenged into the core as the Earth was growing. A large fraction of the mantle inventory of Ru was delivered in the last 0.5% of the Earth's accretion, after core formation had ceased^{14,15}. The isotopic compositions of O, Ca, Ti and Nd versus Ru therefore shed light on very different stages of the Earth's accretion, corresponding to the whole or only the last 0.5% of its mass growth history, respectively.

For moderately siderophile elements such as Cr, Ni and Mo, which display isotopic anomalies, the analysis is more involved because these elements were neither completely retained in the Earth's mantle nor completely partitioned into the Earth's core. Atoms delivered early in the mantle were partially scavenged into the core and replaced by atoms delivered by subsequent impacts, so moderately siderophile elements provide a record of the Earth's accretion that is biased towards late impacts. To quantify precisely what stage of the Earth's accretion is recorded by these elements, it is useful to introduce the concept of the probability density function (PDF) for the delivery of elements in the Earth's mantle. This PDF gives the proportion of atoms in the mantle that were delivered at different stages of the Earth's growth.

The PDF for the accretion of elements in the Earth's mantle can be calculated analytically if one considers that the metal–silicate distribution coefficient D did not change with time, the degree of equilibration of the impactor core with the proto-Earth mantle k_{ic} remained constant, the core mass fraction f remained constant, and the Earth's accretion proceeded by impacts of infinitely small impactors. As discussed below, these assumptions can be relaxed without greatly changing the results. Under these prescriptions, the PDF takes the form (see the 'Supplementary Equations' section of the Supplementary Information for details)

$$\text{PDF}(x) = (1 + \kappa)x^\kappa \quad (1)$$

where x is the fraction of the Earth's final mass and $\kappa = Dfk_{ic}/(1 - f)$. The corresponding cumulative distribution function (CDF) is:

$$\text{CDF}(x) = x^{\kappa+1} \quad (2)$$

I also calculate the mass fraction over which the last 95% of a given element at present in the mantle was delivered, which gives a measure of what stage of the Earth's accretion this element records:

$$x_{0.95} = 1 - 0.05^{\frac{1}{\kappa+1}} \quad (3)$$

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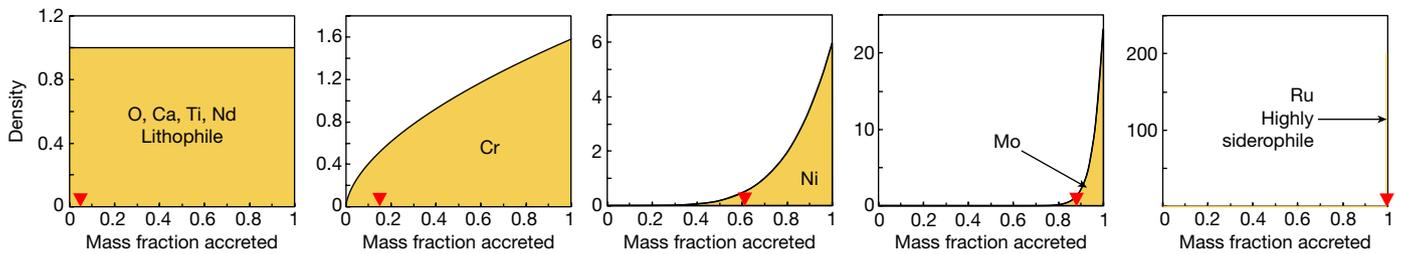


Figure 1 | Model PDFs of O, Ca, Ti, Nd (lithophile elements), Cr, Ni, Mo (moderately siderophile elements), and Ru (highly siderophile element) for the accretion of elements in the Earth's mantle. These curves give, for each element, the proportion of atoms that were delivered to the Earth's mantle at different stages of its accretion. For instance, the fraction of atoms at present in the Earth's mantle that were delivered when the Earth grew from fractions of x_1 to x_2 of its present mass is given by $\int_{x_1}^{x_2} \text{PDF}(u) du$.

The extent to which impactor cores were equilibrated with target mantles (k_{ic}) is estimated using the ^{182}Hf – ^{182}W decay system (lithophile ^{182}Hf decays into moderately siderophile ^{182}W with a half-life of 8.9 million years) to be between 0.3 and 0.8 (refs 16 and 17; a value of 0.4 is adopted here). For metal–silicate distribution coefficients, effective D values corresponding to bulk partitioning between the terrestrial mantle and core were adopted from ref. 18 (that is, 3 for Cr, 26 for Ni, and 120 for Mo). The corresponding PDFs and CDFs are plotted in Fig. 1 and Extended Data Fig. 2, respectively. As expected, for lithophile elements, $D = 0$ corresponds to a uniform PDF, meaning that O, Ca, Ti, and Nd record the full accretion history of the Earth ($x_{0.95} = 0.95$; indicating that 95% of lithophile elements in the modern mantle were delivered in the last 95% of the Earth's accretion). Chromium records the full accretion history, but this is biased towards later events ($x_{0.95} = 0.85$). Nickel records the last 39% or so of the Earth's accretion ($x_{0.95} = 0.39$). Molybdenum records the last 12% or so ($x_{0.95} = 0.12$).

The analytical model yields a simple formula (equation (1)) that shows the dependence of the PDF on impactor core equilibration, metal–silicate partition behaviour, and core mass fraction. To evaluate the robustness of the conclusions drawn from this simple model, I examine two previously published models that avoid some of the assumptions made in deriving equation (1) (for example, that D is constant)^{15,19}.

Badro *et al.*¹⁹ (see Supplementary Equations) consider accretion of small planetesimals that fully equilibrate with the target mantle upon impact. The mantle redox conditions remain near constant (Extended Data Fig. 3) or evolve from an oxidized state to the present values.

Rubie *et al.*¹⁵ (see Supplementary Equations) use the output of N -body simulations to calculate the mantle concentrations of siderophile elements. The impactors comprise large embryos and small planetesimals whose compositions and redox states depend on their distance to the Sun. In this model, metal–silicate equilibration between the impactor core and the Earth's mantle is incomplete.

Both models allow D values to vary as a function of pressure P , temperature T , composition and the redox condition. The PDFs predicted from these more realistic models (Extended Data Figs 4 and 5; see Supplementary Equations) are very similar to those calculated based on equation (1). The conclusion of this comparison is that the accretion age of elements in the mantle is a robust feature that does not depend on the model considered or the assumptions that are made.

The mantle isotopic composition at present can be calculated from the PDF as follows:

$$\epsilon_{\text{mantle}} = \int_0^1 \text{PDF}(x) \epsilon(x) dx \quad (4)$$

The curves were calculated using equation (1) (see Supplementary Equations for details) assuming a constant metal–silicate distribution through time, accretion of infinitely small impactors, and equilibration of 40% of the impactor cores with the target mantle (the remaining 60% of the impactor cores merges with the target core without silicate equilibration). The red arrow on the x -axis marks the position of $x_{0.95}$ (see equation (3)), corresponding to the fraction of the Earth's mass after which 95% of an element at present in the mantle was delivered.

where $\epsilon(x)$ is the isotopic composition of the accreted material when the Earth has reached a fraction x of its present size. Some models consider that the last stages of the Earth's accretion involved volatile-rich oxidized material^{20,21}. To constrain the nature of the Earth's accreting material through time, I consider a simple three-stage accretion model (Supplementary Equations). The first stage (I) comprises the first 60% of the Earth's accretion because Rubie *et al.*²¹ suggested that material accreted after that could have been more oxidized. The second stage (II) comprises 60%–99.5% of the Earth's accretion. The third stage (III) corresponds to the late veneer and comprises the last 0.5% or so of the Earth's accretion. The model considers four components that have isotopic compositions similar to enstatite meteorites (E), ordinary chondrites (O), CI and CO/CV carbonaceous chondrites. These meteorite groups are representative of E-, S- and C-type asteroids, and cover much of the diversity in isotopic compositions recorded in meteorites^{9,10}. The contributions of E, O, CI, and CO/CV are adjusted through a χ^2 -minimization to reproduce the O, Ca, Ti, Cr, Ni, Mo, and Ru isotopic compositions of the Earth's mantle (Fig. 2). The case of ^{142}Nd is treated separately (Extended Data Fig. 6) because its variations can be due to both α -decay of short-lived ^{146}Sm (half-life $t_{1/2} = 68$ or 103 million years)²² and incomplete mixing of the products of stellar nucleosynthesis²³.

The nature of the late veneer (stage III; 99.5%–100%) is primarily constrained from Ru, which calls for 100% E. Stage II (60%–99.5%) is also mostly made of E. This is a robust feature that stems from the fact that Ni and Mo were delivered to the Earth's mantle during that stage. The $\epsilon^{92}\text{Mo}$ value of the Earth's mantle lies at one end of the meteoritic range. Only E approximately matches the mantle composition and no meteoritic mixture can conceivably reproduce this composition. In detail, enstatite chondrites may display small positive $\epsilon^{92}\text{Mo}$ anomalies of about +0.38 (ref. 24), which would call for the contribution of material not yet sampled from known chondrites. The E component also has the same $\epsilon^{64}\text{Ni}$ value as terrestrial mantle rocks while CI, CO/CV and O all display measurable $\epsilon^{64}\text{Ni}$ anomalies.

The nature of the Earth's accreting material during stage I depends on whether $\mu^{142}\text{Nd}$ is used as a constraint in the χ^2 -minimization. If $\mu^{142}\text{Nd}$ is not included, stage I (0%–60%) comprises 51% E + 40% O + 9% COCV ($\chi^2 = 11$). The main reason for the 40% O + 9% COCV contribution is to reproduce the $\epsilon^{48}\text{Ca}$ and $\epsilon^{50}\text{Ti}$ values of the Earth's mantle, which differ slightly from the E component. If $\mu^{142}\text{Nd}$ is included, stage I (0%–60%) comprises 100% E ($\chi^2 = 53$). The reason is that the $\mu^{142}\text{Nd}$ value of the Earth's mantle lies at one end of the meteoritic range, close to E, so any contribution of O, CI or CO/CV degrades the fit. Enstatite chondrites, however, display a small negative $\mu^{142}\text{Nd}$ anomaly of -7 ± 3 relative to mantle rocks, suggesting that either the mantle has a slightly super-chondritic Sm/Nd ratio (that is, the difference is due to ^{146}Sm decay) or a component not sampled by

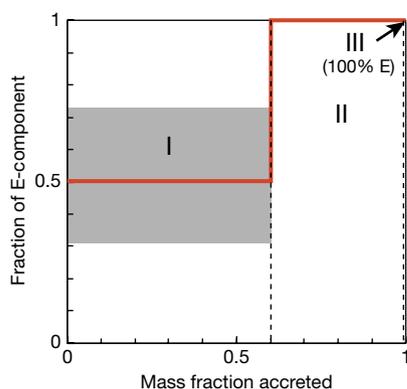


Figure 2 | Proportions of the enstatite (E) component in a three-stage accretion model of the Earth. See Supplementary Equations for details. Note that $\mu^{142}\text{Nd}$ variations were not taken into account in the minimization because they can also arise from ^{146}Sm decay^{22,23} (Extended Data Fig. 6 shows the result of a minimization including $\mu^{142}\text{Nd}$). Stages I, II and III comprise 0–60%, 60–99.5% and 99.5–100% of the Earth's accretion, respectively. The reason for the 60% divide is that previous models have suggested that the material accreted by the Earth could have changed in nature, from more reduced to more oxidized, at 60%–80% accretion²¹. The third stage corresponds to the addition of a late veneer after the completion of core formation¹⁴. The accreted material is assumed to be mixtures of four components with the isotopic compositions of enstatite (E), ordinary (O), and carbonaceous chondrites (CI and CO/CV). The five free parameters of the model are the fractions of E in stages I, II and III, and the proportions of CI and CO/CV in the non-enstatite component. These parameters are estimated using a χ^2 -minimization to reproduce the isotopic composition of the Earth's mantle for $\Delta^{17}\text{O}$, $\epsilon^{48}\text{Ca} + \epsilon^{50}\text{Ti}$, $\epsilon^{54}\text{Cr}$, $\epsilon^{64}\text{Ni}$, $\epsilon^{92}\text{Mo}$, and $\epsilon^{100}\text{Ru}$ (six independent constraints). The influence of composition uncertainties on the best-fitting parameters was assessed using a Monte Carlo simulation (grey bands indicate 95% confidence for the fraction of E). The best-fitting model (red line) corresponds to 51% E + 9% COCV + 40% O during stage I and about 100% E during stages II and III. The calculated isotopic anomalies in the Earth's mantle are close to the terrestrial values (which, by definition, represent no anomaly, meaning a value of 0); $\Delta^{17}\text{O} = +0.02 \pm 0.11$, $\epsilon^{48}\text{Ca} = +0.01 \pm 0.17$, $\epsilon^{50}\text{Ti} = +0.01 \pm 0.18$, $\epsilon^{54}\text{Cr} = 0.00 \pm 0.03$, $\epsilon^{64}\text{Ni} = +0.01 \pm 0.19$, $\epsilon^{92}\text{Mo} = +0.34 \pm 0.37$ and $\epsilon^{100}\text{Ru} = -0.11 \pm 0.08$ ($\chi^2 = 11$).

meteorites contributed to making the Earth (see Extended Data Fig. 6 legend for details).

The large fraction of E in the Earth's building blocks at all stages of its accretion contrasts with the small proportion of E-type asteroids in the present-day main belt. This may stem in part from the fact that chondrites (and presumably many of the asteroids found in the main belt) were formed approximately 2 million years after the birth of the Solar System, while embryos (for example, Mars) and other planetesimals (for example, those sampled by iron meteorites) were formed much earlier^{25,26}. The isotopic composition of the solar nebula may have changed during this timespan of 2 million years, and the building blocks of the terrestrial planets may have been more uniform in their isotopic compositions than is suggested by the compositions of chondrites and asteroids. The small $\Delta^{17}\text{O}$ excess measured in Martian meteorites relative to the Earth requires a greater proportion of O versus E in Mars (for example, 45% E + 55% O)²⁶ compared to the Earth (71% E + 24% O + 5% COCV). The chemical composition of Mercury is consistent with an enstatite chondrite origin²⁷, supporting the view that the inner protoplanetary disk was dominated by E-type material.

Enstatite chondrites are a group of meteorites that are characterized by much lower Mg/Si ratios and $\delta^{30}\text{Si}$ values than terrestrial mantle rocks (note that unlike other isotope systems discussed in this contribution, $\delta^{30}\text{Si}$ denotes mass-dependent fractionation of Si isotopes), which makes them unlikely to have been building blocks of the Earth²⁸. The high $\delta^{30}\text{Si}$ value of the Earth's mantle relative to chondrites of all types may be due to formation of the Earth from precursor materials

enriched through nebular processes in forsterite condensate, which presumably had high Mg/Si and high $\delta^{30}\text{Si}$ (ref. 13). Enstatite chondrites may be the forsterite-poor complementary reservoir to the material that made the Earth, possibly explaining why the Earth and enstatite chondrites share similar isotopic compositions for O, Ca, Ti, Cr, Mo and Ru but have different chemical compositions.

Thus, given that the material accreted by the Earth in the last 40% or so of its growth was isotopically similar to enstatite meteorites, it seems probable that the giant impactor that struck the Earth to form the Moon had a very similar isotopic composition to that of the proto-Earth. In particular, Mo in the Earth's mantle records the last 12% or so of the Earth's accretion, which corresponds to the Moon-forming impact in canonical models of lunar formation (that is, a Mars-size impactor colliding with the Earth just above the escape velocity at a 45° impact angle)²⁹. Its isotopic composition excludes a large contribution of non-E material during that stage. It is well documented that lunar rocks have identical $\Delta^{17}\text{O}$, $\epsilon^{48}\text{Ca}$ and $\epsilon^{50}\text{Ti}$ compositions, and similar $\epsilon^{54}\text{Cr}$ isotopic compositions to those of terrestrial mantle rocks (Supplementary Table 1)^{4–7}. Such a match is problematic in canonical models of lunar formation if one assumes that the impactor had distinct isotopic composition from the proto-Earth¹, because most of the Moon should come from the impactor²⁹.

From the inferred nature of the Earth's building blocks (Fig. 2), the difference in isotopic compositions between lunar and terrestrial rocks can be calculated for a given scenario of lunar formation (see Supplementary Equations). For the canonical model²⁹, the assumptions are that the giant impactor represented 10% of the Earth's final mass and the Moon was made of 60% impactor (E-type) and 40% proto-Earth at 90% accretion (67% E + 27% O + 6% CO/CV). The predicted anomalies in lunar rocks are $\Delta^{17}\text{O} = -0.02 \pm 0.04$, $\epsilon^{48}\text{Ca} = -0.22 \pm 0.11$, $\epsilon^{50}\text{Ti} = -0.11 \pm 0.09$ and $\epsilon^{54}\text{Cr} = +0.03 \pm 0.02$. These calculated compositions are consistent with the values measured in lunar rocks of $\Delta^{17}\text{O} = -0.001 \pm 0.005$, $\epsilon^{48}\text{Ca} = -0.24 \pm 0.24$, $\epsilon^{50}\text{Ti} = -0.03 \pm 0.04$ and $\epsilon^{54}\text{Cr} = +0.16 \pm 0.08$ (refs 4–7; Supplementary Table 1), bearing in mind that the lunar $\epsilon^{54}\text{Cr}$ value may be affected by cosmogenic effects. The present analysis suggests that the similar O, Ca, Ti and Cr isotopic compositions of the Moon and the Earth may have been inherited, in part, from shared E-type precursors, which relaxes the constraints on models of lunar formation^{1,11,12,29}.

A difficulty remains, however, because the $\epsilon^{182}\text{W}$ values and Hf/W ratios of the terrestrial and lunar mantles are also very similar^{30,31}. Unlike isotopic anomalies, ^{182}W is the decay product of ^{182}Hf and it would take special coincidences for the two bodies to end up with matching compositions³². This similarity is also a potential problem for alternative models of the formation of the Moon, involving Earth–Moon equilibration¹, collision of two half-Earth-size progenitors¹² or collision between a small hypervelocity impactor with a fast-spinning proto-Earth¹¹; this is because the final $\epsilon^{182}\text{W}$ value and Hf/W ratio in the Earth's mantle will depend on the extent and conditions of metal-silicate equilibration in the lunar and terrestrial mantles, which may require fine-tuning to explain the similar $\epsilon^{182}\text{W}$ values and Hf/W ratios.

Further measurements of elements with various lithophile–siderophile affinities in the terrestrial mantle and characterization of the isotopic composition of Venus will enable direct testing of the idea that the inner Solar System accreted mostly from material of enstatite meteorite isotopic composition. More extensive isotopic studies of elements in Martian meteorites will similarly unravel the accretion history of Mars.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Data availability The author declares that data supporting the findings of this study are available within the paper, its Supplementary Information files and its Extended Data. All other data are available from the corresponding author upon reasonable request.

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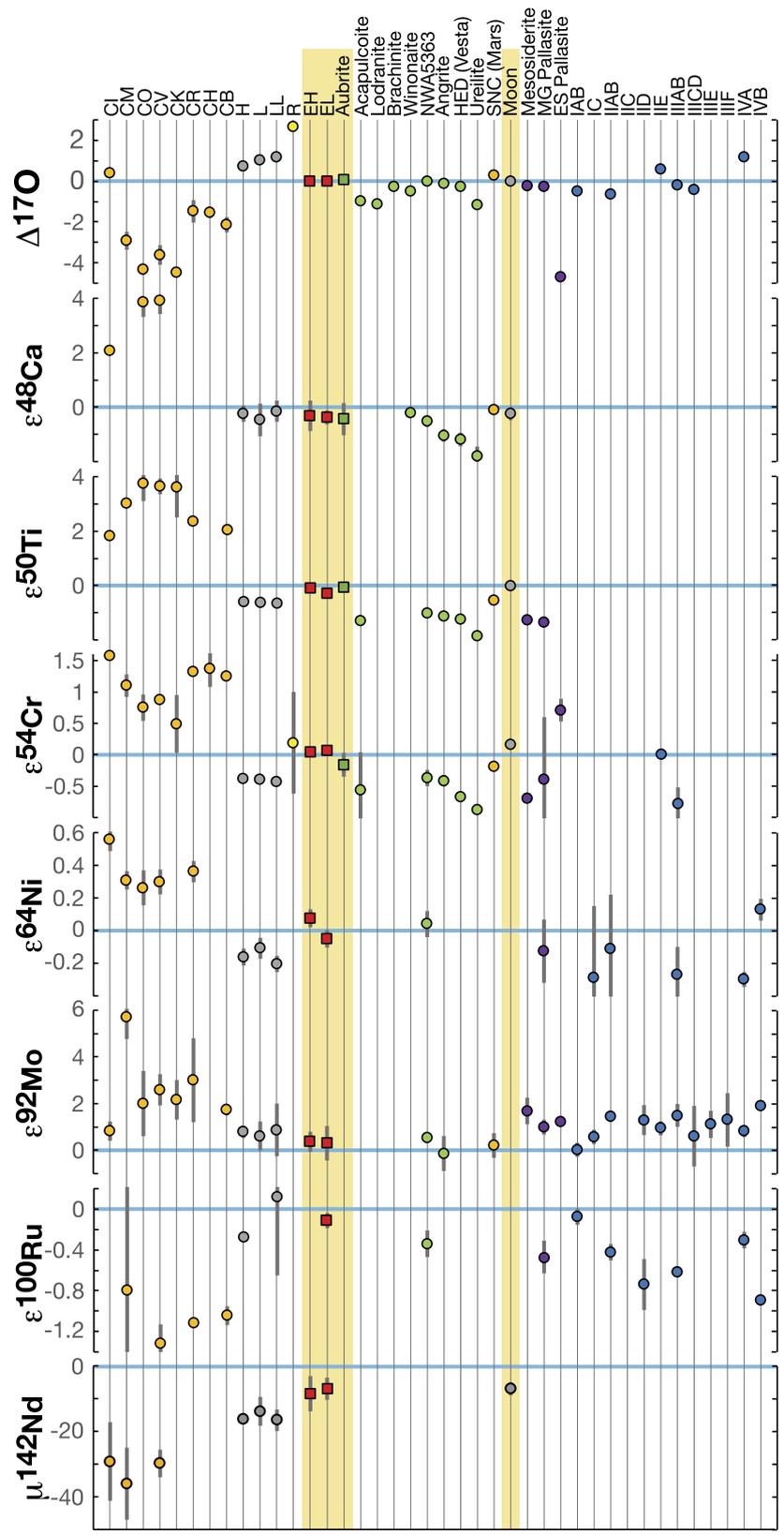
- Pahlevan, K. & Stevenson, D. J. Equilibration in the aftermath of the lunar-forming giant impact. *Earth Planet. Sci. Lett.* **262**, 438–449 (2007).
- Mastrobuono-Battisti, A., Perets, H. B. & Raymond, S. N. A primordial origin for the compositional similarity between the Earth and the Moon. *Nature* **520**, 212–215 (2015).
- Kaib, N. A. & Cowan, N. B. The feeding zones of terrestrial planets and insights into Moon formation. *Icarus* **252**, 161–174 (2015).
- Young, E. D. *et al.* Oxygen isotopic evidence for vigorous mixing during the Moon-forming giant impact. *Science* **351**, 493–496 (2016).
- Zhang, J., Dauphas, N., Davis, A. M., Leya, I. & Fedkin, A. The proto-Earth as a significant source of lunar material. *Nat. Geosci.* **5**, 251–255 (2012).
- Dauphas, N., Chen, J. & Papanastassiou, D. Testing Earth–Moon isotopic homogenization with calcium-48. *Lunar Planet. Sci. Conf. XXXVI*, 2436 (2015).
- Qin, L., Alexander, C. M. D., Carlson, R. W., Horan, M. F. & Yokoyama, T. Contributors to chromium isotope variation of meteorites. *Geochim. Cosmochim. Acta* **74**, 1122–1145 (2010).
- Javoy, M. *et al.* The chemical composition of the Earth: enstatite chondrite models. *Earth Planet. Sci. Lett.* **293**, 259–268 (2010).
- Warren, P. H. Stable-isotopic anomalies and the accretionary assemblage of the Earth and Mars: a subordinate role for carbonaceous chondrites. *Earth Planet. Sci. Lett.* **311**, 93–100 (2011).
- Dauphas, N. & Schauble, E. A. Mass fractionation laws, mass-independent effects, and isotopic anomalies. *Annu. Rev. Earth Planet. Sci.* **44**, 709–783 (2016).
- Čuk, M. & Stewart, S. T. Making the Moon from a fast-spinning Earth: a giant impact followed by resonant despinning. *Science* **338**, 1047–1052 (2012).
- Canup, R. M. Forming a Moon with an Earth-like composition via a giant impact. *Science* **338**, 1052–1055 (2012).
- Dauphas, N., Poitrasson, F., Burkhardt, C., Kobayashi, H. & Kurosawa, K. Planetary and meteoritic Mg/Si and $\delta^{30}\text{Si}$ variations inherited from solar nebula chemistry. *Earth Planet. Sci. Lett.* **427**, 236–248 (2015).
- Bottke, W. F., Walker, R. J., Day, J. M., Nesvorný, D. & Elkins-Tanton, L. Stochastic late accretion to Earth, the Moon, and Mars. *Science* **330**, 1527–1530 (2010).
- Rubie, D. C. *et al.* Highly siderophile elements were stripped from Earth's mantle by iron sulfide segregation. *Science* **353**, 1141–1144 (2016).
- Rudge, J. F., Kleine, T. & Bourdon, B. Broad bounds on Earth's accretion and core formation constrained by geochemical models. *Nat. Geosci.* **3**, 439–443 (2010).
- Nimmo, F., O'Brien, D. & Kleine, T. Tungsten isotopic evolution during late-stage accretion: constraints on Earth–Moon equilibration. *Earth Planet. Sci. Lett.* **292**, 363–370 (2010).
- Siebert, J., Corgne, A. & Ryerson, F. J. Systematics of metal–silicate partitioning for many siderophile elements applied to Earth's core formation. *Geochim. Cosmochim. Acta* **75**, 1451–1489 (2011).
- Badro, J., Brodholt, J. P., Piet, H., Siebert, J. & Ryerson, F. J. Core formation and core composition from coupled geochemical and geophysical constraints. *Proc. Natl Acad. Sci. USA* **112**, 12310–12314 (2015).
- Schönbächler, M., Carlson, R., Horan, M., Mock, T. & Hauri, E. Heterogeneous accretion and the moderately volatile element budget of Earth. *Science* **328**, 884–887 (2010).
- Rubie, D. C. *et al.* Accretion and differentiation of the terrestrial planets with implications for the compositions of early-formed Solar System bodies and accretion of water. *Icarus* **248**, 89–108 (2015).
- Boyet, M. & Carlson, R. W. ^{142}Nd evidence for early (>4.53 Ga) global differentiation of the silicate Earth. *Science* **309**, 576–581 (2005).
- Burkhardt, C. *et al.* A nucleosynthetic origin for the Earth's anomalous ^{142}Nd composition. *Nature* **537**, 394–398 (2016).
- Render, J., Fischer-Gödde, C., Burkhardt, C. & Kleine, T. Molybdenum isotopes and the building blocks of the Earth. *Lunar Planet. Sci. Conf. XXXVII*, 2639 (2016).
- Dauphas, N. & Chaussidon, M. A perspective from extinct radionuclides on a young stellar object: the Sun and its accretion disk. *Annu. Rev. Earth Planet. Sci.* **39**, 351–386 (2011).
- Tang, H. & Dauphas, N. ^{60}Fe – ^{60}Ni chronology of core formation in Mars. *Earth Planet. Sci. Lett.* **390**, 264–274 (2014).
- Nittler, L. R. *et al.* The major-element composition of Mercury's surface from Messenger X-ray spectrometry. *Science* **333**, 1847–1850 (2011).
- Fitoussi, C. & Bourdon, B. Silicon isotope evidence against an enstatite chondrite Earth. *Science* **335**, 1477–1480 (2012).
- Canup, R. M. & Asphaug, E. Origin of the Moon in a giant impact near the end of the Earth's formation. *Nature* **412**, 708–712 (2001).
- Kruijer, T. S., Kleine, T., Fischer-Gödde, M. & Sprung, P. Lunar tungsten isotopic evidence for the late veneer. *Nature* **520**, 534–537 (2015).
- Touboul, M., Puchtel, I. S. & Walker, R. J. Tungsten isotopic evidence for disproportional late accretion to the Earth and Moon. *Nature* **520**, 530–533 (2015).
- Dauphas, N., Burkhardt, C., Warren, P. H. & Fang-Zhen, T. Geochemical arguments for an Earth-like Moon-forming impactor. *Phil. Trans. R. Soc. Lond. A* **372**, 20130244 (2014).

Supplementary Information is available in the online version of the paper.

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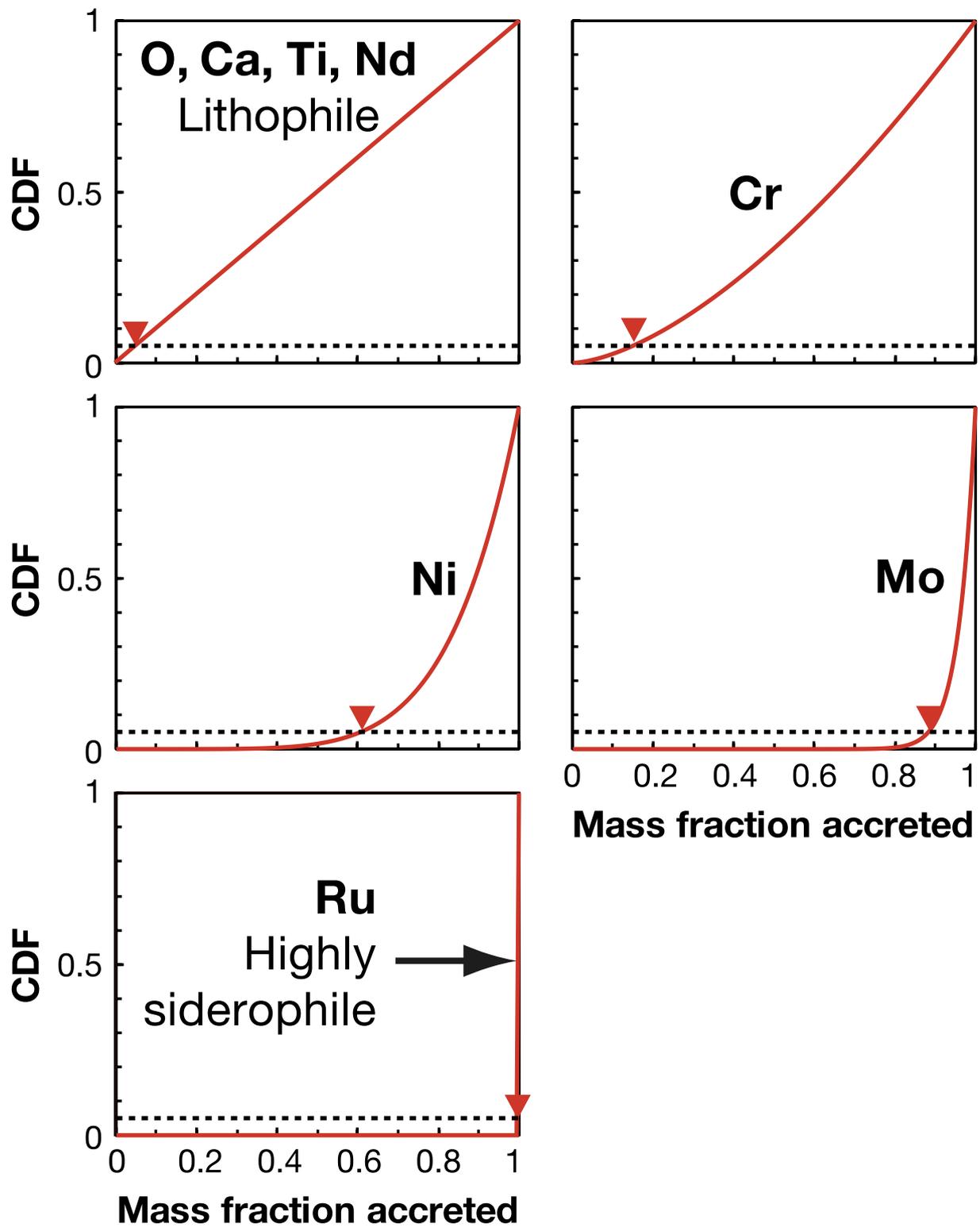
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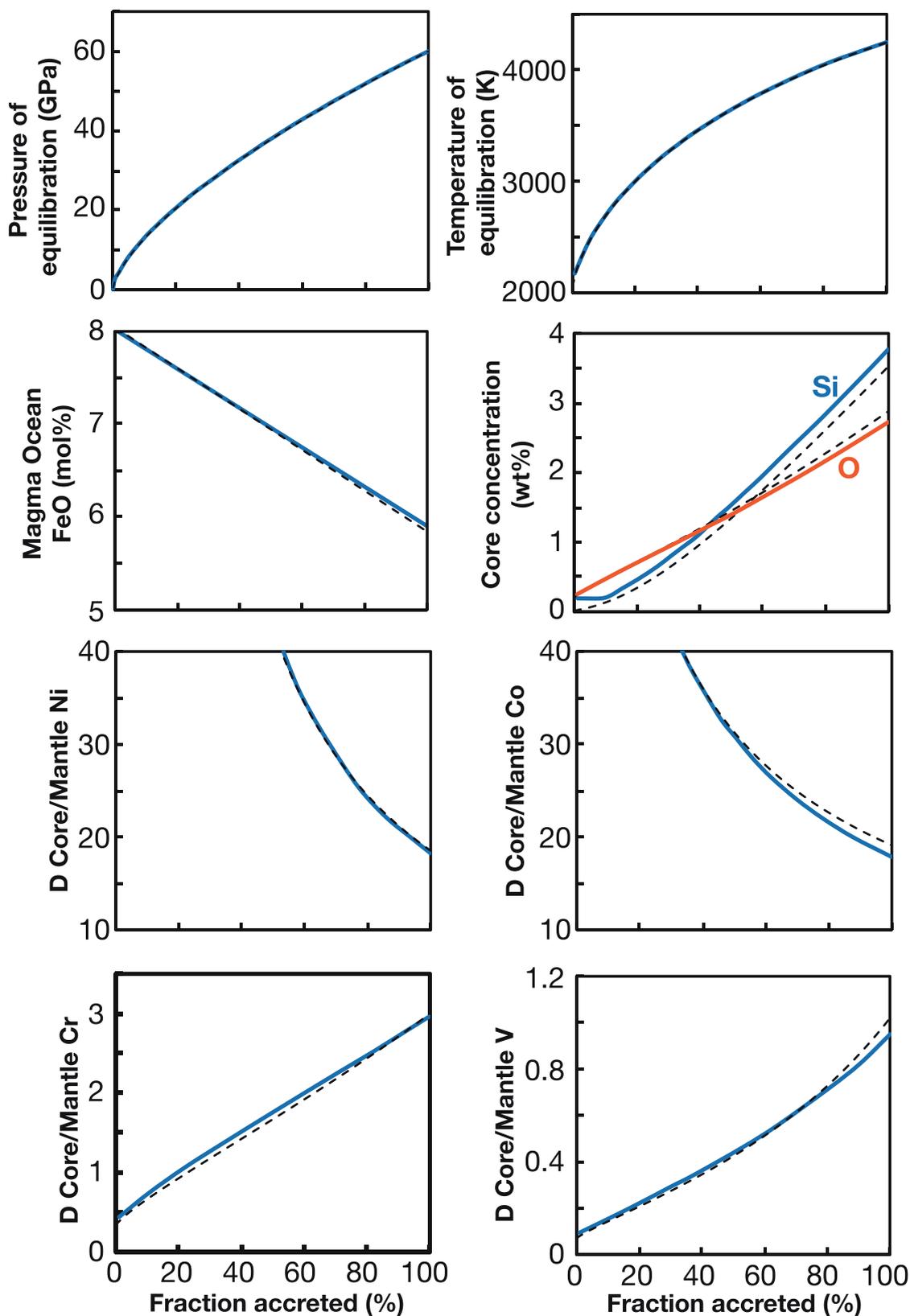
Extended Data Figure 1 | Isotopic anomalies for $\Delta^{17}\text{O}$, $\epsilon^{48}\text{Ca}$, $\epsilon^{50}\text{Ti}$, $\epsilon^{54}\text{Cr}$, $\epsilon^{64}\text{Ni}$, $\epsilon^{92}\text{Mo}$, $\epsilon^{100}\text{Ru}$ and $\mu^{142}\text{Nd}$ in bulk meteorites and planetary materials. See Supplementary Table 1. Enstatite meteorites (EH and EL chondrites, aubrite achondrites) and lunar samples have isotopic

compositions (yellow shading) that are identical or very similar to the terrestrial mantle composition. Other meteorites and planetary materials display isotopic anomalies in one or several elements. The terrestrial mantle composition is, by definition, at 0 (blue horizontal lines).



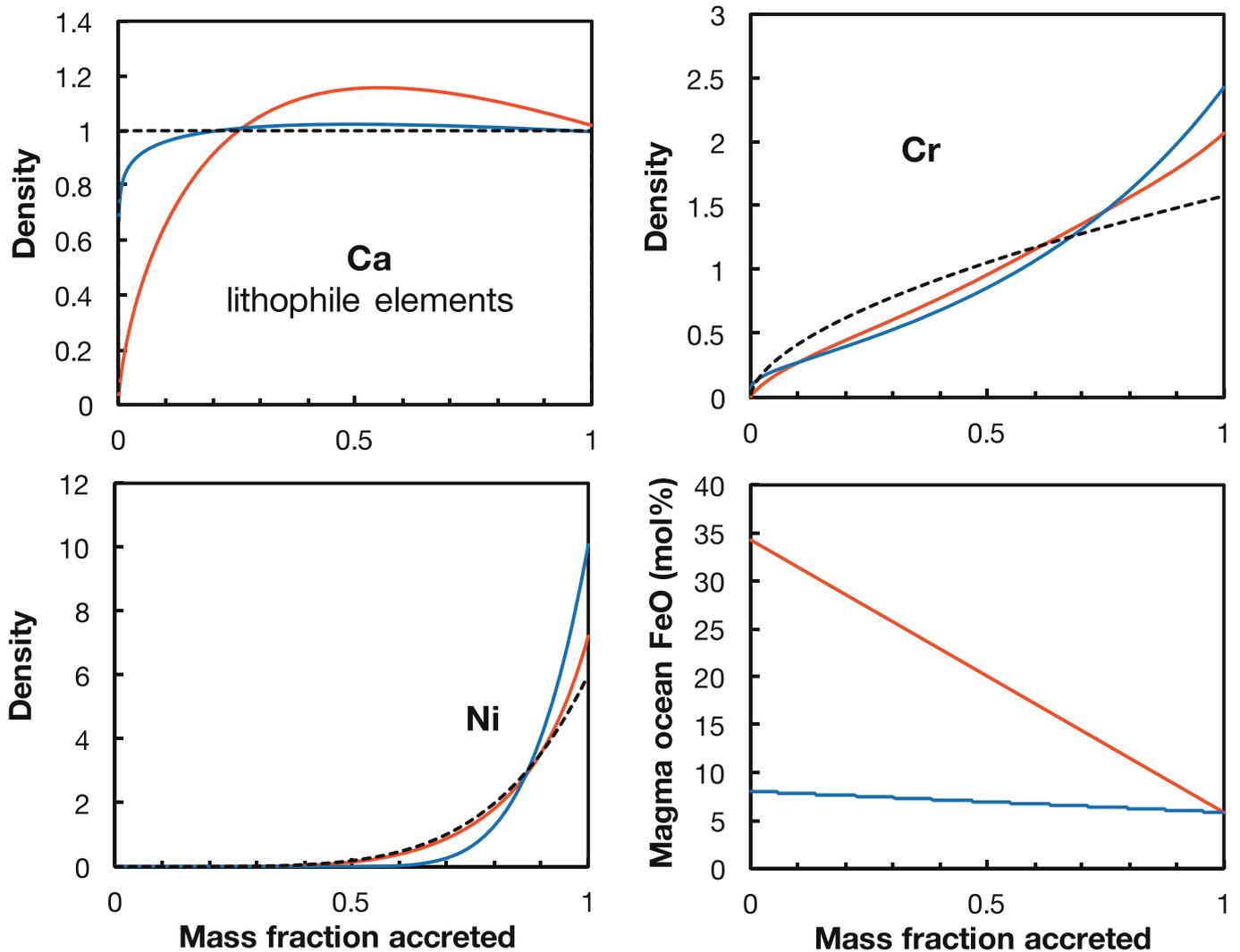
Extended Data Figure 2 | CDFs of lithophile O, Ca, Ti and Nd, moderately siderophile Cr, Ni and Mo and siderophile Ru atoms in the present terrestrial mantle. See equation (2) and Fig. 1 for the corresponding PDFs and details. For each element, the horizontal dashed

line at $CDF = 0.05$ gives the fraction of the Earth's final mass after which 95% of an element at present in the mantle was delivered (the red triangles mark $x_{0.95}$ as given by equation (3)).



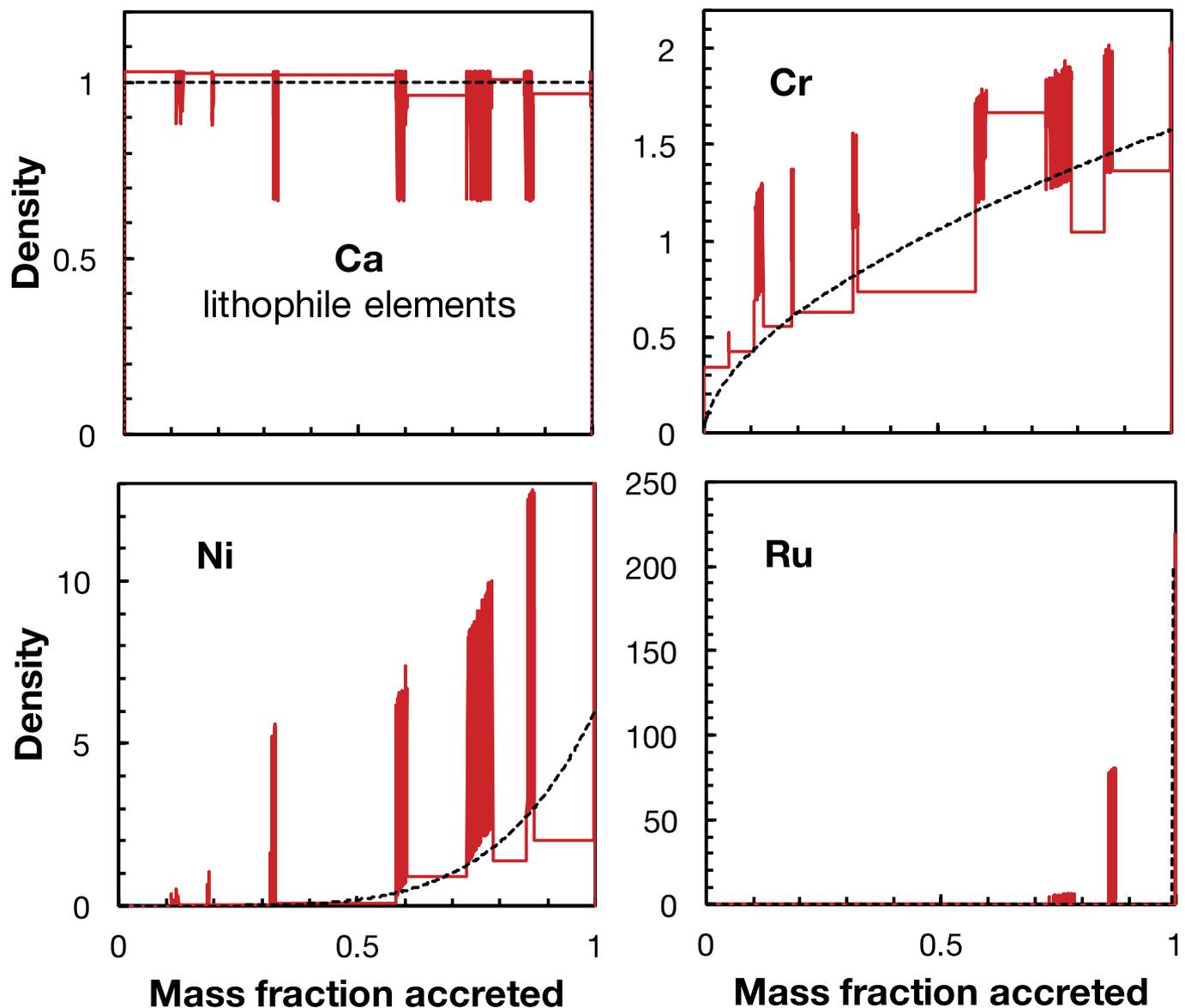
Extended Data Figure 3 | Example of terrestrial accretion and core partitioning for a scenario from ref. 19 of near-constant mantle redox evolution. The blue and red lines correspond to model outputs from ref. 19 (updated from their supplementary figure 2) while the dashed black lines are from a Mathematica code developed for this study (available in the Supplementary Information) that makes the same assumptions as ref. 19 (see Supplementary Equations). The simulations use a final

equilibration pressure of 60 GPa, a FeO mol% concentration in the magma ocean that decreases linearly with the accreted fraction from 8% to 5.8% (see the oxygen fugacity path 6 in figure 1 of ref. 19) and an equilibration temperature that follows the 'hot liquidus' of ref. 19. As shown, there is excellent agreement between ref. 19 and the present study. 'D Core/Mantle' refers to the ratio of the concentrations in the core and mantle.



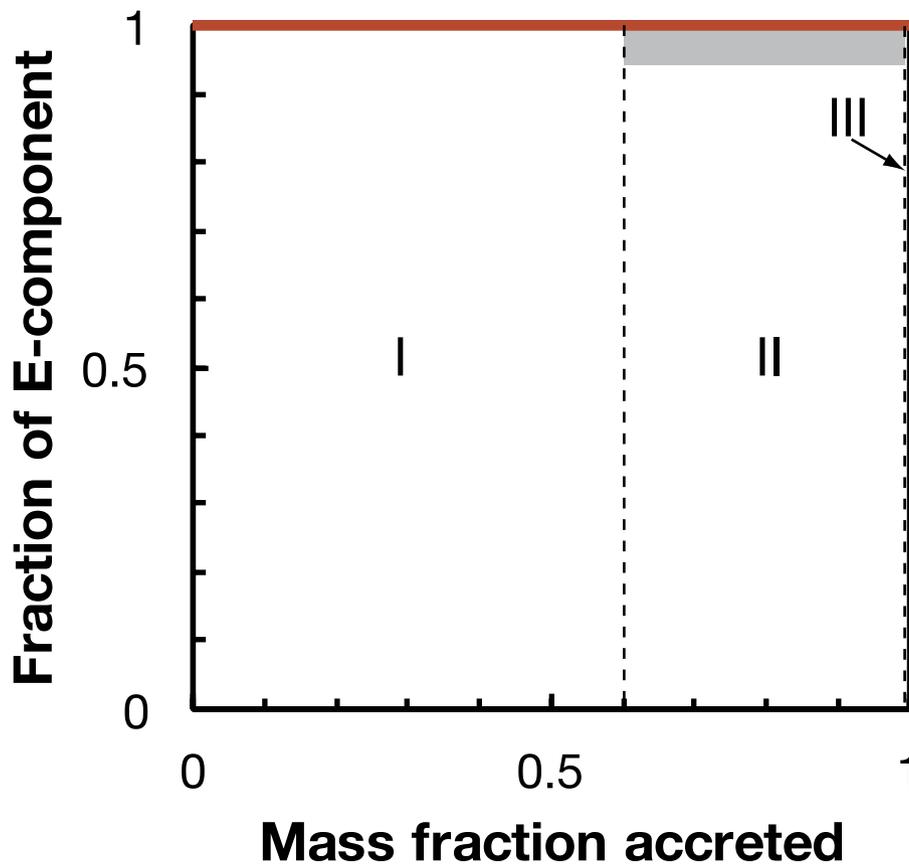
Extended Data Figure 4 | PDFs of Ca (lithophile), Cr, and Ni (moderately siderophile) for the accretion of elements in the Earth's mantle in the model of ref. 19. See Supplementary Equations for details. The blue and red curves correspond to two endmember accretion scenarios that can reproduce geophysical and geochemical constraints for the Earth's core and mantle. The red curves correspond to a scenario wherein the mantle FeO concentration evolves from about 34 mol% to 5.9 mol%; the blue curves correspond to a scenario wherein the mantle FeO evolves from 8 mol% to 5.9 mol% (bottom right panel; FeO path numbers 13 and 6 in ref. 19). The black dashed curves are the predictions

from equation (1). The non-flat density of Ca is an artefact due to the fact that the FeO concentration of the mantle is arbitrarily prescribed, such that in the scenarios investigated, the CaO concentration of the accreted material would need to increase as the FeO decreases. This model assumes full impactor core-target mantle equilibration and considers small impactors (1/1,000th the size of the present Earth). The metal-silicate distribution coefficients evolve as a function of the evolving pressure-temperature-composition-oxygen fugacity conditions. The values of $x_{0.95}$ for Cr and Ni in the near-constant FeO model of Badro *et al.*¹⁹ are 0.81 and 0.23, respectively (compared to 0.85 and 0.39 for equation (3)).



Extended Data Figure 5 | PDFs of Ca (lithophile), Cr, Ni (moderately siderophile), and Ru (highly siderophile) for the accretion of elements in the Earth's mantle in the model of ref. 15. The red curves are from the model¹⁵; see Supplementary Equations for details. The black dashed curves are the predictions from equation (1). The model of ref. 15 uses a dynamical simulation (Grand Tack 4:1-0.5-8) as input that gives the mass and heliocentric distance of each embryo or planetesimal that is accreted by the Earth as a function of time. Embryos and planetesimals closer to the Sun are assumed to be more reduced while those further away are assumed to be more oxidized. Following each impact, the impactor mantle is assumed to merge with the target mantle without metal equilibration,

a fraction of the impactor core merges with the target core without silicate equilibration, and fractions of the impactor core and target mantle are allowed to equilibrate before the equilibrated metal sinks to the Earth's core and the equilibrated silicate mixes with the rest of the Earth's mantle. The metal–silicate distribution coefficients evolve as a function of the evolving pressure–temperature–composition–oxygen fugacity conditions. The values of $x_{0.95}$ for Cr and Ni in the model of Rubie *et al.*¹⁵ are 0.88 and 0.41, respectively (compared to 0.85 and 0.39 for equation (3)). Note that according to this model, half of the Ru in the mantle could have been delivered before the late veneer; $x_{0.95} = 0.14$.



Extended Data Figure 6 | Proportions of the E component in a three-stage accretion model of the Earth. See Supplementary Equations and Fig. 2 legend for details. Unlike in Fig. 2, $\mu^{142}\text{Nd}$ variations were taken into account in the minimization. Stages I, II and III comprise 0%–60%, 60%–99.5%, and 99.5%–100% of the Earth's accretion. The accreted material is assumed to be mixtures of four components with the isotopic compositions of enstatite (E), ordinary (O), and carbonaceous chondrites (CI and CO/CV). The five free parameters of the model are the fractions of E in stages I, II and III, and the proportions of CI and CO/CV in the non-enstatite component. These parameters are estimated using a χ^2 -minimization to reproduce the isotopic composition of the Earth's mantle for $\Delta^{17}\text{O}$, $\epsilon^{48}\text{Ca} + \epsilon^{50}\text{Ti}$, $\epsilon^{54}\text{Cr}$, $\epsilon^{64}\text{Ni}$, $\epsilon^{92}\text{Mo}$, $\epsilon^{100}\text{Ru}$ and $\mu^{142}\text{Nd}$ (seven independent constraints). The best-fitting model corresponds to about 100% E during all three stages, with up to 6% of O during stage II.

The calculated isotopic anomalies in the Earth's mantle are those of E-chondrites: $\Delta^{17}\text{O} = -0.01 \pm 0.06$, $\epsilon^{48}\text{Ca} = -0.37 \pm 0.24$, $\epsilon^{50}\text{Ti} = -0.19 \pm 0.27$, $\epsilon^{54}\text{Cr} = +0.06 \pm 0.04$, $\epsilon^{64}\text{Ni} = +0.01 \pm 0.19$, $\epsilon^{92}\text{Mo} = +0.34 \pm 0.37$, $\epsilon^{100}\text{Ru} = -0.11 \pm 0.08$, and $\mu^{142}\text{Nd} = -7 \pm 3$ ($\chi^2 = 53$). These match approximately the terrestrial composition (that is, no anomaly by definition). Note that the fit is much worse than when $\mu^{142}\text{Nd}$ is not included ($\chi^2 = 11$), in part because all chondrite groups (including E) display resolvable negative $\mu^{142}\text{Nd}$ anomalies. This can be explained if a component not sampled in chondrites contributed to making the Earth²³ or if the accessible Earth has a slightly superchondritic Sm/Nd ratio²². Existing data on $\mu^{145}\text{Nd}$, $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ yield a $\mu^{142}\text{Nd}$ value corrected for the presence of nucleosynthetic anomalies of -5 ± 2 , suggesting that the shift in $\mu^{142}\text{Nd}$ between E-chondrites and the Earth's mantle of -7 ± 3 could be due in part to ^{146}Sm decay²³.