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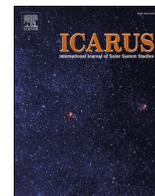
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Letter

Zinc isotope anomalies in primitive meteorites identify the outer solar system as an important source of Earth's volatile inventory

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ABSTRACT

The source of and timing of delivery of the volatile elements to Earth is a question that is fundamental to understanding how our planet evolved. Here, we show that primitive meteorites have resolved mass-independent Zn isotope anomalies from the terrestrial reservoir. Carbonaceous chondrites (CC), likely originating from the outer Solar System are distinct from non-CC, and Earth is intermediate between these two components. Modelling based on these data indicates that around 30% of Earth's budget of Zn and other moderately volatile material derives from the participation of 6% of CC-like materials during Earth's accretion, with the remaining coming from NC meteorites. This implies that, despite the relatively minor mass of Earth thought to derive from CC-like material, the CC component of Earth was relatively and significantly volatile-enriched; this is in line with the observation that the terrestrial elemental abundance pattern of moderately volatile elements could be explained by a carbonaceous source, and with the carbonaceous chondrite-like isotopic budget of more volatile-rich material accreted later in Earth's accretion history (e.g. Hg, Se, N, noble gases).

1. Introduction

Nucleosynthetic isotope variations measured in meteorites provide crucial information for studying pre- and early Solar System conditions and processes. They can place quantitative constraints on the history and variety of stellar sources of material delivered to the pre-solar molecular cloud and/or planetary accretion, and reveal the degree of heterogeneity in the proto-planetary nebula (Spitzer et al., 2020; Trinquier et al., 2007, 2009). They are also an important means of fingerprinting meteorite groups and, as a corollary, identifying those primitive meteorite groups that represent material that accreted to form differentiated bodies, including the Earth (Javoy et al., 2010; Warren, 2011).

Such anomalies have been measured in extra-terrestrial materials within the iron peak (IP) element isotope systems (Fe, Ca, Cr, Ni, Ti, Zn; see e.g. Bermingham et al., 2020 for review); these elements are the final products of fusion reactions in the cores of massive stars or during explosive nucleosynthesis (Clayton, 2003). For those systems where resolvable anomalies have been measured, Earth is intermediate between carbonaceous chondrites (i.e. outer solar system material) and ordinary chondrites (i.e. inner solar system material); this difference is often referred to as the "CC-NC dichotomy" (e.g. Budde et al., 2019;

Kleine et al., 2020; Nanne et al., 2019; Schiller et al., 2018, 2020; Trinquier et al., 2009). For these isotope systems, the enstatite chondrites are typically not anomalous with respect to Earth, leading to the view that Earth accreted from predominantly EC-like material. As a corollary, for these refractory isotope systems, material from the outer solar system is not required to have played a major role in Earth's accretion (e.g. Dauphas, 2017). However, these more refractory elements give us limited information about the source timing of volatile accretion to Earth, and could perhaps underestimate the importance of outer solar system material in Earth's volatile budget.

Among iron peak elements, Zn (T_{C50} , temperature at which 50% of its mass is calculated to have condensed from a gas of solar composition condensation = 726 K Lodders, 2003) is the most volatile. Therefore, Zn isotopes in primitive meteorites could provide an important source of information about the source of (moderately volatile) element delivery to Earth. To date, however, Zn is the only multi-isotope iron-peak element for which isotopic anomalies have not been measured in bulk meteorites; Moynier et al. (2009) found no resolvable anomalies on the bulk scale for both carbonaceous and ordinary chondrites – although there are hints of a ^{66}Zn excess in CO3 Ornans, and a ^{66}Zn deficit in H4 Forest Vale. To a certain extent, the measurement of both positive and

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negative ^{66}Zn anomalies in CAIs (Völkering and Papanastassiou, 1990) suggests that such anomalies should be present in some (particularly CAI-rich) primitive meteorites although these have not, so far, been found; either because the anomalies have been completely overwhelmed by ‘common’ Zn, or are too small for the previous measurement precisions to resolve. The identification of Zn isotopic anomalies could be used to place strong constraints on its origin in terrestrial planets together with other moderately volatile elements. Here, we reappraise the existence, magnitude and potential carrier phase(s) of Zn isotope anomalies in primitive meteorites, with the benefit of improved analytical precision and uncertainties, through the analysis of a representative suite of carbonaceous, ordinary and enstatite chondrites including bulk-rock and leachate measurements as well as terrestrial samples.

2. Results

Sample materials and methods are described in detail in the SOM. Zinc isotope measurements were corrected for mass-dependent fractionation using the exponential law (Russel et al., 1978). Two normalizing ratios were used in this work, $^{68}\text{Zn}/^{64}\text{Zn}$ ($R_c = 0.3856$) and $^{67}\text{Zn}/^{64}\text{Zn}$ ($R_c = 0.0843$; Rosman, 1972). This is because, although ratioing to $^{68}\text{Zn}/^{64}\text{Zn}$ gives slightly better precision on the calculated ϵZn values (both ^{68}Zn and ^{64}Zn are relatively abundant and counting statistics are improved; see Table S2 in SOM), we interpret ^{68}Zn as

carrying an anomaly, and so normalizing with $^{68}\text{Zn}/^{64}\text{Zn}$ reduces the magnitude of both $\epsilon^{66}\text{Zn}$ and $\epsilon^{67}\text{Zn}$ values.

Zinc anomalies are quantified using the epsilon notation relative to the terrestrial standard BHVO-2, defined as follows:

$$\epsilon \quad (2)$$

Where $x = 66, 67, 68$ or 70 , c is the normalizing ratio, and the isotope ratios have been corrected for mass-dependent fractionation. The long-term precision (2se) on the bracketing standard is $\epsilon^{66}\text{Zn} \pm 0.011$, $\epsilon^{67}\text{Zn} \pm 0.018$, $\epsilon^{70}\text{Zn} \pm 0.074$ when normalizing to $^{68}\text{Zn}/^{64}\text{Zn}$, and $\epsilon^{66}\text{Zn} \pm 0.015$, $\epsilon^{68}\text{Zn} \pm 0.026$, $\epsilon^{70}\text{Zn} \pm 0.076$ when normalizing to $^{67}\text{Zn}/^{64}\text{Zn}$ ($n = 105$). The Zn isotope data for bulk meteorites and terrestrial standards are presented in Table S2, and leaching experiment data in Table S3.

2.1. Terrestrial standards

Assuming all the terrestrial samples are derived from the same Zn reservoir, and there are no known terrestrial processes which can mass-independently fractionate Zn isotopes, there should be no resolvable Zn anomalies between terrestrial rocks and the bracketing standard. This is the case, with the average terrestrial composition determined from the 4 rocks giving $\epsilon^{66}\text{Zn}_{68/64} = 0.015 \pm 0.075$, $\epsilon^{67}\text{Zn}_{68/64} = -0.037 \pm 0.099$, $\epsilon^{70}\text{Zn}_{68/64} = 0.046 \pm 0.710$ (all 2sd, Table S2, Fig. 1a; N.B. a different

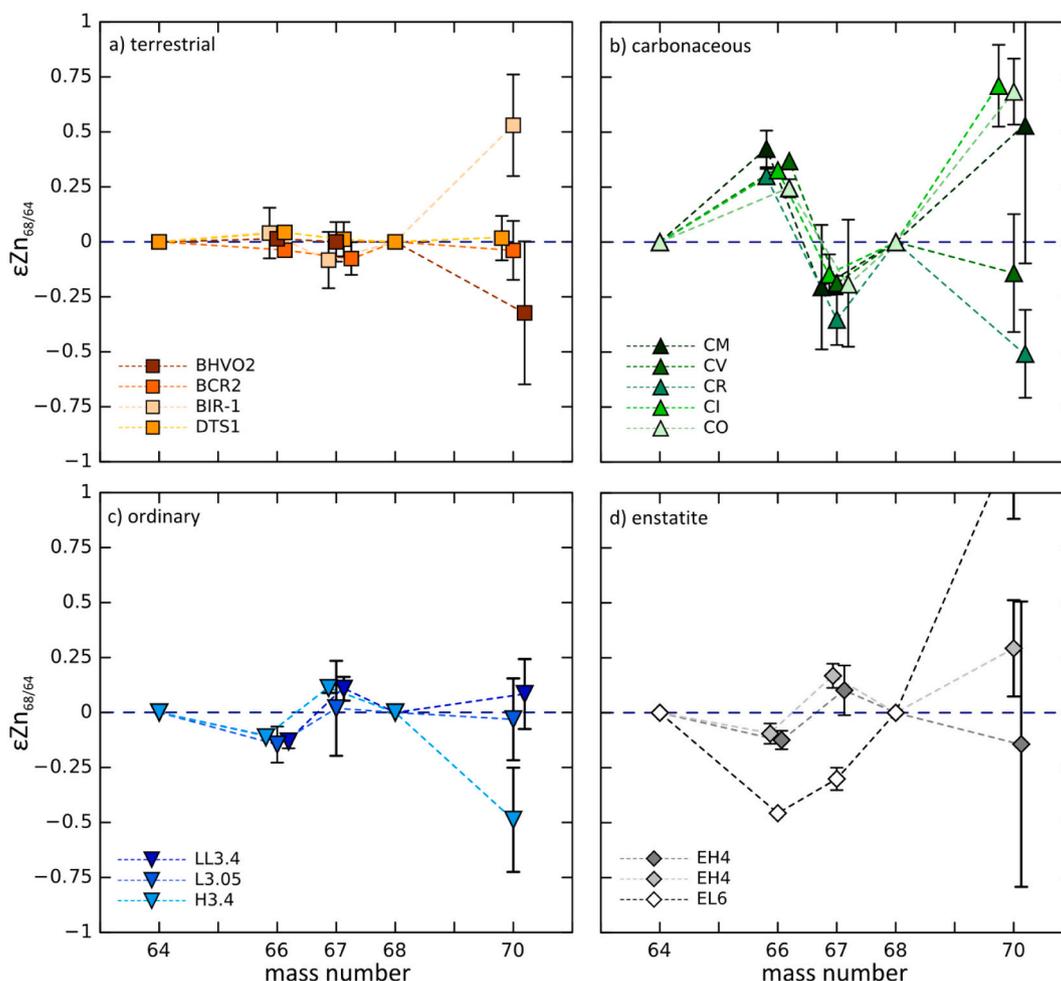


Fig. 1. Zinc isotopic ratio (reported as the per ten thousand deviations from the BHVO-2 terrestrial sample after a normalization to $^{68}\text{Zn}/^{64}\text{Zn} = 0.385564$), for a) terrestrial samples (one BHVO-2 was analyzed as an unknown, b) individual carbonaceous chondrites c) individual ordinary chondrites and d) individual enstatite chondrites. Meteorite names can be found in the SOM. Carbonaceous chondrites are enriched in ^{66}Zn and depleted in ^{67}Zn compared to terrestrial rocks, while ordinary and enstatite chondrites show a mirror pattern, with a depletion in ^{66}Zn and enrichment in ^{67}Zn .

BHVO-2 aliquot was prepared and analyzed as an unknown and is included in this average). Normalizing data with $^{67}\text{Zn}/^{64}\text{Zn}$ gives similar results (Table S2). For all ratios except $^{70}\text{Zn}/^{64}\text{Zn}$, the spread of data is also very limited, all centred around zero, as would be expected. The $\epsilon^{70}\text{Zn}$ values, however, define a larger spread, with one standard, BIR-1, apparently demonstrating a resolvable ^{70}Zn excess. This is difficult to explain without calling upon some unresolved interference or matrix effect that is having a detrimental effect on the measurement of this isotope ratio. In practice, this means that only large ($>1\epsilon$) ^{70}Zn anomalies are detectable. In contrast, analyses of terrestrial samples indicate that $>0.1\epsilon$ anomalies can be accurately resolved on the ^{66}Zn , ^{67}Zn and ^{68}Zn isotopes (depending on the chosen normalizing ratio).

2.2. Bulk meteorites

When normalized to $^{68}\text{Zn}/^{64}\text{Zn}$, all CC display very similar isotope anomaly patterns (Fig. 1b, Table S2), having resolved positive ^{66}Zn anomalies ($\epsilon^{66}\text{Zn}_{68/64} = 0.245$ to 0.424) and negative ^{67}Zn ($\epsilon^{67}\text{Zn}_{68/64} = -0.143$ to -0.343) anomalies. There are, potentially, differences between CC groups in terms of $\epsilon^{66}\text{Zn}_{68/64}$, which is in line with other iron-peak isotope systems, however, further analyses would be required to confirm this. In this normalization scheme, there are no resolvable ^{70}Zn carbonaceous chondrite anomalies, which is consistent with literature (Moynier et al., 2009), although the meteorite group averages do hint at the possibility of anomalies on this isotope (Fig. S1).

Both ordinary and enstatite chondrites have negative ^{66}Zn anomalies; these anomalies are smaller than, and the opposite sense compared to those measured in CC (Fig. 1c and d, S1, Table S2). A repeat dissolution and chemical processing of QUE 97008.45 shows identical ^{66}Zn and ^{67}Zn anomalies to the original analysis, but has a different $\epsilon^{70}\text{Zn}$ magnitude, confirming the robustness of this method for all isotopes except ^{70}Zn (Table S2).

The EL6 anomaly pattern is markedly different to EH chondrites (Fig. 1d); this is the only case where the groups within a meteorite class display markedly different anomaly patterns. This is unlikely to represent an original variation in isotope abundances between the different enstatite chondrite parent bodies. EL6 are depleted in refractory lithophile elements (Boyett et al., 2018; Rubin et al., 2009) and extremely depleted in volatile elements compared to EH, likely due to impact loss on the parent body (Moynier et al., 2011), which has caused significant, kinetic, mass-dependent Zn isotope fractionation. Hence, normalization using the exponential fractionation law has not adequately corrected for the mass-dependent isotope variations in this case.

To investigate the statistical significance of the bulk anomalies, two-tailed, two-sample, unequal variance Student's *t*-tests (Welch's *t*-tests) were performed on the data. Given the similarity of anomaly patterns within each meteorite class the means of each class were used in the tests, compared each time to the mean of the terrestrial samples analyzed (Fig. S1). In all cases of class averages for $\epsilon^{66}\text{Zn}_{68/64}$, $\epsilon^{66}\text{Zn}_{67/64}$, $\epsilon^{67}\text{Zn}_{68/64}$ and $\epsilon^{68}\text{Zn}_{67/64}$ anomalies, all *p*-values are below 0.05, i.e. these anomalies are statistically significant (Table S2). For ^{70}Zn , none of the group averages appear to have significant anomalies relative to terrestrial at the currently attainable method precision.

2.3. Leaching experiments

Zinc isotope anomalies for the different leaching steps for both Murchison CM2 and the selection of EH3 chondrites are given in Table S3 and Fig. S2; as with the bulk meteorite data, the ratios have been normalized to $^{68}\text{Zn}/^{64}\text{Zn}$. Also shown for comparison on Fig. S2 are the bulk analyses for each of the meteorite groups (dotted lines). For Murchison, measurable Zn was present to analyse the isotope compositions of the carbonate, sulphate, sulphide, metal and silicate phases, with most of the Zn budget ($\sim 88\%$) contained with the sulphates and sulphides; for the EH3 meteorites, Zn was present in the sulphide, metal, and combined silicate and refractory phases, although in this case, the

metal phase tended to dominate the Zn budget (see Table S3, SOM).

First, in all analyses, and for all isotopes, the largest anomalies are found in the most labile phases (i.e. carbonates, sulphides and sulphates) and, in general, the magnitude of anomalies reduces as the strength of acid increases. However, in terms of $\epsilon^{66}\text{Zn}$, no phase apart from the silicate +refractory in one EH3 meteorite (ALHA 77295, Fig. S2) has a terrestrial composition; moreover, no specific phase seems to contain the anomaly i.e. in most meteorites studied, the entire Zn budget appears anomalous.

3. Discussion

Zinc isotope anomalies in primitive meteorites follows the fundamental “dichotomy” between carbonaceous chondrites (CC) and non-carbonaceous (NC) meteorites whatever the normalization scheme used (Fig. 3), as has already observed for various iron-peak and s-process isotope systems (Budde et al., 2019; Kleine et al., 2020; Nanne et al., 2019; Schiller et al., 2018, 2020; Trinquier et al., 2009). We also see a broad positive correlation with anomalies in ^{66}Zn and other neutron-rich isotope anomalies in the same meteorites (^{48}Ca , ^{50}Ti , ^{54}Cr , ^{62}Ni ; Fig. S3). An exception to this is the EL6, which has unique isotopic anomaly pattern (Fig. 2).

Zinc isotopes can be highly mass-dependently fractionated during evaporation, affecting the normalization scheme, as for EL6 data (Fig. 1D). There are a number of empirical laws that can be employed to correct for both natural and instrumentally-induced isotope fractionation, (e.g. (Habfast, 1998; Maréchal et al., 1999)), although the exponential law is the most commonly employed, as this provides a correction most consistent with natural fractionation (Maréchal et al., 1999). At low degrees of isotope fractionation from a standard, there are no differences between the sense and magnitude of the isotope ratio corrections introduced by each the laws.

The same is not true when each of the laws are applied to the data acquired for EL6 Atlanta which has an extremely heavy Zn isotope composition ($\delta^{66}\text{Zn} = 7.01 \pm 0.13$). This likely reflects a preferential escape of the lighter isotopes during volatile impact loss on the EL parent body (Moynier et al., 2011). Applying the exponential law here does not adequately correct for the degree of isotope fractionation that affected this meteorite. Different fractionation laws generate larger anomaly magnitudes on each isotope, with the power law reversing the sense of the pattern (Fig. S4).

Also applied to the EL6 data is the exponential law with a modified fractionation coefficient (Habfast, 1998). This was formulated to take into account the unrealistic assumption of complete mixing of a sample during evaporation using TIMS, whereby an evaporating surface reservoir was continually being fed by an unfractionated, unevaporated, reservoir. A similar phenomenon likely occurred on the EL parent body (Moynier et al., 2011) as Zn was evaporated in likely a similar regime. Here, the top and bottom of the ratio *x* defined in Eq. (1) are modified thusly:

$$x = \frac{\ln \left[K \left(\sqrt{m_2/m_1} - 1 \right) + 1 \right]}{\ln \left[K \left(\sqrt{m_3/m_1} - 1 \right) + 1 \right]} \quad (3)$$

where *K* is an arbitrary number ($0 \leq K \leq 1$) which defines the mixing regime in the sample; when *K* = 1, complete mixing between the two reservoirs occurs, and the fractionation coefficient is unaffected. Applying this correction to the EL6 data, the value for *K* = 0.87 was taken to force the ^{67}Zn anomaly through zero (terrestrial). In this instance, both ^{66}Zn and ^{70}Zn anomalies are significantly reduced (Fig. S1, the results labelled “exponential-red-b”); the ^{70}Zn anomaly is within error of terrestrial, and there is only a small negative ^{66}Zn anomaly (similar to the negative anomalies found in EH chondrites, Fig.1d). This correction corroborates previous suggestions (Moynier

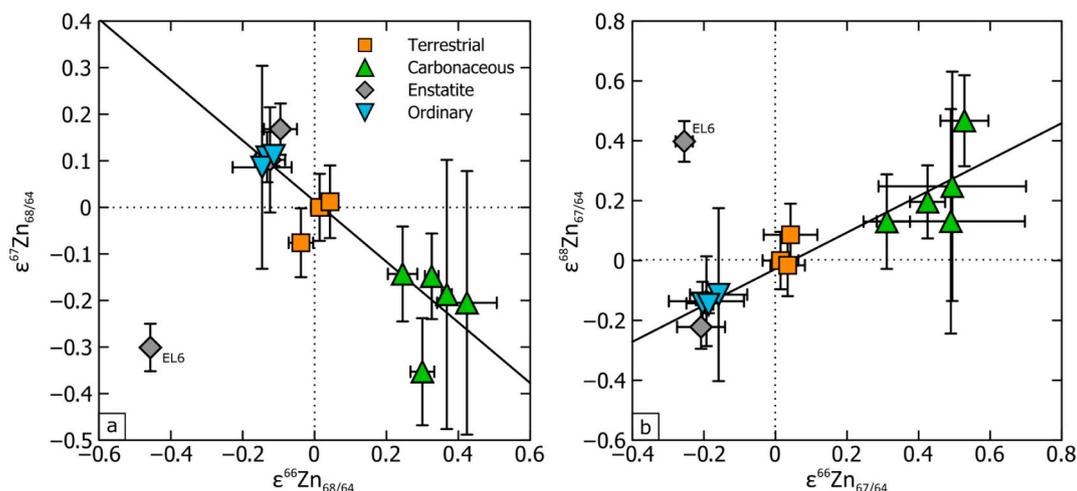


Fig. 2. $\epsilon^{67}\text{Zn}_{68/64}$ plotted against $\epsilon^{66}\text{Zn}_{68/64}$ (a) and $\epsilon^{68}\text{Zn}_{67/64}$ plotted against $\epsilon^{66}\text{Zn}_{67/64}$. Terrestrial, carbonaceous (CC) and non-carbonaceous (NC) follow a similar trend. Terrestrial samples have an intermediary Zn isotopic composition between CC and NC, in the two schemes of normalization. The EL6 sample is an exception that plots off the trend because of an incomplete correction of the large mass-fractionation of this sample (see text for detail).

et al., 2011) that the process of Zn loss from the EL6 was evaporative. Crucially, whichever process generated the highly fractionated Zn isotope composition of the EL6, it does not appear to have occurred to any significant degree on the other chondrite parent bodies. The distinctive Zn isotope anomaly pattern of the EL6 meteorites seems to rule out any significant involvement of similar material in the source of terrestrial Zn.

The higher volatility of Zn compared to the other IP elements poses a conundrum as to how anomalous Zn survived transport from its host star to the solar nebula, and the subsequent homogenisation therein. One possibility is sulphide, either as coatings on presolar grains or inclusions that survived within more refractory material (Haenecour et al., 2016). Presolar silicates could also be Zn-carriers; although condensation calculations suggest that most Zn condenses into troilite, olivine can take up some Zn (Wood et al., 2019), albeit at the ppm-level. This predicted low Zn concentration in presolar silicates makes it difficult to explain solar-system scale meteorite anomalies. A related question is which phase(s) currently control(s) the Zn isotopic anomalies. The largest Zn anomalies are always found in the most labile phases of the sequentially leached phases for both enstatite and carbonaceous meteorites (Fig. S2) which could lend support to a sulphide carrier phase; this is especially obvious in the EH3 meteorites where, even though the sulphide phases do not dominate the Zn budget in these meteorites, they have the largest anomalies. However, the comparable and relatively constant magnitude isotopic composition of all phases implies that the Zn anomalies have been redistributed via secondary processes, or that all Zn in the region of meteorite condensation was anomalous. Aqueous alteration is an efficient way of mobilising Zn, in the case of the carbonaceous chondrites, however, for the EH3 chondrites, Zn redistribution is more difficult to explain. Because of these complexities, although no strong constraints can be placed on the potential carrier(s) of the Zn anomalies at this stage, the EH3 meteorite leachate data might suggest that sulphides phases are the major carrier.

Given the stochastic nature of planetary accretion (Chambers, 2004; Walsh et al., 2011) and the significant variability of isotope anomalies in meteorites, both with respect to Earth and between groups (Dauphas et al., 2014), it is likely that no one meteorite group represents the Earth composition both in terms of isotopic and elemental composition. While enstatite chondrites are the isotopically closest to Earth (Javoy et al., 2010), these meteorites are chemically distinct (in particular in their very low Mg/Si ratio) to Earth and so a mixture of primitive meteorites or meteorite-like material is normally proposed, which best matches the chemical and/or isotopic composition of Earth (Dauphas et al., 2014;

Lodders, 2000; Mezger et al., 2021; Warren, 2011). The mixture is therefore model-dependent (we also note here that this sort of mixing model is not successful for s-process isotope anomalies, where Earth appears to be an end-member e.g. Kleine et al., 2020); nevertheless, the more isotope anomalies that are identified, the more constraints that can be placed on Earth's building blocks. For example, a mixture of 75% enstatite, 19% ordinary, 2% CI and 4% CO-CV chondrites to form Earth was proposed to generate the current terrestrial isotopic composition (Dauphas et al., 2014). Applying this mixture to the Zn anomaly data provides novel insight into Zn Earth's moderately volatile element accretionary history.

Firstly, the solution of Dauphas et al. (2014) requires 75% of enstatite chondrites in the mixture—the reason that this was not separated into EH and EL groups is because these two groups generally display similar anomaly patterns. Zinc is an exception, with EL6 having a very different pattern compared to EH (and all other) chondrites (Fig. 3). Because of this, EL6 chondrites are almost certainly not a component of Earth's building blocks; furthermore, because volatile loss is almost certainly the reason why EL6 chondrites have such fractionated Zn isotopes (Moynier et al., 2011), the lack of parity between EL6 and terrestrial patterns suggests that the volatile-poor nature of Earth compared to most chondritic materials is not due to volatile loss, but incomplete accretion of the volatile elements (Albarede et al., 2011; Braukmüller et al., 2019; Vollstaedt et al., 2020). Some of the strongest evidence for this is based on the mass-dependent Zn isotopic data (Luck et al., 2005; Pringle et al., 2017; Sossi et al., 2018); the least volatile-depleted (CI chondrites) are the isotopically heaviest while the most volatile-depleted (CV chondrites) are the isotopically lightest, the Earth being even isotopically lighter than the CV chondrites. This pattern is opposite to that which would be expected from evaporative loss of Zn after or during planetary formation and rather suggest that the Earth Zn reflects the composition of its accreting material.

If Zn behaved as a lithophile element, the Zn isotopic composition of the Earth mantle should reflect an average along Earth's accretion history (e.g. Dauphas, 2017). Furthermore, if EL6 meteorites are ruled out from Earth's building blocks, the preponderance of enstatite chondrite-like (and to a lesser extent, O-like) material in the mixture to explain the isotopic composition of the Earth (Boyett et al., 2018; Dauphas et al., 2014) allows further insight. Crucially, because terrestrial rocks have a distinct Zn isotope budget from both EH and O chondrites, the material that accreted to form Earth must have included a fraction of CC (i.e. outer solar system) material to generate Earth's Zn isotope composition, which is intermediate between NC (inner solar system) and CC (Fig. 2).

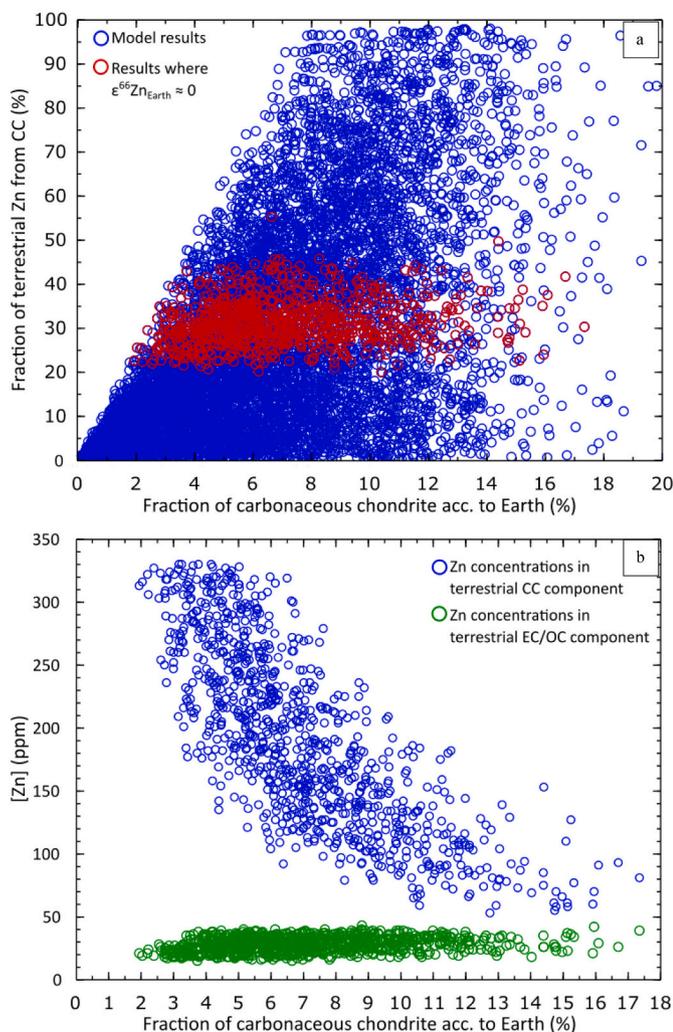


Fig. 3. Results of the Monte Carlo simulations of mixing between CC and NC materials to reproduce the Zn isotopic composition of the Earth. a) The amount of terrestrial Zn that would be delivered from CC is reported against the fraction of outer solar system (CC) material delivered to Earth. Between 0 and 100% of terrestrial Zn could be delivered from outer solar system material (blue dots) but only the red dots represent the model outputs with “terrestrial” Zn isotopic composition. b) The concentration of Zn coming from outer solar system (blue) and inner solar system (green) as a function of the amount of outer solar system material accreted to Earth-for the “terrestrial” (red) scenarios shown in panel a. The Zn concentration of inner solar system material must be depleted in Zn, to some extents by an order of magnitude, compared to that from the outer solar system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Applying a simple accretion mixture (e.g. 75% EC, 19% OC, 6% CC; Dauphas et al., 2014) to the Zn isotope data, weighting each anomaly by average meteorite group Zn abundance (Lodders and Fegley Jr, 1998), the resulting anomaly pattern does not match the terrestrial composition (i.e. $\epsilon^{\text{Zn}} \equiv 0$) as it would be dominated by the Zn isotopic composition of NC meteorites. This is because EH (and EL3) chondrites have relatively high concentrations of Zn (~ 250 ppm for EH and 100 to 220 ppm for EL3, Lodders and Fegley Jr, 1998; Rubin et al., 2009) and therefore dominate the mixing calculation. It could be that the material that accreted to form the Earth was isotopically similar but chemically different to the current inventory of primitive meteorites. Notably, it has been suggested that Earth material could have been akin to EH chondrite isotopic composition but condensed at higher temperature (Morbidelli et al., 2020), which would reduce the amount of Zn contribution from enstatite chondrite component by, for example, an order of magnitude

(~ 25 ppm instead of 250 ppm).

To explore this potential further, we apply a Monte Carlo mixing model to explore the Zn concentrations and fraction of terrestrial Zn input from the likely end-members during terrestrial accretion. Because of the similarity of inner solar system (NC) Zn isotope anomalies, an average of all these meteorites is used ($\epsilon^{66}\text{Zn} = -0.201 \pm 0.021$, 2sd). Again, although there is more variability in the CC Zn anomaly data, most individual CC $\epsilon^{66}\text{Zn}$ values are in error of each other, and a bulk average $\epsilon^{66}\text{Zn}$ “outer solar system” value of $+0.452 \pm 0.177$ (2sd) is utilised. The other input parameters are the approximate abundance of inner (EC/OC) material in the Earth (Dauphas et al., 2014) best estimate ($94.6 \pm 4.0\%$), and the maximum concentration of Zn from the inner (290 ppm) and outer (330 ppm) solar system material based on the highest concentrations of Zn measured in bulk enstatite and carbonaceous meteorites (Rubin et al., 2009; Wasson and Kallemeyn, 1988). The model inputs were allowed to vary around the 2sd precisions for $\epsilon^{66}\text{Zn}$ anomalies, from 80% to 100% for the amount of inner solar system accreted to Earth, and from 1 ppm to maximum Zn concentrations specified. At this stage, the only constraint on the model outputs was that final bulk terrestrial Zn concentration ranged from 45 to 80 ppm (this range is based on the potential that some Zn may have partitioned into the core; Mahan et al., 2018). If this constraint was not met, that run of the model was discarded.

The outputs of the model are shown in Fig. 3a, in terms of the amount of outer solar system (CC) material delivered to Earth vs. the amount of terrestrial Zn that would be delivered from this outer solar system material. At this stage, the model suggests that between 0 and 100% of terrestrial Zn can be delivered from outer solar system material. However, coloured in red are those model outputs whose final “terrestrial” Zn isotope anomaly is calculated to be $\epsilon^{66}\text{Zn} = 0.000 \pm 0.025$. These “terrestrial” scenarios are plotted in Fig. 3b. This figure shows the predicted concentration of Zn derived from outer solar system (blue) and inner solar system (green) material as a function of the amount of outer solar system material accreted to Earth. For all successful models, the Zn concentration of inner solar system material needs to be depleted in Zn compared to that from the outer solar system – this is in line with most assertions that the material delivered from outer solar system material should be more volatile-rich. What is also striking is how invariant the successful modelled Zn concentration from inner solar system material is – even though this parameter could vary freely from 1 to 290 ppm, all successful scenarios fall between 15 and 43 ppm Zn, with an average of 25 ppm. This is consistent with the suggestion that high temperature condensates from the inner solar system represent a bulk of Earth’s ingredients (Wanke and Dreibus, 1988; Morbidelli et al., 2020).

With reference to the amount of Zn (and by corollary, other MVE) that was accreted to Earth from carbonaceous sources, the outputs of the successful model results are summarised in Fig. 4 which show the mass fraction of carbonaceous chondrites accreted to Earth, as well as the mass fraction of terrestrial Zn this would represent. In terms of the amount of material accreted to Earth, the output distribution peak sits at 5.8% (range of 1.8 to 17.4%) which is very close to the outcome of outer solar system material predicted by other isotopic systems (e.g. Dauphas, 2017) and is therefore not in conflict with other isotope mixing models. In terms of the amount of terrestrial Zn that was delivered by outer solar system material, the successful model results suggest that at least 20% of terrestrial Zn comes from the outer solar system, with the peak at 29.9%. This value is in excellent agreement with the study of Sossi et al. (2018), who argue based on an elemental MVE mixing model, that a maximum of 35% of Earth’s Zn was delivered by a carbonaceous-like component. To summarise, Zn isotope anomalies imply that even though outer solar system material makes up $<10\%$ of the mass of material accreted to form the Earth, this material likely delivered a significant ($\sim 1/3$) amount of Earth’s budget of moderately volatile elements. This fraction of Zn is consistent with the posited late delivery of most terrestrial N, C, and noble gases (Marty, 2012), Hg (Meier et al., 2016; Moynier et al., 2020), S, Se and Te (Wang and Becker, 2013) and potentially with a large

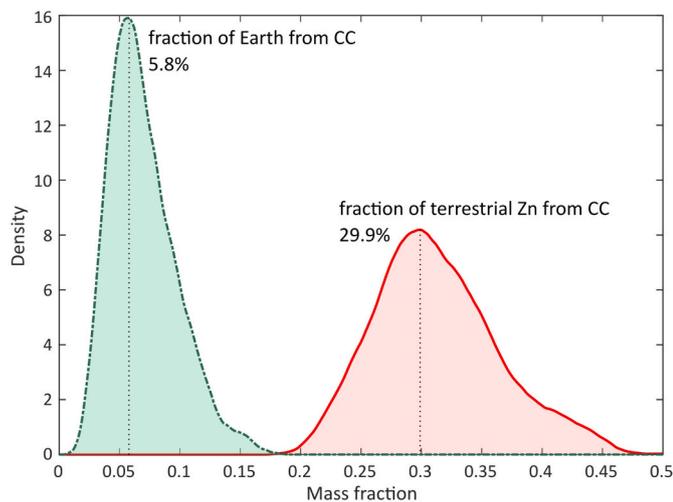


Fig. 4. Mass fraction of carbonaceous chondrites accreted to Earth, as well as the mass fraction of terrestrial Zn this would represent calculated to reproduce the Zn isotopic composition of the Earth. 5.8% of the Earth material must have been delivered as CC, which is very close to the outcome of outer solar system material predicted based on other isotopic compositions (Dauphas et al., 2014).

fraction of Ag, Cu and Fe (Savage et al., 2015; Schiller et al., 2020; Schonbachler et al., 2010) – this is assuming that a large component of Earth’s volatiles were delivered by a CC-like, more oxidised component. Particularly, if Zn did partition into the core during differentiation (Mahan et al., 2018), this small amount of CC-like material needed to be delivered late, as otherwise this signature would be mostly subsumed into the core. Finally, up to 10% of carbonaceous chondrite-like material needed to account for the Zn isotopic composition of the Earth is fully consistent with the assertion that carbonaceous chondrites represent a significant component of the terrestrial MVE abundances (Braukmüller et al., 2019).

Author contributions

Conceptualization: FM, PS, MB
 Methodology: PS, FM
 Analysis: PS.
 Interpretations: PS, FM, MB.
 Supervision: FM
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Declaration of Competing Interest

Authors declare that they have no competing interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.icarus.2022.115172>.

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