

Nucleosynthetic zinc isotope anomalies reveal a dual origin of terrestrial volatiles

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ABSTRACT

Determining the provenance of volatile elements in Earth is key for understanding the processes that led to its formation as a habitable planet. We show that the moderately volatile element zinc exhibits an isotopic dichotomy between non-carbonaceous and carbonaceous meteorites, which presumably derive from the inner and outer Solar System, respectively. Terrestrial zinc has an intermediate isotopic composition, demonstrating that Earth accreted about 70% of its zinc from inner Solar System bodies. Using literature data, we find the same proportions for the more volatile elements hydrogen and nitrogen, suggesting Earth's volatile elements predominantly derive from inner Solar System objects and not, as often assumed, from the outer Solar System. Thus, Earth may have evolved to a habitable planet even without the contributions it received from the outer Solar System.

1. Introduction

Determining the processes by which Earth accreted volatile elements is key for understanding terrestrial planet formation and a possible pathway for the emergence of a habitable planet. Volatile elements are defined as having half-mass condensation temperatures (T_C) from a gas of solar composition below those of the major rock-forming elements Mg, Si, and Fe, and are subdivided into moderately ($T_C > \sim 670$ K) and highly volatile elements ($T_C < \sim 670$ K) (Palme and O'Neill, 2014). In Earth, all volatile elements are depleted compared to the primordial material of the solar accretion disk as recorded in the composition of the Sun and the most primitive meteorites, the CI (Ivuna-type) carbonaceous chondrites (Palme and O'Neill, 2014). In spite of this depletion, Earth contains volatile elements with $T_C < 750$ K in approximately CI-chondritic relative abundances, suggesting it accreted from a mixture of volatile-poor and volatile-rich building materials (Braukmüller et al., 2019; Mezger et al., 2021; Sossi et al., 2018). However, the provenance of the volatile-rich building blocks and whether they derive from the inner or outer Solar System is debated. It has been suggested that the isotopic composition of the highly volatile elements H and N in Earth's mantle and hydrosphere points towards derivation from volatile-rich CI and CM (Mighei-type) chondrites, which formed in the outer Solar System beyond the water ice line (Alexander et al., 2012; Marty, 2012).

However, more recent work has shown that the H and N isotopic composition of Earth's mantle overlaps with that of enstatite chondrites, which formed in the inner Solar System (Piani et al., 2020). Thus, because the H and N isotope compositions of Earth's mantle and hydrosphere overlap with both enstatite and carbonaceous chondrites, distinguishing between an inner and outer Solar System origin of Earth's volatile elements is difficult based solely on these two elements. The source of terrestrial volatiles may instead be determined using moderately volatile elements, because any material that delivered the highly volatiles must have also delivered elements with higher condensation temperatures.

Nucleosynthetic isotope anomalies offer the most direct way of identifying the origin of the material accreted by Earth. These anomalies arise through the heterogeneous distribution of presolar matter in the solar accretion disk, making them powerful tracers of genetic links among planetary building blocks (Burkhardt et al., 2021; Dauphas, 2017). These isotope anomalies reveal a division of the disk into the non-carbonaceous (NC) and carbonaceous (CC) reservoirs (Budde et al., 2016; Kruijjer et al., 2017; Warren, 2011), which have been suggested to represent the inner and outer Solar System, respectively. Proposed mechanisms for the separation of these two reservoirs include the early formation of Jupiter (Kruijjer et al., 2017), a structured protoplanetary disk (Brasser and Mojzsis, 2020; Charnoz et al., 2021; Morbidelli et al.,

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Table 1

Mass-independent Zn isotope compositions of meteorites and terrestrial samples. $\mu^{6x}\text{Zn} = [({}^{6x}\text{Zn}/{}^{64}\text{Zn})_{\text{sample}}/({}^{6x}\text{Zn}/{}^{64}\text{Zn})_{\text{SRM683}} - 1] \times 10^6$ with $x = 6, 7, 8$, after mass-bias correction by internal normalization to either ${}^{68}\text{Zn}/{}^{64}\text{Zn}$ or ${}^{67}\text{Zn}/{}^{64}\text{Zn}$. All uncertainties are two-sided Student's-t 95% confidence intervals.; n is the number of repeat analyses.

Sample	Group/type	${}^{67}\text{Zn}/{}^{64}\text{Zn}$ int. norm.		${}^{68}\text{Zn}/{}^{64}\text{Zn}$ int. norm.		n
		$\mu^{67}\text{Zn}$	$\mu^{68}\text{Zn}$	$\mu^{67}\text{Zn}$	$\mu^{68}\text{Zn}$	
<i>Terrestrial samples</i>						
BCR-2	Basalt	-10 ± 3	-5 ± 7	-7 ± 3	4 ± 5	26
BHVO-2	Basalt	-8 ± 3	-2 ± 5	-7 ± 2	1 ± 4	43
JA-2	Andesite	-11 ± 6	-4 ± 10	-9 ± 2	3 ± 8	14
Average BSE		-9 ± 2	-3 ± 4	-7 ± 1	2 ± 3	
<i>Carbonaceous chondrites</i>						
Orgueil	CI1	27 ± 5	11 ± 8	21 ± 3	-8 ± 6	16
Tarda	C2-ung.	34 ± 6	18 ± 6	24 ± 6	-14 ± 5	15
J. Winselwan	CM2	32 ± 5	16 ± 10	24 ± 2	-12 ± 7	20
Allende	CV3	34 ± 2	16 ± 4	25 ± 1	-13 ± 3	68
Vigarano	CV3	34 ± 4	12 ± 7	28 ± 2	-9 ± 5	15
Kainsaz	CO3	29 ± 4	14 ± 6	23 ± 3	-10 ± 4	18
<i>CC iron meteorites</i>						
Carbo	IID	30 ± 4	12 ± 9	23 ± 3	-9 ± 7	18
<i>Ordinary chondrites</i>						
Beaver Creek	H4	-31 ± 5	1 ± 7	-32 ± 6	-1 ± 5	13
Bjurböle	L/LL4	-23 ± 5	-6 ± 6	-20 ± 3	4 ± 4	14
NWA 5206	LL3.05	-22 ± 12	-12 ± 13	-16 ± 10	9 ± 10	5
Parnallee	LL3	-36 ± 5	-7 ± 11	-32 ± 4	6 ± 9	8
Ragland	LL3.4	-30 ± 9	-18 ± 19	-20 ± 6	14 ± 14	6
Soko Banja	LL4	-35 ± 9	-22 ± 23	-24 ± 5	16 ± 17	5
Tennasilm	L4	-35 ± 10	-15 ± 15	-27 ± 3	12 ± 11	6
Umm Ruaba (B)	L4	-43 ± 8	-30 ± 15	-28 ± 5	23 ± 11	5
Average OC		-32 ± 6	-14 ± 8	-25 ± 5	10 ± 6	
<i>Enstatite chondrites</i>						
Almahata Sitta MS-150	EL6	-21 ± 6	-8 ± 10	-17 ± 3	6 ± 8	8
Indarch	EH4	-26 ± 3	-14 ± 6	-19 ± 3	11 ± 5	18
MAC 02837	EL3	-20 ± 11	-9 ± 18	-15 ± 8	7 ± 14	6
PCA 91020	EL3	-24 ± 4	-13 ± 6	-17 ± 2	10 ± 5	19
Sahara 97,072	EH3	-23 ± 4	-9 ± 8	-18 ± 3	7 ± 6	14
Average EC		-23 ± 3	-11 ± 3	-17 ± 2	8 ± 3	
<i>NC iron meteorites</i>						
Canyon Diablo	IAB	-34 ± 5	-5 ± 7	-32 ± 4	3 ± 6	14
Henbury	IIIAB	-36 ± 5	-4 ± 10	-34 ± 6	3 ± 7	14
Saint-Aubin	IIIAB	-37 ± 17	-19 ± 32	-27 ± 12	14 ± 24	1
Mt. Dooling	IC	-41 ± 4	-22 ± 9	-30 ± 3	16 ± 7	12
<i>Ureilites</i>						
ALH 77257	Ureilite	-42 ± 7	-22 ± 9	-31 ± 5	16 ± 7	9
EET 96293	Ureilite	-45 ± 10	-24 ± 14	-33 ± 5	18 ± 11	7
GRO 95575	Ureilite	-39 ± 11	-11 ± 10	-34 ± 6	8 ± 7	6
LAP 03587	Ureilite	-45 ± 6	-18 ± 10	-36 ± 2	14 ± 7	18
NWA 5938	Ureilite	-40 ± 10	-14 ± 23	-33 ± 5	11 ± 17	7
Average Ureilite		-42 ± 4	-18 ± 7	-33 ± 2	13 ± 5	

2022), and migration of the water ice line leading to planetesimal formation at distinct radial locations in the disk (Lichtenberg et al., 2021). Regardless of the exact mechanism by which the NC and CC reservoirs were separated, identifying a NC-CC dichotomy for volatile elements would provide a powerful tool for determining the provenance of these elements in Earth and whether they derive from the inner (NC reservoir) or outer (CC reservoir) Solar System. However, until now nucleosynthetic isotope anomalies have been identified exclusively for non-volatile elements (Kleine et al., 2020) and are thought to be absent for volatile elements, which owing to their lower condensation temperatures may have been more readily homogenized throughout the disk (Vollstaedt et al., 2020). A recent study suggested that isotope variations in the volatile element K ($T_C \sim 993$ K) are nucleosynthetic in origin (Ku and Jacobsen, 2020), but these variations show no clear NC-CC

dichotomy and may also reflect mass-dependent isotope fractionation (Tian et al., 2021).

The moderately volatile element Zn ($T_C \sim 704$ K) is a promising target to search for nucleosynthetic isotope anomalies, because it belongs to the Fe-peak elements which show abundant isotope anomalies (Trinquier et al., 2009) and because it exhibits isotope anomalies in some Ca,Al-rich inclusions (CAI) from primitive chondrites (Loss and Lugmair, 1990; Volkening and Papanastassiou, 1990). Such CAI typically carry isotope anomalies for several non-volatile elements (Brennecka et al., 2020), and all these elements reveal the NC-CC dichotomy among bulk meteorites (Nanne et al., 2019). Here we show that Zn exhibits the same fundamental isotopic dichotomy between NC and CC materials as non-volatile elements, and use this observation to constrain the provenance of volatile elements in Earth.

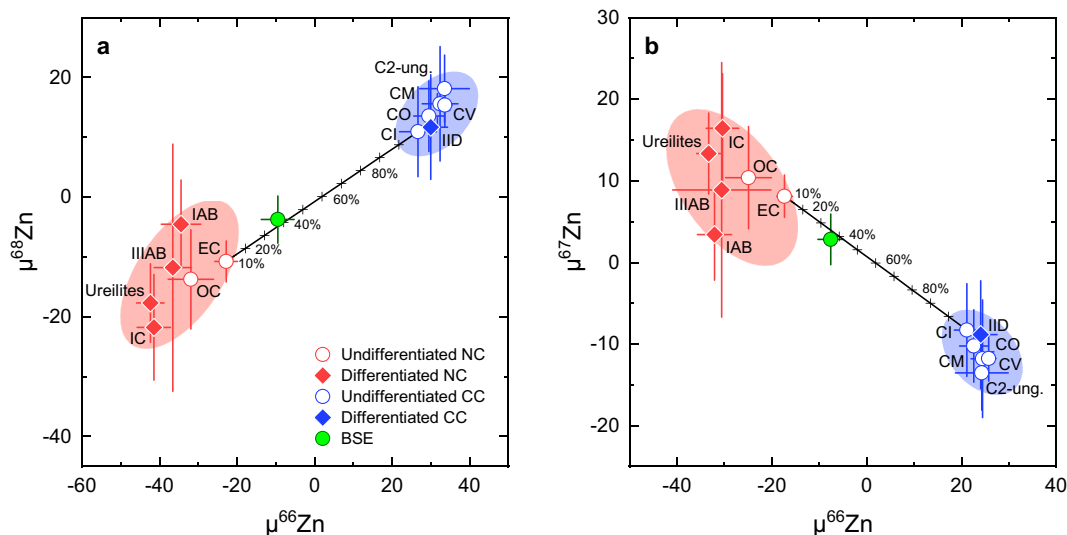


Fig. 1. Zinc isotope anomalies of meteorites and terrestrial samples. NC (inner Solar System) and CC meteorites (outer Solar System) exhibit distinct Zn isotope compositions. This distinction exists regardless of whether the data are internally normalized to $^{67}\text{Zn}/^{64}\text{Zn}$ (a) or $^{68}\text{Zn}/^{64}\text{Zn}$ (b). The bulk silicate Earth (BSE) has an intermediate Zn isotope composition and can be reproduced by a $\sim 70:30$ mixture of Zn from the NC and CC reservoirs (black solid line). This mixing line connects enstatite and CI chondrites, but other mixing lines connecting the NC and CC fields result in similar proportions of NC- and CC-derived Zn. See text for details. Error bars are 95% confidence intervals.

2. Nucleosynthetic zinc isotope dichotomy

2.1. Zinc isotope results

We measured the Zn isotope composition of several NC and CC meteorites as well as terrestrial rock samples (see Table 1). The sample set includes meteorites of different accretion ages (iron meteorites, chondrites) of both NC and CC heritage, and samples with the most extreme nucleosynthetic isotope anomalies from a given reservoir, such as ureilites and enstatite chondrites from the NC reservoir, and CI and CV (Vigarano-type) chondrites from the CC reservoir. This comprehensive sample set allows assessing how any nucleosynthetic Zn isotope heterogeneity among and between the NC and CC reservoirs may have evolved in time and space. The Zn isotopic data are internally normalized to a defined $^{67}\text{Zn}/^{64}\text{Zn}$ to correct for instrumental and natural mass-dependent fractionation using the exponential law, and are reported as $\mu^{66}\text{Zn}$ and $\mu^{68}\text{Zn}$ values, which are the parts-per-million deviations of a sample's $^{66}\text{Zn}/^{64}\text{Zn}$ and $^{68}\text{Zn}/^{64}\text{Zn}$ ratios from those of the standard (see supplementary materials). To assess internal consistency, the data are also reported as $\mu^{66}\text{Zn}$ and $\mu^{67}\text{Zn}$ values after internal normalization to a defined $^{68}\text{Zn}/^{64}\text{Zn}$. No data are reported for the low abundance isotope ^{70}Zn (0.62%), because the analytical setup did not allow for the simultaneous measurement of all Zn isotopes.

The NC and CC meteorites from this study have systematically different Zn isotopic compositions, where all NC meteorites exhibit negative $\mu^{66}\text{Zn}$ (from approximately -42 to -23 ppm) and $\mu^{68}\text{Zn}$ (from about -18 to -11 ppm), while all CC meteorites are characterized by positive $\mu^{66}\text{Zn}$ and $\mu^{68}\text{Zn}$ values of about $+30$ and $+15$ ppm, respectively (Table 1, Fig. 1). In addition, there are small variations among the NC meteorites, with ureilites having the largest and enstatite chondrites the smallest ^{66}Zn and ^{68}Zn deficits (Fig. 1a). By contrast, all CC meteorites, including various chondrites and one iron meteorite, have indistinguishable Zn isotope compositions, although CI chondrites may have slightly smaller $\mu^{66}\text{Zn}$ and $\mu^{68}\text{Zn}$ values than the other CC meteorites. The meteorites also fall into two clusters when the Zn isotope data are normalized to $^{68}\text{Zn}/^{64}\text{Zn}$ instead of $^{67}\text{Zn}/^{64}\text{Zn}$. For this alternative normalization NC meteorites exhibit negative $\mu^{66}\text{Zn}$ (from about -33 to -17 ppm) and positive $\mu^{67}\text{Zn}$ values (from about 8 to 13 ppm), while CC meteorites have complementary positive $\mu^{66}\text{Zn}$ and negative $\mu^{67}\text{Zn}$

values of approximately $+24$ and -12 ppm, respectively (Fig. 1b). Thus, NC and CC meteorites have systematically distinct Zn isotopic compositions regardless of the particular normalization of the data.

The terrestrial samples exhibit small ^{66}Zn and ^{68}Zn deficits compared to the standard (Fig. 1), which likely result from isotopic fractionation of Zn during production of the high-purity standard (supplementary materials), as has been observed for several other elements (Budde et al., 2019; Steele et al., 2011; Zhang et al., 2012). Regardless of this small offset, both the terrestrial samples and the solution standard used in this study plot between the NC and CC compositional fields.

2.2. Origin of zinc isotope anomalies

Before the Zn isotope anomalies among meteorites can be interpreted in terms of nucleosynthetic variability, it is important to consider other potential processes that may have resulted in the observed isotope variations. For instance, apparent isotope anomalies may arise from non-exponential mass-dependent isotope fractionation that is not fully corrected for using the internal normalization of the data (Tang and Dauphas, 2012). However, this process would result in Zn isotope correlations that are almost perpendicular to those observed among the meteorites (supplementary materials). Moreover, the mass-dependent Zn isotope variations among most of the samples of this study are smaller than 0.5 ‰/amu (Table S1), such that any improper correction for non-exponential mass fractionation would result in $\mu^{66}\text{Zn}$ shifts of only <8 ppm (supplementary materials). Thus, neither the ~ 70 ppm $\mu^{66}\text{Zn}$ difference between NC and CC meteorites nor the ~ 20 ppm $\mu^{66}\text{Zn}$ variations among the NC meteorites reflect unaccounted mass fractionation effects. Isotope anomalies may also arise from mass-independent fractionation by the nuclear field shift effect (Nishizawa et al., 1993), but this would result in larger variations in $\mu^{67}\text{Zn}$ and $\mu^{68}\text{Zn}$ compared to $\mu^{66}\text{Zn}$, which is opposite to the relative magnitude of Zn isotope anomalies observed among the meteorites (Fig. S2). Finally, the interaction with galactic cosmic rays (GCR) may also lead to isotope anomalies. However, the CC iron meteorite Carbo (group IID) is one of the most strongly irradiated iron meteorites known (Krujjer et al., 2013) but its Zn isotope composition is indistinguishable from those of the carbonaceous chondrites analyzed in this study, all of which are characterized by much shorter cosmic ray exposure times. Thus, GCR-

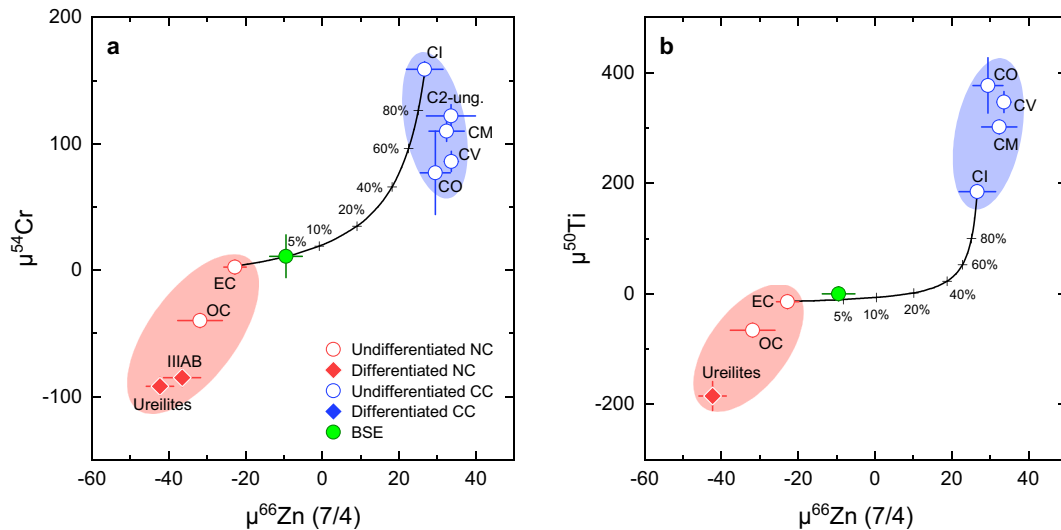


Fig. 2. Relation of Cr, Ti, and Zn isotope anomalies among meteorites and the bulk silicate Earth (BSE). Isotope anomalies in the moderately volatile element Zn are correlated with anomalies in the non-volatile elements Cr (a) and Ti (b). The BSE is offset from the NC correlations and its isotopic composition can be accounted for by admixture of ~5 wt.-% CI-like material to a proto-BSE having an enstatite chondrite-like isotopic composition and Zn, Cr, and Ti concentrations calculated by subtracting the amount of added CI-derived element from the present-day BSE concentrations. Cr and Ti isotope data from compilation in Spitzer et al. (2020). Error bars are 95% confidence intervals.

induced shifts also cannot be responsible for the observed Zn isotope variations among meteorites. The Zn isotope anomalies are, therefore, best understood as being nucleosynthetic in origin.

This interpretation is supported by the observation that the Zn isotope compositions of meteorites define two distinct clusters that correspond to the NC-CC dichotomy (Fig. 1) as defined by nucleosynthetic isotope anomalies of other elements such as Cr and Ti. Accordingly, in diagrams of $\mu^{66}\text{Zn}$ versus $\mu^{50}\text{Ti}$ or $\mu^{54}\text{Cr}$, NC and CC meteorites plot in two distinct fields corresponding to the NC and CC groups (Fig. 2). Moreover, among the NC meteorites the $\mu^{66}\text{Zn}$ variations are correlated with those in $\mu^{50}\text{Ti}$ or $\mu^{54}\text{Cr}$ (Fig. 2). Thus, Zn does not only show the same fundamental NC-CC dichotomy previously observed for non-volatile elements, but it also conforms to the ubiquitous multi-element co-variations of isotope anomalies among NC meteorites (Burkhardt et al., 2021; Spitzer et al., 2020).

The need for internal normalization of the isotopic data to correct for instrumental mass fraction makes it difficult to identify which of the Zn isotopes are enriched or depleted relative to the terrestrial standard. Nevertheless, the finding that ^{66}Zn excesses are coupled with ^{68}Zn excesses and ^{67}Zn deficits indicates that more than one Zn isotope is anomalous, because variations in solely ^{64}Zn would result in negative $\mu^{66}\text{Zn}$ and positive $\mu^{68}\text{Zn}$ values ($^{67}\text{Zn}/^{64}\text{Zn}$ normalization) or negative $\mu^{66}\text{Zn}$ and $\mu^{67}\text{Zn}$ ($^{68}\text{Zn}/^{64}\text{Zn}$ normalization), which is inconsistent with the observed Zn isotope patterns (Fig. 1; Fig. S3). Moreover, the occurrence of ^{66}Zn excesses in CC meteorites in both normalizations suggests that CC meteorites are indeed characterized by enrichments in ^{66}Zn . Although more complex mixtures of isotope anomalies cannot be excluded, the observed Zn isotope pattern would be consistent with coupled ^{66}Zn and ^{68}Zn enrichments, or ^{66}Zn excesses combined with ^{67}Zn deficits (Fig. S3). It is noteworthy that coupled ^{66}Zn and ^{68}Zn enrichments are predicted to occur by nuclear statistical equilibrium during explosive Si burning in massive stars, which also produces excesses in the neutron-rich isotopes of other Fe-group elements such as ^{50}Ti and ^{54}Cr (Hartmann et al., 1985). As such, the coupled ^{50}Ti , ^{54}Cr , and $^{66,68}\text{Zn}$ excesses in CC meteorites are consistent with the observation that the CC reservoir in general is enriched in nuclides produced in neutron-rich stellar environments (Budde et al., 2016; Kleine et al., 2020; Nanne et al., 2019).

The finding that the volatile element Zn exhibits the same fundamental NC-CC isotopic dichotomy previously observed for non-volatile

elements reveals that the nucleosynthetic isotope variability among meteorites does not primarily depend on an element's volatility. Nevertheless, the isotope variability among bulk meteorites for Zn is smaller (~70 ppm range for $\mu^{66}\text{Zn}$) than for other elements like Ti and Cr (~500 ppm range for $\mu^{50}\text{Ti}$; ~250 ppm range for $\mu^{54}\text{Cr}$). This may reflect more efficient homogenization of isotopically anomalous presolar carriers for volatile elements like Zn than for more refractory elements like Ti and Cr. However, Ni displays a similar overall isotopic variability (~100 ppm range for $\mu^{64}\text{Ni}$) as Zn, although it is more refractory and has a similar condensation temperature as Cr. Overall, these observations are difficult to reconcile with an origin of this variability by thermal processing in the disk, but are consistent with a model in which the NC-CC dichotomy is governed by mixing between two isotopically distinct but chemically unfractionated disk reservoirs, where the presence of the dichotomy depends on whether or not an element is isotopically anomalous in CAI (Burkhardt et al., 2019; Nanne et al., 2019).

3. Mixed NC-CC heritage of moderately volatile elements in Earth

In terms of nucleosynthetic isotope anomalies, the bulk silicate Earth (BSE) is expected to be largely homogeneous, and so the terrestrial rocks analyzed in this study provide a good proxy for the Zn isotope composition of the entire BSE. This composition is offset from the NC compositional range (Fig. 1), and plots off the $\mu^{50}\text{Ti}$ - $\mu^{66}\text{Zn}$ and $\mu^{54}\text{Cr}$ - $\mu^{66}\text{Zn}$ NC correlations towards the composition of CC meteorites (Fig. 2). Thus, terrestrial Zn has a mixed NC-CC heritage, implying that Earth accreted volatiles from different areas of the disk, which most likely included the inner (NC reservoir) and outer (CC reservoir) Solar System.

To quantify the relative contributions of NC- and CC-derived Zn to Earth, it is useful to assume that terrestrial Zn is a simple two-component mixture of NC and CC materials. As a moderately volatile element, Zn is depleted in the BSE, and so the Zn concentrations of the NC and CC bodies accreted by Earth are likely variable. As such, the amount of NC- and CC-derived Zn in the BSE cannot be calculated by assuming chondritic Zn concentrations for the material accreted by Earth. Instead, it is useful to determine the mass fraction of CC-derived Zn in the BSE, which can be calculated independently of the Zn concentrations as follows (supplementary materials):

$$f_{CC}(Zn)_{BSE} = \frac{\mu^{66}Zn_{BSE} - \mu^{66}Zn_{NC}}{\mu^{66}Zn_{CC} - \mu^{66}Zn_{NC}}$$

Using the average $\mu^{66}Zn_{NC} = -33 \pm 17$ (2 s.d.), $\mu^{66}Zn_{CC} = 31 \pm 6$ (2 s.d.), and $\mu^{66}Zn_{BSE} = -9 \pm 2$ (2 s.d.) determined in this study, a mass fraction of CC-derived Zn in the BSE of 0.36 ± 0.19 (2 s.d.) is computed.

This value does not change significantly if other specific Zn isotope compositions for the NC and CC materials are used. For instance, for most elements, the BSE is isotopically most similar to enstatite chondrites, which has been interpreted to indicate that Earth predominantly accreted from material with this particular isotope composition (Dauphas, 2017). Alternatively, enstatite chondrites may merely record the average isotopic composition of the heterogeneous NC material accreted by Earth (Burkhardt et al., 2021). This is supported by the observations that the isotope anomalies among NC meteorites are linearly correlated for elements of different geo- and cosmochemical character (Spitzer et al., 2020) and that the BSE consistently plots close to these correlations, indicating that as soon as the BSE is isotopically similar to enstatite chondrites for one element, it will be so for other elements (Burkhardt et al., 2021). Thus, because the Zn isotope anomalies among NC materials are also correlated with those in other elements (Fig. 2), it is reasonable to assume that the NC-derived terrestrial Zn on average had an enstatite chondrite-like isotopic composition. This is also consistent with the position of the BSE in the $\mu^{66}Zn$ versus $\mu^{54}Cr$ and $\mu^{50}Ti$ diagrams, because mixing lines connecting other NC compositions with the CC field do not pass consistently through the BSE's isotopic composition (Fig. 2). Note that assuming an enstatite chondrite-like isotopic composition for the NC-derived Zn does not mean that this Zn was delivered by enstatite chondrites themselves, but merely that it comes from bodies whose isotopic composition is on average enstatite chondrite-like. Using $\mu^{66}Zn_{NC} = -23 \pm 3$ (2 s.d.) as measured here for enstatite chondrites results in a mass fraction of CC-derived Zn in the Earth of 0.26 ± 0.06 (2 s.d.). This value changes to 0.28 ± 0.07 (2 s.d.) if $\mu^{66}Zn_{CC} = 27 \pm 5$ as measured for CI chondrites is used for the CC-derived Zn. Thus, regardless of the particular Zn isotope composition assumed for the NC and CC materials that delivered Zn to Earth, we consistently find that only ~30% of the terrestrial Zn derives from the CC reservoir, while ~70% is from the NC reservoir.

The fractions of NC- and CC-derived Zn calculated above do not correspond to the mass fractions of NC and CC bodies accreted by Earth, because these bodies likely were variably depleted in volatile elements like Zn. Consequently, calculating the fractions of NC and CC bodies accreted by Earth from the Zn isotope data requires assumptions about the Zn concentrations of these bodies. For instance, the mass fraction of CC bodies accreted by Earth can be calculated as follows (supplementary materials):

$$f_{CC}(Earth) = f_{CC}(Zn)_{BSE} \cdot \frac{[Zn]_{BSE}}{[Zn]_{CC}}$$

where $[Zn]_{BSE}$ is the known Zn concentration of BSE of 54 ± 10 ppm (Palme and O'Neill, 2014), and $[Zn]_{CC}$ is the average Zn concentration of the accreted CC material. Using a CI chondrite-like Zn concentration for this material results in a CC mass fraction in Earth of 0.05 ± 0.02 (2 σ), while using a lower, CV chondrite-like Zn concentration results in a value of 0.12 ± 0.04 (2 σ) (in both cases using the $\mu^{66}Zn$ of enstatite chondrites for the NC-derived Zn). The CC mass fractions would increase further when even lower Zn concentrations are assumed, but several observations indicate that this is unlikely. First, given that CC bodies formed at greater heliocentric distances than NC bodies, it seems quite unlikely that the CC material was characterized by stronger average volatile element depletions than the NC material accreted by Earth. Second, the BSE displays CI-chondritic relative abundances of volatile lithophile elements with condensation temperatures (T_C) below 750 K, indicating that these elements, including Zn, were added to Earth by objects with unfractionated volatile element abundances (Braukmüller et al., 2019). Moreover, for elements with $T_C < 750$ K, all carbonaceous

chondrites are characterized by CI-chondritic relative but variable absolute abundances, where CV chondrites display the lowest volatile element abundances (Alexander et al., 2012; Hellmann et al., 2020). Thus, the CC mass fraction of 0.12 ± 0.04 as calculated using a CV chondrite-like Zn concentration provides a reasonable upper limit for the amount of CC material accreted by Earth. Finally, using nucleosynthetic isotope anomalies for a comprehensive set of non-volatile elements, it has been shown that Earth accreted only ~4% CC material (<21% at the 2 σ level) (Burkhardt et al., 2021). This mass fraction is remarkably consistent with those calculated above, suggesting not only that the CC-derived Zn in Earth is from objects with carbonaceous chondrite-like Zn contents, but also that the simple two-component mixing model for terrestrial Zn used here is consistent with the BSE's isotopic composition of non-volatile elements. In particular, the BSE's position in the $\mu^{66}Zn$ versus $\mu^{54}Cr$ and $\mu^{50}Ti$ diagrams is consistent with admixture of ~5% CI chondrite-like material to a proto-BSE having an enstatite chondrite-like isotopic composition (Fig. 2).

Although the Zn isotope data do not directly constrain the timing of volatile element delivery to Earth, chemical models for the growth and differentiation of Earth predict that the provenance of Earth's building blocks changed to more oxidized bodies from greater heliocentric distance during the later stages of accretion (e.g., Rubie et al., 2015). This suggests that the CC-derived Zn was added to Earth relatively late, while the NC-derived Zn was already present earlier because it was inherited from Earth's major building blocks. This is consistent with the average enstatite chondrite-like isotopic composition of the NC-derived Zn in Earth (Fig. 2), which also is the average isotopic composition of Earth's major building blocks (Burkhardt et al., 2021; Dauphas, 2017). Moreover, the late delivery of CC-derived Zn is in line with the BS mixed NC-CC Mo isotopic composition, which suggests that Earth accreted CC material during the last ~10% of its growth (Budde et al., 2019). Nevertheless, the CC-derived Zn in Earth may not all derive from accretion of CC bodies themselves, but may also be inherited from building blocks that already had mixed NC-CC signatures as a result of prior collisions between NC and CC bodies.

4. Volatile accretion history of earth

The finding of a mixed NC-CC heritage of terrestrial Zn is consistent with evidence for a mixed NC-CC origin of the highly volatile elements H and N in Earth (Piani et al., 2020). Although the BSE's D/H and $^{15}N/^{14}N$ ratios were originally interpreted to indicate a CI/CM-like source (Alexander et al., 2012; Marty, 2012), it has more recently been shown that the H and N isotopic composition of Earth's mantle is indistinguishable from that of enstatite chondrites (Piani et al., 2020). These authors also showed that the H and N isotopic compositions of Earth's surficial reservoirs (atmospheres + oceans) are distinct from enstatite chondrites and seem to require the contribution from CI-like material (Piani et al., 2020). Thus, similar to the Zn isotope data from this study, the BSE's H and N isotopic composition also point towards a mixed origin consisting of enstatite chondrite- and CI chondrite-like materials.

To facilitate direct comparison of the H and N results with the Zn isotope results of this study, we applied the same mixing model as for Zn isotopes to the highly volatile elements H and N. As noted above, this mixing model is independent of the absolute concentrations of the elements considered and, therefore, does neither depend on the assumed concentrations of these elements in the NC and CC materials accreted by Earth, nor on the poorly known concentrations of H and N in bulk Earth. A further advantage of this model is that it provides direct information on the extent of volatile element depletion of the NC and CC materials accreted by Earth, because for any volatile-depleted material the mass fractions of H and N would be lower than for the less volatile Zn.

Using the previously reported characteristic D/H and $^{15}N/^{14}N$ ratios of the BSE (which for highly volatile elements includes mantle, crust, oceans, and atmosphere), CI and enstatite chondrites (supplementary materials), our mixing model reveals that only about 30% of the

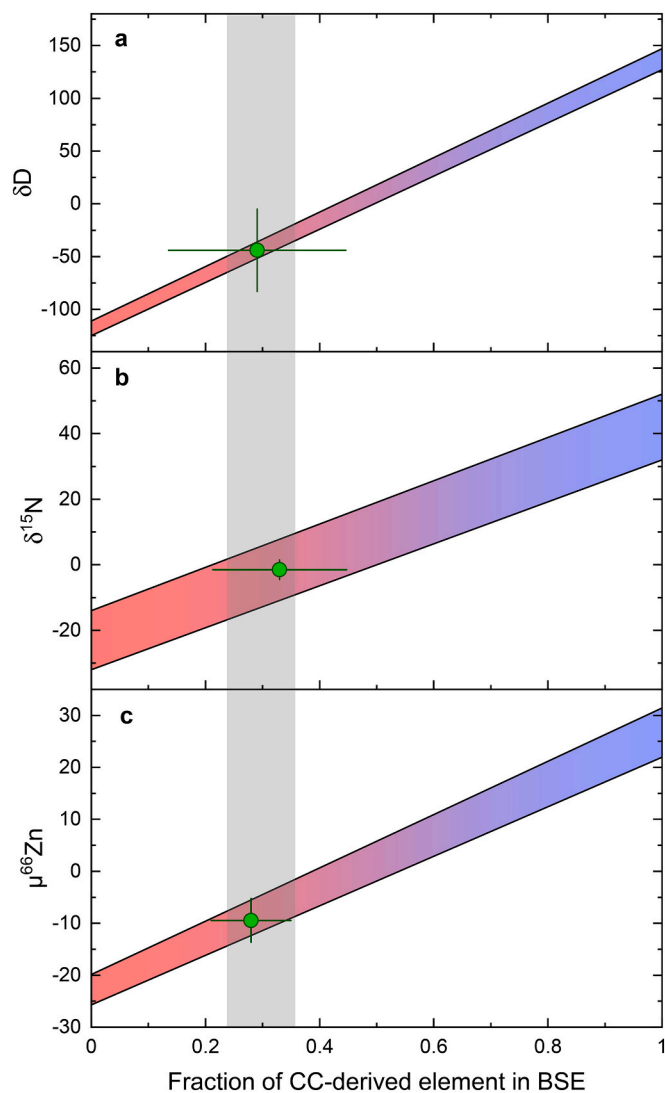


Fig. 3. Mixing relations between enstatite chondrite- and CI chondrite-like materials and how they link to the N, H, and Zn isotope composition of the bulk silicate Earth (BSE). The red and blue colors indicate NC and CC heritage, where the two endmembers used in this model have enstatite chondrite-like and CI chondrite-like isotopic compositions, respectively. The isotopic composition of BSE is consistent with about 30% of N, H, and Zn originating from CI chondrite-like material, while the remainder would derive from inner Solar System material with an on average enstatite chondrite-like isotopic composition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

terrestrial N and D derive from the CC reservoir, while the remainder comes from the NC reservoir. Thus, despite the large range in volatility of Zn, N, and H, the NC- and CC-derived proportions of these elements in Earth are the same (Fig. 3). This suggests strongly that these elements were added to Earth together and, hence, through accretion of the same volatile-undepleted objects from both the NC and CC reservoirs.

The results from this study using Zn isotopes, therefore, show that about 70% of Earth's volatile element inventory comes from the NC reservoir and, hence, the inner disk. It thus appears that the habitability of Earth is not tied to the accretion of volatile-rich, carbonaceous chondrite-like bodies, which likely derive from the outer Solar System, but that the necessary ingredients for the development of life were contributed by Earth's major inner Solar System building blocks.

Declaration of Competing Interest

None.

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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.2022.115171>.

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