

An inner solar system origin of volatile elements in Mars

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ABSTRACT

The origin of volatile elements in Mars and whether these elements derive from the inner or outer solar system is unclear. Here we show that Mars exhibits nucleosynthetic zinc (Zn) isotope anomalies similar to those of non-carbonaceous (NC) but distinct from carbonaceous (CC) meteorites. Like for non-volatile elements, Mars' Zn isotope composition is intermediate between those of enstatite and ordinary chondrites, demonstrating that Mars acquired volatile elements predominantly from its inner solar system building blocks. The Zn isotope data limit the contribution of CI chondrite-like material to Mars to 4% by mass at most and show that Mars accreted less CC material than Earth. The origin of these disparate CC fractions is unclear, but can place constraints on how and when CC-type material was delivered to the inner solar system.

1. Introduction

Determining the provenance of volatile elements in the terrestrial planets is critical for understanding planet formation and a possible pathway for the emergence of habitable planets. Mars is a planetary embryo that accreted within the first ~5–10 million years (Ma) of solar system history (Dauphas and Pourmand, 2011; Kleine et al., 2002; Nimmo and Kleine, 2007) and as such provides a record of volatile element delivery to the inner solar system during the early stages of planet formation. Volatile elements on Mars may derive from its major building blocks or, alternatively, an exogenous source that otherwise contributed only little mass to Mars. Understanding volatile element accretion, therefore, requires assessing as to whether there is a genetic link between Mars' major building material and the source of its volatile elements. This in turn requires identifying the origin and nature of Mars' building materials, and finding a genetic tracer that can link potential volatile element sources to those building materials.

The provenance of volatile elements in the terrestrial planets may be inferred from the isotopic composition of the highly volatile elements H (i.e., D/H) and N (i.e., $\delta^{15}\text{N}$), which show large variations among solar system materials (Alexander et al., 2012; Marty, 2012). For instance, the D/H and $\delta^{15}\text{N}$ of bulk silicate Earth (BSE), comprising its mantle, crust, and hydrosphere, was initially interpreted to indicate a carbonaceous chondrite-like source for these elements (Alexander et al., 2012; Marty, 2012), but more recent work has shown that these signatures rather

point towards an enstatite chondrite-like source with some addition from volatile-rich carbonaceous chondrites (Piani et al., 2020; Steller et al., 2022). For Mars, however, D/H and $\delta^{15}\text{N}$ are less distinctive tracers for the origin of volatile elements, because large isotopic variations exist between the martian crust, mantle, and atmosphere, which makes determining the D/H and $\delta^{15}\text{N}$ of bulk silicate Mars (BSM) quite difficult (Avice and Marty, 2020; Usui et al., 2012). Thus, the provenance of volatile elements on Mars cannot easily be identified using these proxies.

The recent discovery of nucleosynthetic isotope anomalies in the moderately volatile element Zn (Martins et al., 2023; Savage et al., 2022; Steller et al., 2022) offers a new approach to this problem (moderately volatile elements are defined as having half-mass condensation temperatures below those of Mg and Si but above that of FeS). Nucleosynthetic isotope anomalies arise through the heterogeneous distribution of presolar material and reveal that the solar protoplanetary disk can be subdivided into the non-carbonaceous (NC) and carbonaceous (CC) reservoirs (Budde et al., 2016; Warren, 2011), which have been suggested to represent the inner and outer solar system (Kruijer et al., 2017; Morbidelli et al., 2022). The NC-CC dichotomy is well documented for several elements having distinct geochemical and cosmochemical behavior (Bermingham et al., 2020; Kleine et al., 2020; Kruijer et al., 2020b), and so the isotopic composition of a planet's mantle relative to the NC-CC dichotomy provides important information not only about the heritage of a planet's building material, but also how this material

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may have changed as accretion proceeded (Dauphas, 2017). This is because lithophile elements like Cr and Ti trace a planet's entire accretion history, whereas siderophile elements like Mo predominantly record the late stages of accretion (Dauphas, 2017). By contrast, volatile elements like Zn are depleted in Mars (Yoshizaki and McDonough, 2020) and, therefore, provide an isotopic record of only those objects that delivered volatile elements to the planet. Combining nucleosynthetic isotope anomalies for non-volatile and volatile elements, therefore, provides an efficient means for determining the source of a planet's volatile element inventory, and for assessing whether or not these elements were delivered by a planet's major building blocks.

For Earth, it has been shown that the BSE's Zn isotopic composition is intermediate between those of the NC and CC reservoirs, indicating that ~30% of terrestrial Zn derives from the CC reservoir, while the remaining ~70% were provided by Earth's major inner solar system building blocks (Paquet et al., 2022; Savage et al., 2022; Steller et al., 2022). Here, we apply the same approach to Mars and report Zn isotope data for a set of martian meteorites. These data are used to constrain the heritage of volatile elements in Mars, the link of volatile element sources to Mars' main building material, and to assess whether Mars and Earth accreted volatile elements from the same or different sources.

2. Volatile element delivery by Mars' inner solar system building blocks

2.1. Zinc isotopic composition of Mars

We analyzed five martian meteorites, including three shergottites (Tissint, Zagami, NWA 1195) and two nakhlites (Nakhla, MIL 03346). These two groups of martian meteorites derive from distinct mantle sources which were likely established during the early differentiation of Mars, most likely during crystallization of a magma ocean (e.g., Borg and Draper, 2003). The analytical methods for sample digestion, chemical purification of Zn, and isotope measurements by multi-collector inductively coupled plasma mass spectrometry follow those described in Steller et al. (2022). The Zn isotopic data are internally normalized to a fixed $^{67}\text{Zn}/^{64}\text{Zn}$ using the exponential law, to correct for instrumental and natural mass-dependent isotope fractionation, and are reported as $\mu^{66}\text{Zn}$ and $\mu^{68}\text{Zn}$ values (the parts-per-million deviation from the NIST SRM 683 standard). To evaluate internal consistency, the data are also reported as $\mu^{66}\text{Zn}$ and $\mu^{67}\text{Zn}$ values after internal normalization to $^{68}\text{Zn}/^{64}\text{Zn}$.

All five martian meteorites exhibit indistinguishable Zn isotope anomalies relative to the composition of the terrestrial standard and for both internal normalizations plot well inside the NC field, between the compositions of ordinary and enstatite chondrites (Fig. 1). The lack of Zn isotopic variations among the different martian meteorites is consistent with observations for other, non-volatile elements, which also reveal no resolved nucleosynthetic isotope variations among different martian samples (Burkhardt et al., 2021; Kruijjer et al., 2020a). Some martian meteorites show hints of small ^{54}Cr isotope variations, but the origin of these variations and whether they reflect nucleosynthetic heterogeneity is debated (Kruijjer et al., 2020a; Zhu et al., 2022). Either way, given the approximately fourfold larger ^{54}Cr variations among meteorites than ^{66}Zn variations (Steller et al., 2022) and the ubiquitous multi-element isotope correlations among NC meteorites (Spitzer et al., 2020), this potential small ^{54}Cr heterogeneity among martian samples would not result in resolvable $\mu^{66}\text{Zn}$ variations. As such, the mean Zn isotopic composition of the five martian meteorites of this study provides a good estimate for the Zn isotopic composition of bulk silicate Mars (BSM) as sampled by meteorites (Table 1).

2.2. Building material of Mars

On the basis of O isotopes and nucleosynthetic isotope anomalies for non-volatile elements, prior studies have argued that Mars

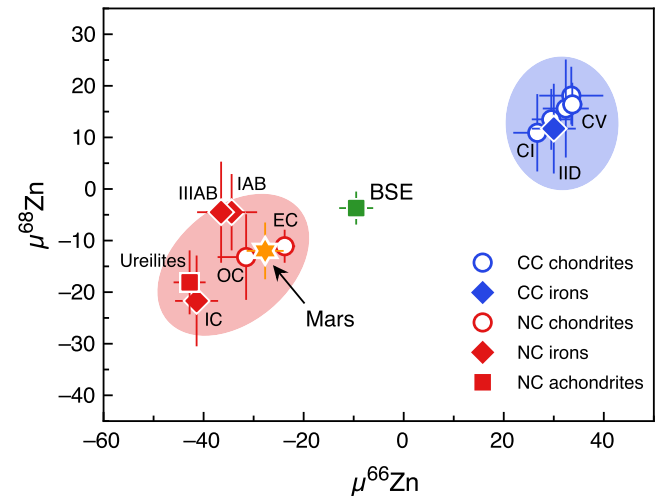


Fig. 1. Zinc isotope composition of Mars compared to meteorites and the bulk silicate Earth (BSE). Mars plots within the compositional field of non-carbonaceous (NC) meteorites and is distinct from carbonaceous (CC) meteorites. By contrast, the BSE plots within an approximately linear trend between ureilites and CI chondrites. EC = enstatite chondrites; OC = ordinary chondrites; CI = Ivuna-type carbonaceous chondrites; CV = Vigarano-type carbonaceous chondrites; IAB, IC, IID, and IIIAB are distinct groups of iron meteorites. Data for meteorites and BSE from Steller et al. (2022).

predominantly accreted from enstatite and ordinary chondrite-like materials (Brasser et al., 2018; Lodders and Fegley, 1997; Sanloup et al., 1999) with only minor contributions (<9% at the 2 σ level) from CC material (Burkhardt et al., 2021). This is consistent with the Zn isotope composition of Mars, which is also intermediate between that of enstatite and ordinary chondrites. However, it has also been suggested that Mars formed as a ~60:40 mixture of materials with ureilite- and CI chondrite-like isotope compositions (Schiller et al., 2018). This model is based on the observation that in plots of $\mu^{48}\text{Ca}$, $\mu^{50}\text{Ti}$, and $\mu^{54}\text{Cr}$ against each other, Mars consistently plots on an approximately linear trend between ureilites and CI chondrites. The data of the present study reveal that this also seems to be the case for Zn, where in the $\mu^{66}\text{Zn}-\mu^{54}\text{Cr}$ plot Mars has an intermediate composition between ureilites and CI chondrites (Fig. 2). However, because of its depletion in volatile elements like Zn, Mars is not expected to plot on linear $\mu^{66}\text{Zn}-\mu^{54}\text{Cr}$ mixing lines connecting the NC and CC fields. This would only occur if throughout Mars' accretion the NC and CC mixing end-members had the same Zn/Cr ratios. This in turn would require that all NC and CC materials accreted by Mars either had chondritic Zn/Cr and that the sub-chondritic Zn/Cr ratio of Mars was only established after accretion, or that the NC and CC materials had the same sub-chondritic Zn/Cr ratios, which would have to be that of BSM. However, given the variable volatile element contents of meteorites and the usually volatile-rich nature of carbonaceous chondrites it is quite unlikely that the NC and CC materials accreted by Mars all had chondritic chemical compositions or all had the same volatile element-depleted compositions.

Instead, any $\mu^{66}\text{Zn}-\mu^{54}\text{Cr}$ mixing line connecting variably volatile-depleted NC materials with CI chondrites is strongly curved and for low to modest CC fractions almost perpendicular to the NC isotope trend (Fig. 2). This is also the case when the less volatile-rich CV chondrites are used as the CC end-member (Fig. 2). Thus, regardless of which carbonaceous chondrite group is used as the CC end-member, and because Mars plots within the NC field, the isotopic composition of the NC end-member must be close to the actual composition of Mars and, therefore, significantly displaced from that of ureilites (Fig. 2). The new Zn isotopic data, therefore, essentially rule out the idea that Mars' isotopic composition reflects the addition of a large fraction of CI material (or other CC material) to an NC body having a ureilite-like isotopic

Table 1

Zn isotope data for martian meteorites. $\mu^{6x}\text{Zn} = [({}^{6x}\text{Zn}/{}^{64}\text{Zn})_{\text{sample}}/({}^{6x}\text{Zn}/{}^{64}\text{Zn})_{\text{SRM683-1}}] \times 10^6$ with $x = 6, 7, 8$, after internal normalization to either ${}^{68}\text{Zn}/{}^{64}\text{Zn}$ (8/4) or ${}^{67}\text{Zn}/{}^{64}\text{Zn}$ (7/4). All uncertainties are 95% confidence intervals; N is the number of repeat analyses.

Sample	Class.	N	$\mu^{66}\text{Zn}$ (8/4) $\pm 2\sigma$	$\mu^{67}\text{Zn}$ (8/4) $\pm 2\sigma$	$\mu^{66}\text{Zn}$ (7/4) $\pm 2\sigma$	$\mu^{68}\text{Zn}$ (7/4) $\pm 2\sigma$
Nakhla	Nakhlite	6	-21 \pm 8	7 \pm 10	-26 \pm 6	-9 \pm 13
MIL 03346	Nakhlite	6	-21 \pm 9	7 \pm 17	-26 \pm 15	-9 \pm 23
NWA 1195	Sherg.	8	-23 \pm 3	15 \pm 11	-33 \pm 8	-20 \pm 14
Tissint	Sherg.	10	-21 \pm 4	9 \pm 7	-27 \pm 6	-11 \pm 9
Zagami	Sherg.	12	-21 \pm 3	8 \pm 8	-27 \pm 6	-11 \pm 11
Mars		5	-22 \pm 1	9 \pm 4	-28 \pm 4	-12 \pm 5

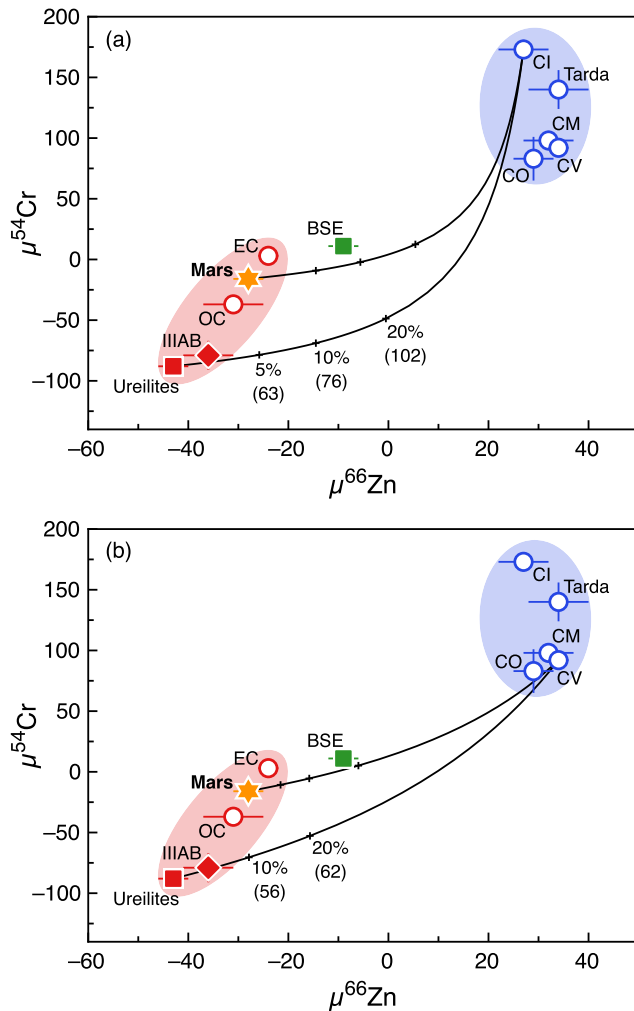


Fig. 2. Relation of $\mu^{66}\text{Zn}$ and $\mu^{54}\text{Cr}$ among meteorites, Mars, and Earth. Mars plots on the $\mu^{66}\text{Zn}$ - $\mu^{54}\text{Cr}$ correlation defined by NC meteorites between the compositions of ordinary (OC) and enstatite (EC) chondrites. Solid lines are mixing lines between NC material having an ureilite-like or Mars-like isotopic composition with (a) CI or (b) CV chondrite-like material. For the NC end-member the Zn (50 $\mu\text{g/g}$) and Cr concentrations (3700 $\mu\text{g/g}$) for ordinary chondrites are assumed (Wasson and Kallemeyn, 1988). Numbers correspond to weight-% of added carbonaceous chondrite-like material, and numbers in parentheses provide the calculated Zn concentration of bulk silicate Mars (BSM). Note that for more than ~ 10 wt.-% CI chondrite-like material the calculated Zn concentration of BSM is higher than the observed value of 56 ± 10 $\mu\text{g/g}$. The shape of the mixing lines reveals that Mars' isotopic composition can only be reproduced if the isotopic composition of its NC end-member is close to the actual composition of Mars, refuting the idea that Mars' isotopic composition reflects the addition of a large fraction of CI material (or other CC material) to an NC body having a ureilite-like isotopic composition. Data for NC and CC meteorites and BSE from Steller et al. (2022).

composition. Instead, these data indicate that Mars formed predominantly from NC materials whose average isotopic composition is intermediate between ordinary and enstatite chondrites, and to which only a very small fraction, if any, of CC material was added (Fig. 2).

To more quantitatively determine the contribution of NC and CC bodies to Mars' building blocks and its volatile element inventory, we will assume a two-component mixing model, where the final planet's bulk composition is a mixture of NC and CC materials. Zinc is assumed to be lithophile, such that the BSM's Zn isotope composition is that of the bulk planet (see Supplementary Materials for justification of this assumption and discussion of the geochemical behavior of Zn on Mars). The concentration of an element i in the planet and in the CC reservoir is denoted by $C_{i,p}$ and $C_{i,CC}$, respectively, and the CC fraction is f_{CC} . The elemental concentration in the NC reservoir, $C_{i,NC}$, is not known a priori but can be solved for by using mass balance for a given f_{CC} :

$$C_{i,NC} = \frac{C_{i,p} - C_{i,CC}f_{CC}}{1 - f_{CC}} \quad (1)$$

The final isotopic composition of the planet $\mu_{i,p}$ is likewise given by mass balance:

$$\mu_{i,p}C_{i,p} = \mu_{i,NC}C_{i,NC}(1 - f_{CC}) + \mu_{i,CC}C_{i,CC}f_{CC} \quad (2)$$

where $\mu_{i,NC}$ and $\mu_{i,CC}$ are the isotopic anomalies of the two end-members. Eqs. (1) and (2) can be combined to solve for f_{CC} :

$$f_{CC} = \frac{C_{i,p} (\mu_{i,p} - \mu_{i,NC})}{C_{i,CC} (\mu_{i,CC} - \mu_{i,NC})} \quad (3)$$

If two different elements are considered, then any successful model must yield the same f_{CC} from eq. (3) for the two elements. This means that

$$\frac{C_{1,p} (\mu_{1,NC} - \mu_{1,p})}{C_{1,CC} (\mu_{1,CC} - \mu_{1,NC})} = \frac{C_{2,p} (\mu_{2,NC} - \mu_{2,p})}{C_{2,CC} (\mu_{2,CC} - \mu_{2,NC})} \quad (4)$$

where the subscripts 1,2 denote the two elements of interest (e.g., Zn and Cr). Given the end-member compositions and a measurement of the planet's isotopic anomaly $\mu_{1,p}$, eq. (4) can be used to calculate the predicted isotopic anomaly for the other element $\mu_{2,p}$. If this matches the measured value within error, then a successful scenario is found and f_{CC} can be calculated from eq. (3). By repeating this process multiple times with randomly assigned end-member compositions, the range of f_{CC} values yielding successful solutions can be determined. Moreover, the range of permissible isotopic compositions of the NC end-member can be determined, i.e., the average isotopic composition of the NC material accreted by Mars. The end-member compositions used in the calculations are provided in the Supplementary Materials.

As expected from Mars' position within the NC field of the $\mu^{66}\text{Zn}$ - $\mu^{68}\text{Zn}$ and $\mu^{66}\text{Zn}$ - $\mu^{54}\text{Cr}$ plots (Figs. 1, 2), eq. (3) returns very low CC fractions in Mars. Using CI chondrites as the CC end-member results in $f_{CC} = 0.005 \pm 0.034$ (2σ), indicating that Mars accreted less than $\sim 4\%$ CI chondrite-like material. Using CV chondrites as the CC end-member gives $f_{CC} = 0.017 \pm 0.084$ (2σ), indicating that a slightly larger CC contribution is possible, but not required for this assumed composition. For these CC fractions, the Zn contents calculated from eq. (1) are within

the range of those observed among NC chondrites. Thus, the NC-like Zn isotopic composition of Mars combined with the observation that BSM plots on the $\mu^{66}\text{Zn}-\mu^{54}\text{Cr}$ correlation defined by NC meteorites indicates that Mars accreted at most $\sim 4\%$ CI chondrite-like material (or at most $\sim 10\%$ CV chondrite-like material). These are upper limits and the contribution of these CC materials to Mars were likely smaller.

Despite this very low CC fraction, Mars appears to have accreted some CC material, as is evident from the BSM's Mo isotopic composition, which is intermediate between those of the NC and CC reservoirs and indicates that $40 \pm 30\%$ (2σ) of the BSM's Mo derives from CC bodies (Burkhardt et al., 2021). As a siderophile element, Mo predominantly records the later stages of accretion, which in detail depends on the siderophilicity of Mo during core formation on Mars (Dauphas, 2017). One problem though is that the abundance of Mo in BSM is not well known, with estimates ranging from $\sim 0.5 \mu\text{g/g}$ (Yoshizaki and McDonough, 2020) to $\sim 0.118 \mu\text{g/g}$ (Wänke et al., 1994) and $\sim 0.019 \mu\text{g/g}$ (Kong et al., 1999). For this range in Mo abundances, the BSM's Mo isotopic composition may record the last $\sim 40\%$ (for $0.5 \mu\text{g/g}$ in BSM), $\sim 20\%$ (for $0.118 \mu\text{g/g}$) or $\sim 3\%$ (for $0.019 \mu\text{g/g}$) of Mars' accretion [calculated using the formalism of Dauphas, 2017]. Taking the $40 \pm 30\%$ CC-derived Mo in the BSM from above, this corresponds to the accretion of as much as $16 \pm 12\%$ to as little as $1.2 \pm 0.9\%$ CC material to Mars. This highlights that the Mo isotopic data alone cannot precisely constrain the amount of CC material accreted by Mars, and that the BSM's Mo isotopic composition is consistent with the very low CC fraction inferred from the combined $^{66}\text{Zn}-^{54}\text{Cr}$ systematics.

In summary, the new Zn isotope data, together with isotopic data for non-volatile elements, demonstrate that Mars formed predominantly from NC materials with an average isotopic composition between that of ordinary and enstatite chondrites. Any contribution of CC material from the outer disk was minor ($\sim 4\%$ CI chondrite-like material at most) and occurred during the later stages of Mars' accretion, as recorded in the Mo isotopic composition of martian meteorites.

2.3. Origin of volatile elements in Mars

The low CC mass fraction in Mars combined with the observation that the BSM's Zn isotopic composition is intermediate between ordinary and enstatite chondrites provides two key insights into the origin of volatile elements on Mars. First, taking the upper limit of 4% CI chondrite-like material in Mars together with the known Zn concentrations in BSM and CI ($[\text{Zn}]_{\text{BSM}} = 56 \mu\text{g/g}$, $[\text{Zn}]_{\text{CI}} = 309 \mu\text{g/g}$) reveals that at most $\sim 22\%$ of the martian Zn derives from the CC reservoir. This is an upper limit and the fraction of CC-derived Zn in Mars is likely smaller and may be zero. Using another composition for the CC end-member will not change this result, because the maximum CC fraction in Mars would also change accordingly. Terrestrial Zn has a mixed NC-CC heritage (Martins et al., 2023; Savage et al., 2022; Steller et al., 2022), indicating that compared to Mars, Earth received a larger share of its moderately volatile elements from the CC reservoir. Yet, Earth exhibits a stronger depletion in moderately volatile elements than Mars (Yoshizaki and McDonough, 2020). Together this demonstrates that CC bodies, despite their presumably volatile-rich nature, are not a major source of volatile elements in the terrestrial planets. Second, for non-volatile lithophile elements such as Cr, Ti, and Zr, which trace the isotopic composition of a planet's bulk building material, Mars' isotopic composition is consistently between those of ordinary and enstatite chondrites (Burkhardt et al., 2021; Kruijer et al., 2020a; Render et al., 2022). This is also the case for Mars' O isotope composition (Lodders and Fegley, 1997; Sanloup et al., 1999). Importantly, the BSM's Zn isotopic composition is also intermediate between ordinary and enstatite chondrites, indicating that Zn (and by implication other moderately volatile elements) were delivered to Mars by its main inner solar system building materials, whereas any contribution from exotic, outer solar system sources, were minor to absent.

The limited contribution of CC material to martian Zn (and other

moderately volatile elements) raises the question of whether the highly volatile elements (e.g., H, N) in Mars were also predominantly delivered by NC bodies. In detail, this depends on the volatile depletion pattern of those objects that contributed volatile elements to Mars. For instance, if most of these objects were depleted in more strongly volatile elements (e.g., H, N), then a larger share of Mars' highly volatile elements may derive from CC bodies. Conversely, if volatile elements were predominantly delivered by volatile-unfractionated objects (i.e., objects with solar or CI chondrite-like relative volatile element abundances), then the relative contributions of NC and CC bodies to Mars' volatile element budget would be the same for the moderately and highly volatile elements. For Earth it has been shown that the CC-derived fraction of Zn, H, and N is consistently about 30% , indicating that these volatile elements, despite their different condensation temperatures, derive from the same mixture of volatile-unfractionated objects (Steller et al., 2022). For Mars, this comparison cannot easily be made because unlike for BSE, the BSM's H and N isotopic compositions are not well known. However, the observation that Earth appears to have received about 70% of moderately and highly volatile elements (i.e., Zn, H, and N) from its main inner solar system building blocks (Piani et al., 2020; Steller et al., 2022) indicates that volatile-rich and -unfractionated bodies existed in the terrestrial planet region. This is consistent with the broadly chondritic relative abundances of moderately volatile elements in the BSE, which also suggests that these elements were added to Earth by volatile-unfractionated objects (Braukmüller et al., 2019; Hin et al., 2017; Mezger et al., 2021). This combined with the observation that Earth and Mars, despite their distinct isotopic compositions, shared at least some building material (Burkhardt et al., 2021), suggest strongly that Mars, like the Earth, also accreted highly volatile elements from its main inner solar system building blocks.

3. Distinct accretion histories of Earth and Mars

A key result of this study is that Mars and Earth have distinct Zn isotopic compositions, not only in terms of their Zn isotope anomalies, but most importantly with respect to the NC-CC dichotomy: Whereas Mars plots well within the NC field, Earth plots between the NC and CC fields. This is true not only for Zn isotopes alone (Fig. 1), but also for the $\mu^{66}\text{Zn}-\mu^{54}\text{Cr}$ diagram, where the BSE plots to the right of the NC field, along a mixing line between NC material having an enstatite chondrite-like isotopic composition and the CC field (Fig. 2). Applying the two-component mixing model of this study to Earth using the BSE's Zn and Cr isotopic compositions and abundances (see Supplementary Materials) we find $f_{\text{CC}} = 0.060 \pm 0.024$ (2σ) assuming CI chondrites and $f_{\text{CC}} = 0.154 \pm 0.064$ (2σ) assuming CV chondrites as the CC end-member, consistent with results of prior studies using the same data and a similar model (Savage et al., 2022; Steller et al., 2022). These calculations reveal that for a given CC end-member, Earth accreted more CC material than Mars did (Fig. 3).

The higher CC fraction in Earth compared to Mars is unexpected, because Earth and Mars should have accreted roughly the same amount of CC material from roughly the same regions during the waning stages of accretion (Fischer et al., 2018; O'Brien et al., 2006; Raymond and Izidoro, 2017). If this material consisted of small planetesimals, then one would expect a roughly equal fraction of CC material to have been delivered to both bodies. There are several possible solutions to this apparent paradox. One is that Mars was less able to retain volatile elements delivered during high-velocity impacts. Evaporative escape is a strong function of planetary mass (Young et al., 2019), so this idea is qualitatively plausible, but it is not clear whether it works quantitatively. A second possibility is that the delivery of CC material to the inner solar system post-dated the formation of Mars, which was mostly complete by ~ 5 Ma (Dauphas and Pourmand, 2011). It is unclear, however, how this scenario can be reconciled with the Mo isotopic evidence that Mars accreted some CC material during the late stages of accretion (Burkhardt et al., 2021) and nor does it explain why the CC accretion to

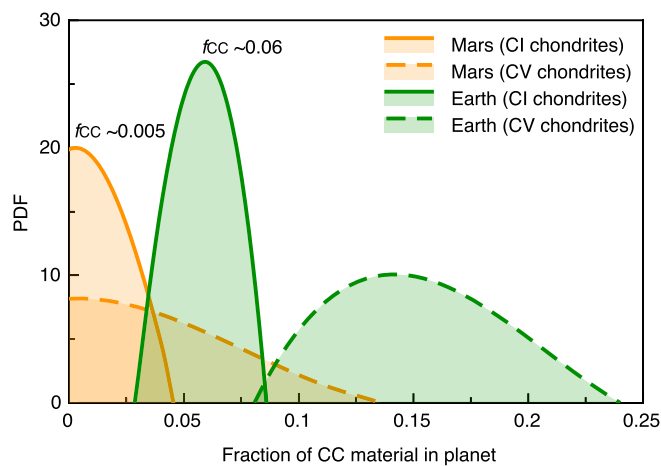


Fig. 3. PDFs for the fraction of CC material in Mars and Earth calculated using a two-component mixing model. For details about the model see text and supplementary materials. The end-member compositions used in the mixing calculations are summarized in Table S1. For a given composition of the CC end-member, Mars accreted less CC material than Earth did.

Mars ceased. Finally, the nearly-complete Earth may have been struck by one or a few large CC embryos—one of which may have been the Moon-forming impactor (Budde et al., 2019)—while Mars was not. This statistical argument is similar to that made by Bottke et al. (2010) concerning the delivery of highly siderophile elements to the Earth and Moon during late accretion. This scenario resembles some prior models, which based on the chemical composition of the BSE argued for a volatile-rich, relatively oxidized nature of the Moon-forming impactor (Mezger et al., 2021), attributes that may link this impactor to the CC reservoir. However, because of the low probability of collision between Earth and large, CC-like objects (Morbidelli et al., 2018), this scenario would require the survival of hundreds or thousands of such objects in the asteroid belt, which are not observed at present. Thus, while this scenario appears plausible from a chemical and isotopic standpoint, it will require further investigation with planetary accretion models. Nonetheless, the very low CC fraction found at Earth and Mars must reflect a generally low abundance of CC-type material in the inner solar system and will therefore place constraints on how and when this material was delivered.

Declaration of Competing Interest

None.

Data availability

Data will be made available on request.

Acknowledgements

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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.2023.115519>.

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