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## Earth's volatile element depletion pattern inherited from a carbonaceous chondrite-like source

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### Abstract

Earth's volatile element abundances (e.g., sulfur, zinc, indium and lead) provide constraints on fundamental processes such as planetary accretion, differentiation, and the delivery of volatile species, like water, which contributed to Earth becoming a habitable planet. The composition of the silicate Earth suggests chemical affinity but isotopic disparity to carbonaceous chondrites, meteorites that record the earliest element fractionations in the protoplanetary disk. However, the volatile element depletion pattern of the silicate Earth is obscured by core formation. Another key problem is the overabundance of indium, which could not be reconciled with any known chondrite group. Here we complement recently published volatile element abundances for carbonaceous chondrites with high precision sulfur, selenium, and tellurium data. We show that both Earth and carbonaceous chondrites exhibit a unique hockey stick volatile element depletion pattern where volatile elements with low condensation temperatures (750 - 500 K) are unfractionated from each other. This abundance plateau accounts for the apparent overabundance of indium in the silicate Earth without the need of exotic building materials or vaporization from precursors or during the Moon-forming impact and suggests the accretion of 10-15 % CI-like material before core formation ceased. Finally, more accurate estimates of volatile element abundances in the core and bulk Earth can now be provided.

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The chemical composition of the terrestrial planets is controlled by the composition of their planetary building blocks. All known inner solar system bodies, including Earth, Moon, Mars and the different meteorite parent bodies, are depleted in volatile elements (e.g., Cd, In, S, Cl) relative to the bulk solar system composition as represented by CI chondrites<sup>1,2</sup>.

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#### Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files.

#### Author Contributions

FW and CM designed the project. CF carried out the ICP-MS analyses for Se, Te and S. NB compiled the data, did the calculations and wrote the manuscript with substantial contributions from FW and CM. All authors contributed to the discussion of the results and editing of the manuscript.

#### Competing interests

The authors declare no competing interests.

The volatile element depletion pattern constrains the nature of Earth's building blocks and may serve as a tracer for the delivery of water during Earth's growth<sup>3–5</sup>. Although Earth's isotope composition cannot be reproduced by mixing known meteorites<sup>1,6–9</sup>, comparisons between Earth's chemical composition and those of undifferentiated meteorites (chondrites), in particular for volatile elements, suggest that Earth's building blocks experienced similar nebular fractionation processes as carbonaceous chondrites but different to those observed in ordinary and enstatite chondrites<sup>1,2,10</sup>. For example, ratios between lithophile volatile and lithophile refractory elements (e.g., K/U) for the bulk silicate Earth (BSE) always plot at the volatile-depleted end of a trend defined by carbonaceous chondrites<sup>2</sup>. Furthermore, Zn and Rb stable isotope compositions of the BSE follow the carbonaceous chondrite trend of increasingly light isotope compositions with increasing degree of volatile element depletion<sup>10,11</sup>.

Earth's primary volatile element depletion pattern is obscured by the additional depletion of siderophile and chalcophile volatile elements in the BSE that is generally attributed to their partitioning into Earth's core<sup>1,12</sup>. However, numerous metal-silicate partitioning experiments have thus far been unable to consistently reproduce the siderophile and chalcophile element depletion pattern observed in the BSE<sup>13–16</sup>. This is especially true regarding the abundance of the volatile element In in the BSE, which appears to be overabundant relative to the carbonaceous chondrite-like volatile element depletion pattern<sup>14,17,18</sup>. Therefore, it was concluded that Earth's volatile element abundances were modified by post-nebular processes such as vaporization on precursor bodies and possibly during the giant Moon-forming impact, late accretion, or collisional erosion<sup>3,17,19</sup>. Alternatively, it was proposed that volatile element abundances evolved differently in the inner solar system, where the vast majority of Earth's building materials originate<sup>14,18</sup>. There are several arguments against secondary volatile element loss related to Earth's accretion, e.g.: (i) variations in <sup>53</sup>Cr induced by the decay of the now extinct <sup>53</sup>Mn ( $T_{1/2} = 3.7$  Myr) suggest that Mn/Cr fractionation and therefore volatile element depletion in the precursor materials of Earth, Mars and the different meteorite parent bodies occurred early in the protoplanetary disk within about 2 Myr of CAI formation<sup>20</sup>, rather than during planetary growth, (ii) the chondritic Mn/Na of Earth argues against post nebular volatile-loss as opposed to the high Mn/Na of other differentiated rocky bodies (e.g. Mars, Moon, achondrites)<sup>19,21</sup> and (iii) evaporative loss of volatile elements should lead to stable isotope fractionation resulting in an enrichment of heavy isotopes in the residue, which is not observed on Earth<sup>10,11,22–24</sup>. Since post-nebular volatile element loss was seemingly restricted on Earth, volatile element abundances must mirror the composition of Earth's building blocks. Here we reassess Earth's volatile element depletion pattern based on recently available volatile element data for carbonaceous chondrites<sup>25,26</sup> complemented with new high precision S, Se and Te data.

## Terrestrial hockey stick volatile element depletion pattern

It is generally assumed that volatile element abundances in carbonaceous and ordinary chondrites decrease gradually with increasing volatility of the elements (as commonly defined by 50% condensation temperatures ( $T_{50\%}$ ))<sup>27,28</sup>. However, recent high precision data<sup>25</sup> confirm earlier suggestions<sup>29,30</sup> that volatile elements with  $T_{50\%} < 750$  K are

depleted by a constant factor in carbonaceous chondrites relative to CI chondrites. Thus, CI-normalized volatile element abundances plotted versus  $T_{50\%}$  define a hockey stick depletion pattern for all investigated carbonaceous chondrite groups (Fig. 1), where *slope volatile elements* with  $T_{50\%}$  between 1250 - 750 K follow the previously suggested gradual depletion trend, whereas volatile elements with  $T_{50\%}$  between 750 - 500 K are essentially unfractionated from each other and are now defined as *plateau volatile elements*<sup>25</sup>. Sulfur, Se and Te belong to the plateau volatile elements and our new isotope dilution data confirm their CI-chondritic relative abundances in all investigated carbonaceous chondrite groups (Supplementary Fig. 1). In contrast, ordinary and enstatite chondrite samples display no clear plateau, but more complex volatile element abundance pattern<sup>31,32</sup> that result at least partly from additional high temperature processes as evident by their strongly fractionated Cd and Zn stable isotope compositions in comparison to carbonaceous chondrites<sup>33–35</sup>.

The volatile element depletion pattern for Earth can only be deduced from predominantly lithophile volatile element abundances in the BSE. Among the plateau volatile elements, these are In, Zn, Cl, Br and I, the abundances of which have been recently revised in both, the BSE and chondrites<sup>14,25,26</sup>. Importantly, all five elements are unfractionated from each other (CI-like) in the BSE within analytical uncertainty<sup>14,18,26</sup> (Fig. 1) and (2). When combined with the abundances of lithophile slope volatile elements in the BSE, this reveals that Earth also displays hockey stick volatile element depletion pattern (Fig. 1). Recognition of this plateau in Earth's volatile element depletion pattern means that In is no longer overabundant in the BSE, obviating the need for terrestrial building blocks with unusual In enrichments<sup>14,18</sup> or processes, such as melting and volatile loss from precursor bodies or during the Moon-forming impact<sup>17</sup> to explain Earth's volatile element depletion pattern.

## Plateau volatile element abundances in bulk Earth and core

Recognition of the hockey stick volatile element depletion pattern allows to improve estimates of plateau volatile element abundances in bulk Earth and its core (Table 1). Bulk Earth abundances are derived from the plateau level in the BSE as defined by the lithophile elements Zn and In, whereas the core abundances are calculated from the inferred bulk Earth abundances and the depletions of siderophile and chalcophile elements relative to the BSE plateau level (Fig. 3).

Our estimates of bulk Earth and core abundances hinge on the lithophile behaviour of In and Zn during core formation, but metal-silicate partition experiments revealed siderophile tendencies for both elements<sup>14,16,36</sup>. Therefore, a substantial fraction of In and Zn could have been sequestered into the core, which would drive estimates of their abundances in bulk Earth higher. Since In is considered more siderophile than Zn<sup>14,16</sup>, partitioning of Zn and In into the core, while maintaining CI-chondritic In/Zn ratios in the BSE appears possible only in extreme cases with equilibrium pressures exceeding 30 - 60 GPa during core formation<sup>16</sup>. Experiments also suggest that In is more siderophile than Cd<sup>14</sup>, which is depleted by core formation (Fig. 3). If true, In must have become even more depleted during core formation and Earth's building materials must be characterized by suprachondritic In/Cd to accommodate the observed In/Cd in the BSE<sup>14</sup>. However, experiments conducted at high sulfur fugacities reveal that Cd is more chalcophile than In<sup>15,37,38</sup>. Furthermore, dissolved

Si in the metal reduces the In partition coefficient more than that of Cd<sup>39</sup> and Zn<sup>40</sup>. Consequently, a S- and Si-bearing core could explain the relative abundances of Zn, In and Cd observed in the BSE. Moreover, the lithophile behaviour of In and Zn during core formation is supported by the Cs abundance in the BSE (Fig. 1). The slope volatile element Cs plots close to the plateau level or slightly above in different carbonaceous chondrites (Fig. 1). In the BSE the lithophile element Cs plots within uncertainty at the same level as Zn and In (Fig. 1, 3) and not above. This supports the notion that both Zn and In remained largely in the silicate Earth during core formation and that both elements serve as a robust baseline for the calculation of plateau volatile element abundances in the BSE.

Based on the new hockey stick volatile element depletion pattern, we can re-evaluate plateau volatile element partitioning into the core. To this end, we calculated core and bulk Earth compositions (Table 1) for two end-member cases: 1) Zn and In did not partition into the core; and 2) there are 50 µg/g Zn in the core, which is the lower estimate of core formation models based on recent experimental data<sup>36</sup>. The latter results in significantly higher concentrations for siderophile plateau volatile elements in bulk Earth and the core. Differences to previous estimates on bulk Earth and core volatile element abundances<sup>12</sup> result from (i) the newly recognized plateau region where volatile element depletion is the same and thus independent from uncertainties in  $T_{50\%}$ , (ii) the observation that Ag belongs to the plateau region<sup>25,41</sup> and (iii) updated chemical compositions for CI chondrites and the BSE (Supplementary Table 1). Our new data confirm that the S abundance in the core cannot contribute substantially to the outer core density deficit<sup>12,42</sup> and reveal the extent to which Pb and other moderately siderophile and chalcophile plateau volatile elements were sequestered into the core (Table 1; Fig. 3).

## Terrestrial building materials and volatile element delivery

In carbonaceous chondrites the unfractionated plateau volatile element pattern can be explained by the presence of material with a CI-like composition in their matrices<sup>25,43</sup>. Accordingly, the unfractionated plateau volatile element abundances in Earth most likely reflect the presence of CI-like material within some of Earth's building blocks. The abundances of the dominantly lithophile plateau volatile elements Zn, Cl, Br, I and In in the BSE allow an estimate on the maximum amount of CI-like material in Earth, which is 10-15 wt.% (Fig. 3). The depletion of siderophile and chalcophile volatile elements relative to the plateau implies that the CI-like material was accreted before core formation and sulfide segregation<sup>44,45</sup> ceased.

In contrast, the abundances and chondritic ratios of highly siderophile elements (HSE) and the chalcogens S, Se and Te are best explained by late accretion of ~0.5 wt.% CM-like material<sup>3</sup> (equivalent to ~0.25 wt.% CI-like material<sup>25</sup>) to a mantle that was virtually completely stripped of HSE and chalcogens during core formation (Fig. 3). Plateau volatile elements other than the chalcogens are less chalcophile and siderophile and were therefore affected to a lesser degree by metal or sulfide segregation. The depletion of Pb and Sn, however, is much smaller than predicted by equilibrium partitioning which indicates that the accretion of the CI-like material was biased towards the end of Earth's main accretion phase<sup>13</sup>, when the composition of Earth's building blocks shifted from reduced refractory

matter to more oxidized and volatile-rich material<sup>47,48</sup>. Likewise, the overall stronger volatile element depletion of Earth compared to most carbonaceous chondrites is best explained by a mix of early refractory building materials with late volatile-rich materials<sup>47</sup>. Independent of the exact timing, the recognition that the CM-like material delivered during late accretion is also characterized by a hockey stick volatile element depletion pattern (Fig. 3), indicates that some of Earth's building materials were chemically similar to carbonaceous chondrites during Earth's main and late accretion phases.

There is an ongoing debate on whether Earth is made of carbonaceous chondrite-like<sup>1,2</sup> or enstatite chondrite-like material<sup>7,49</sup>. Mass-independent isotope compositions for oxygen and several refractory elements in the BSE are indistinguishable or close to those of enstatite chondrites and clearly different from carbonaceous chondrites<sup>6–9</sup>. Consequently, it was proposed that the vast majority of Earth's building blocks formed in the same region of the solar nebula as enstatite chondrites and cannot comprise significant amounts of carbonaceous chondrites<sup>7</sup>. In this case, however, a substantial amount of these terrestrial building blocks must be characterized by a hockey stick volatile element depletion pattern, which is so far not observed in enstatite chondrites. Alternatively, the similar mass-independent isotope composition of Earth and enstatite chondrites results from admixing carbonaceous chondrite material to non-carbonaceous material<sup>50</sup>. In this model, Earth's average building material could comprise up to 32 wt.% of carbonaceous chondrite material while still keeping non-carbonaceous isotope compositions for oxygen and refractory elements<sup>50</sup>. Earth's endmember composition for Mo, Ru and Nd isotopes<sup>6,8,9</sup>, would then require the presence of building materials with isotope compositions that are not present in our meteorite collections. The delivery of volatiles such as water and N<sub>2</sub> by 2–4% carbonaceous chondrite material<sup>4,5</sup> suggests that at least a fraction of volatile elements was added by carbonaceous chondrites.

In summary, carbonaceous chondrites and Earth display a unique, hockey stick-like volatile element depletion pattern where the most volatile elements are depleted to the same extent. This is in stark contrast to the long-standing paradigm of ever increasing depletion with elemental volatility. As a consequence, abundances of the plateau volatile elements in bulk Earth and in the core have been re-evaluated, providing a new framework for studies constraining terrestrial core formation conditions and planetary differentiation in general.

## Methods

### Isotope dilution analysis of S, Se and Te

Selenium and Te abundances (Extended Data Table 2) were determined by isotope dilution multiple collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS). Sulfur abundances were determined using an Element XR™ sector field-inductively coupled plasma-mass spectrometry (SF-ICP-MS)<sup>51–53</sup>. Three isotope tracer solutions (spikes) enriched in <sup>34</sup>S, <sup>77</sup>Se and <sup>125</sup>Te, containing 1195 ± 26 µg/g S, 420.1 ± 2.7 ng/g Se and 56.97 ± 0.83 ng/g Te (2 SD intermediate precision) were used. The intermediate precision given for the spike concentrations refers to repeated calibrations against two commercial Merck and Alfa Aesar element solutions. The isotope tracer solutions were added to ~50 mg chondrite powders. A mixture of two ml of 14 M HNO<sub>3</sub> and 24 M HF was added for sample

digestion and capped beakers were placed onto a hot plate at 120 °C for 48 h. For the determination of S contents an aliquot containing about 15 µg of S was dried down, dissolved in 0.14 M HNO<sub>3</sub> and diluted to final S concentrations of about 1 µg/g.

For Se and Te analyses, the sample solution was dried down, taken up in 2 ml 6 M HCl and refluxed for 24 h at 80 °C to ensure complete conversion of Se (VI) and Te (VI) to the 4+ oxidation state<sup>54</sup>. Solutions were dried down again, taken up in 6 ml 6 M HCl and refluxed for another 24 h at 80 °C. After cooling, the samples were diluted with ultrapure water (18.2 MΩ\*cm) to achieve 36 ml of sample solutions in 1 M HCl. Thiol cotton fibre (TCF) was employed for the separation of Se and Te from sample matrices. Preparation of TCF followed published protocols<sup>55–58</sup>. Diluted sample solutions were then loaded onto 5 ml polypropylene columns<sup>55</sup>. While all major elements pass through, Se (IV) and Te (IV) have strong affinities for the functional groups on the thiol cotton fibres<sup>56</sup>. The remaining matrix elements were then eluted with 2 ml 6 M HCl and 4 ml H<sub>2</sub>O, respectively. Subsequently, the TCF was transferred to 10 ml test tubes and attacked with 0.5 ml 7 M HNO<sub>3</sub> in order to elute Se and Te. Test tubes were capped and placed into a boiling water bath for 20 min. Subsequently, samples were diluted by the addition of 4.6 ml ultrapure water. For Se and Te analyses, the solution was split and 0.25 ml 10 M HCl was added to both aliquots to ensure that Se and Te remain in the 4+ state.

For Se and Te isotope ratio measurements a Neptune MC-ICP-MS equipped with an ESI SC-2 autosampler and a homemade hydride generator was used<sup>52,59</sup>. A 1 µg/g solution yields about 20 mV for <sup>82</sup>Se and 400 mV for <sup>128</sup>Te with 1011 Ω resistors. The cup configuration includes <sup>76</sup>Se, <sup>77</sup>Se, <sup>78</sup>Se and <sup>82</sup>Se and <sup>124</sup>Te, <sup>125</sup>Te, <sup>126</sup>Te, <sup>128</sup>Te and <sup>130</sup>Te. Each analysis comprised 20 cycles with an integration time of 4.2 s. Because Se and especially Te can be rather sticky in the sample introduction system, rinsing with 0.56 M HNO<sub>3</sub> takes up to 20 min. The background was determined right before every standard and sample analysis. Measured background intensities were subtracted offline from sample signal intensities. Instrumental mass bias was monitored externally by repeated analyses of standard solutions and corrected using the natural <sup>77</sup>Se/<sup>82</sup>Se of 0.87447 and <sup>125</sup>Te/<sup>126</sup>Te of 0.37668860.

The intermediate precision of measurement is given here as two relative standard deviations (RSD) for repeated measurements of the Murchison CM2 chondrite and a slightly weathered piece of the Allende CV3 chondrite (n = number of measurements; d = number of digestions). Repeated analyses of S yielded ±1.5% (n=11; d=4) for Murchison CM2 and ±4.0% (n=20; d=8) for Allende CV3. For Se, the intermediate precision was ±1.5% for Murchison CM2 (n=5; d=5) and ±2.9% for the weathered Allende CV3 sample (n=16; d=14). The intermediate precision for Te was ±2.4% for Murchison CM2 (n=5; d=5) and ±4.7% for Allende CV3 (n=16; d=14). For S, Se and Te the precision of the measurement results from the same aliquot measured in different sessions is generally better than the intermediate precision based on repeated digestions. Thus the intermediate precision including repeated digestions is very likely compromised by sample heterogeneity between different powder aliquots. We decided to use Murchison CM2 for the estimate of the intermediate precisions for samples given in Supplementary Table 2, since the Allende CV3 test sample yielded low S (6160 µg/g) and Se (4.5 µg/g) abundances and may suffer from

heterogeneities due to weathering. Procedural blanks for S, Se and Te were variable and always <90 ng for S, <0.6 ng for Se and <0.4 ng for Te. The maximum blank does not contribute significantly to S, up to 0.3% to Se and up to 1.8% to Te for the most depleted CR chondrite sample.

### Calculation of core and bulk Earth plateau volatile element abundances

Core and bulk Earth plateau volatile element abundances reported in Table 1 are calculated based on their abundance in the BSE and the uniform depletion of plateau volatile elements relative to CI chondrites (Fig. 3). The extent of plateau volatile element depletion (VED<sub>BE</sub>) in the bulk Earth is derived from the Mg and CI normalized abundances of the dominantly lithophile plateau volatile elements In and Zn in the BSE, which yields 0.067 for Case 1 and 0.100 for Case 2 (Table 1). All other plateau volatile elements are depleted relative to this plateau level in a Mg and CI normalized plot (Fig. 3), suggesting that the missing complement of these elements resides in the core. The respective bulk Earth abundances for plateau elements El (in µg/g) are calculated as  $El_{BE} = VED_{BE} \times Mg_{BSE} \times (El_{CI}/Mg_{CI}) \times 0.675$ , where 0.675 refers to the silicate Earth mass fraction<sup>43</sup>. The core element abundances in µg/g are then calculated by mass balance as  $El_C = (El_{BE} - 0.675 \times El_{BSE})/0.325$ .

### Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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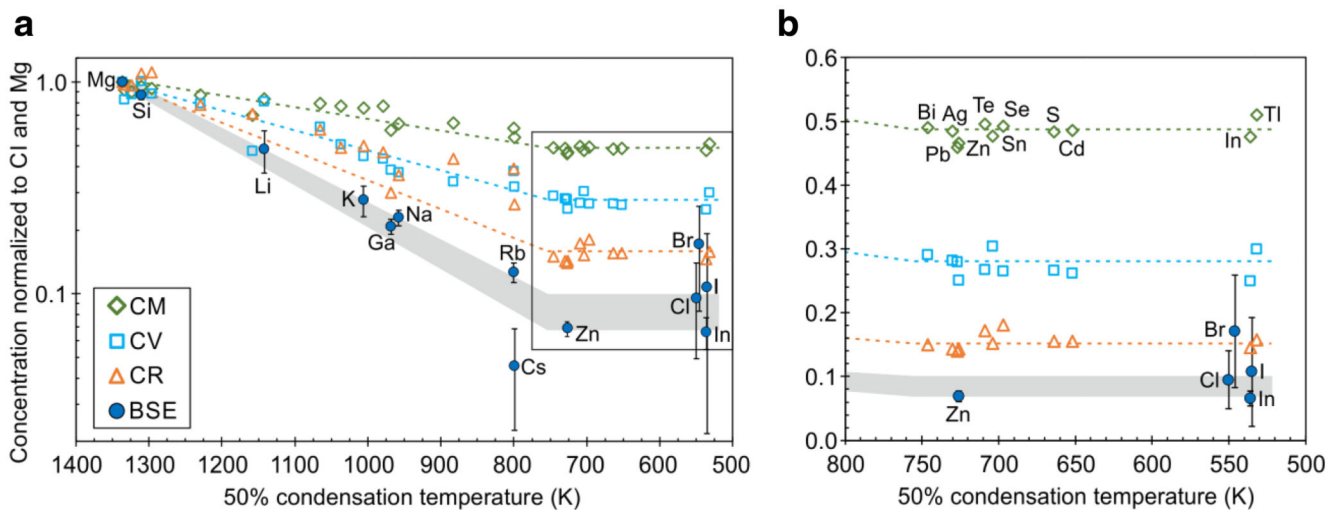
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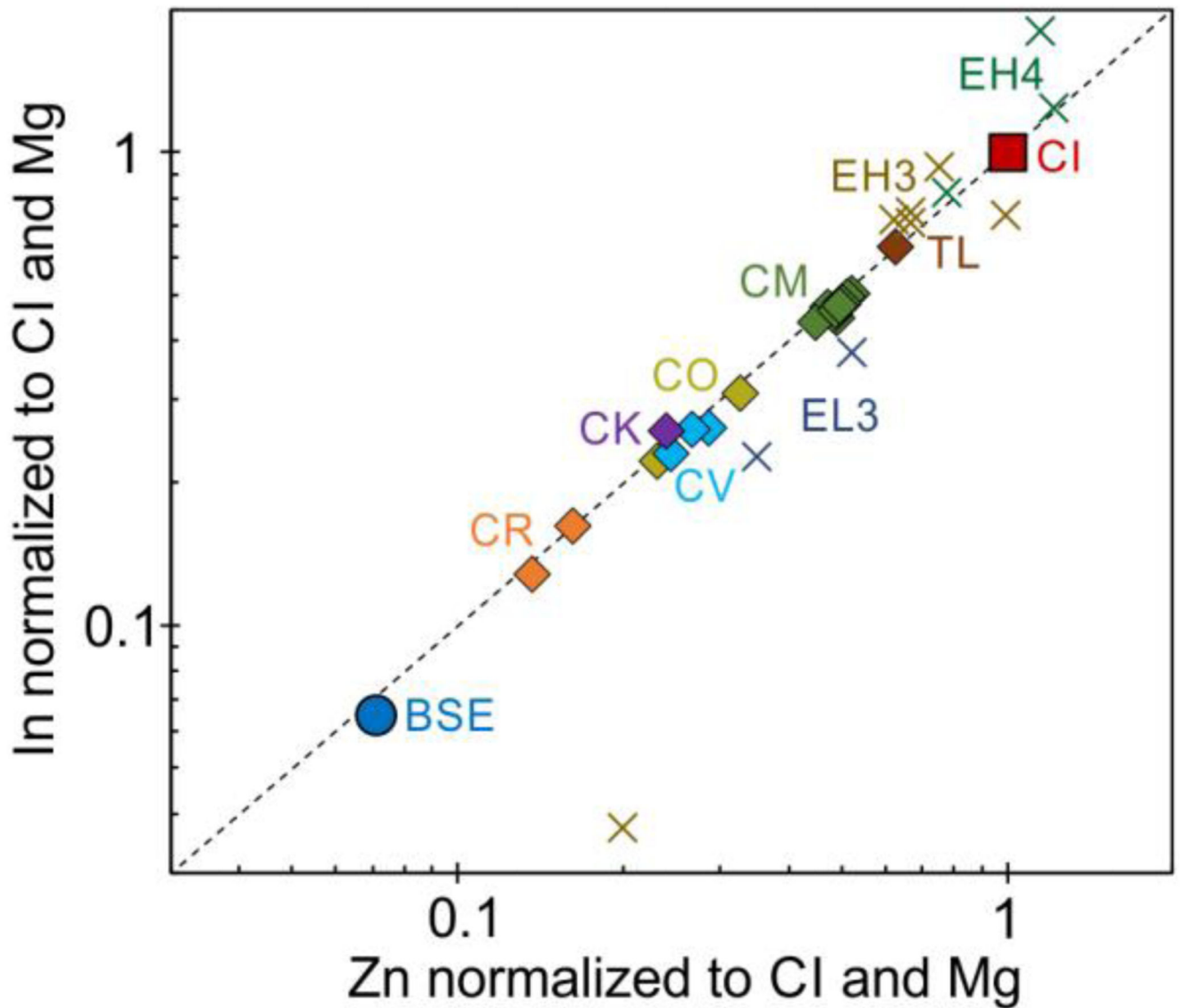
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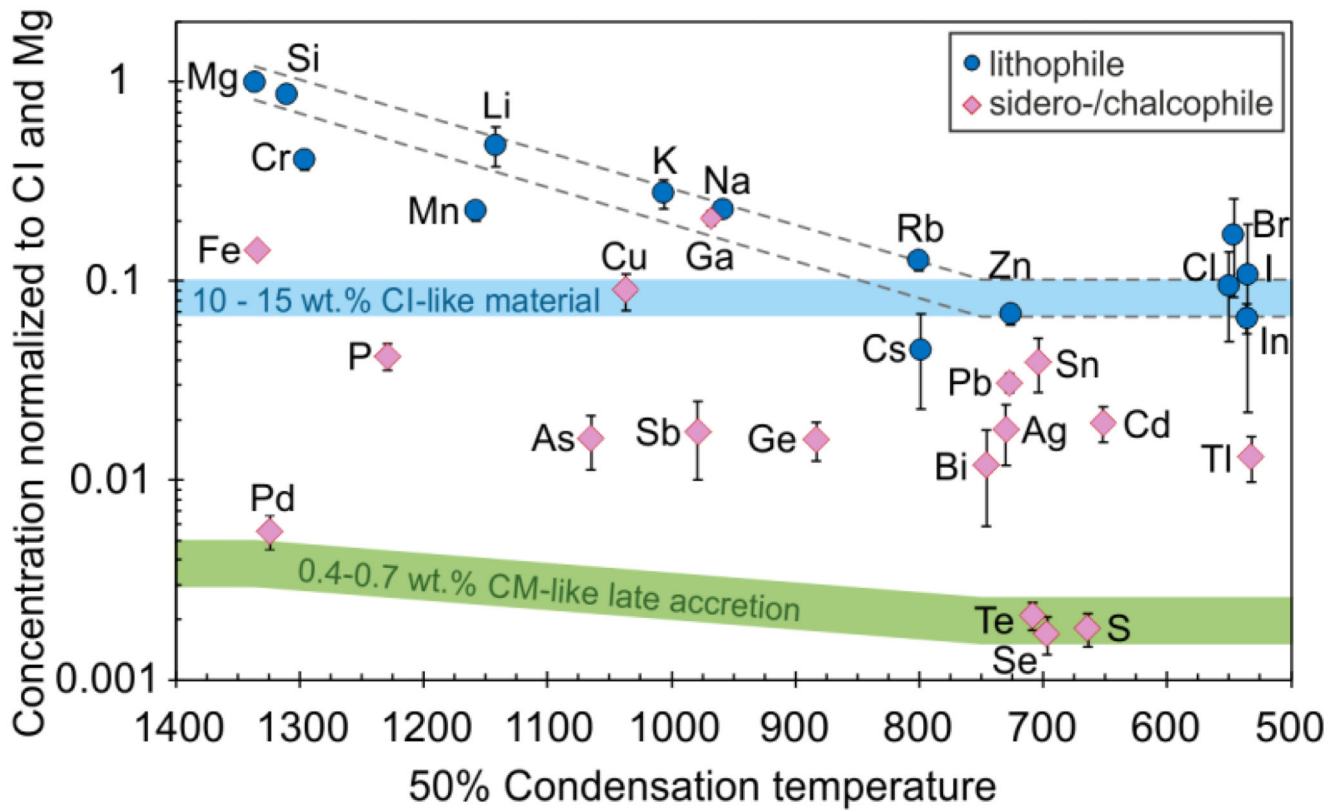
**Figure 1. Volatile element depletion pattern for different carbonaceous chondrite groups and the bulk silicate Earth (BSE).**

(a) CI chondrite and Mg normalized volatile element abundances in carbonaceous chondrites and lithophile volatile element abundances in the BSE define a hockey stick depletion pattern in a semilog plot. (b) Zoom-in on plateau region of the hockey stick. Error bars represent the propagated uncertainties of CI chondrite and CM, CV, CR or BSE concentrations, respectively. For data sources see Supplementary Table 1.



**Figure 2. Indium and Zn abundances normalized to CI chondrites and Mg in chondrites and the BSE.**

Carbonaceous chondrites<sup>25</sup> and the BSE<sup>14</sup> have a CI-chondritic In/Zn ratio as marked by the dashed line, whereas unequilibrated enstatite chondrites<sup>31</sup> scatter around the CI-chondritic ratio. Because of the large scatter of In abundances in ordinary chondrites, representative In/Zn cannot be inferred<sup>14,18</sup>. Since the In/Zn ratio of the BSE plots on the CI-chondritic ratio, it is concluded that In and Zn both behaved predominantly lithophile during core formation.



**Figure 3. Magnesium normalized volatile element abundances in the BSE relative to CI as a function of their 50% condensation temperature<sup>26,41,46</sup>.**

Lithophile plateau volatile element abundances in the BSE ( $TC < 750$  K) can be explained by the addition of 10 - 15 wt.% CI-like material within Earth's building blocks before core formation ceased. Sulfur, Se and Te were likely completely stripped of the mantle during this event before late accretion of 0.4 - 0.7 wt.% CM-like material<sup>3</sup>. Error bars represent the propagated uncertainties of CI chondrite and BSE concentrations. For data sources see Supplementary Table 1.

**Table 1**  
**Bulk Earth and core abundances for plateau volatile elements.**

	Bulk Earth [ $\mu\text{g/g}$ ]			Core [ $\mu\text{g/g}$ ]			Core/BSE	
	Case 1	Case 2	Ref. 12	Case 1	Case 2	Ref. 12	Case 1	Case 2
Bi	0.012	0.017	0.010	0.029	0.046	0.030	9.7	15
Ag	0.023	0.034	0.050	0.052	0.086	0.15	5.8	9.5
Pb	0.27	0.40	0.23	0.46	0.86	0.40	2.5	4.6
Zn	35	52	40	0	50	0	-	0.91
Te	0.24	0.35	0.30	0.71	1.06	0.85	65	97
Sn	0.16	0.24	0.25	0.21	0.44	0.50	1.5	3.2
Se	2.2	3.2	2.7	6.5	9.6	8.0	81	120
S	5300	7900	6400	16000	24000	19000	76	113
Cd	0.073	0.11	0.10	0.16	0.27	0.15	5.1	8.6
In	0.0083	0.012	0.007	0	0.013	0	-	1.08
Tl	0.014	0.021	0.014	0.035	0.056	0.030	8.6	14

Case 1 assumes an entirely lithophile behaviour of Zn and In, while Case 2 assumes that the core contains 50  $\mu\text{g/g}$  Zn<sub>36</sub>. Bulk Earth abundances normalized to CI and Mg yield a plateau at 0.067 for Case 1 and 0.100 for Case 2. For details of the calculation procedure see method section.