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The origin of unequilibrated EH chondrites - constraints from *in-situ* analysis of Si isotopes, major and trace elements in silicates and metal

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Abstract: Various lines of evidence suggest that material isotopically similar to enstatite chondrites may have accreted to the terrestrial planets. However, the enrichment of light Si isotopes in bulk enstatite chondrites is not easy to reconcile with the heavy Si isotopic composition of the Bulk Silicate Earth (BSE). To investigate the origin of the light Si isotopic composition of enstatite chondrites, we have obtained *in-situ* Si isotope data and simultaneously major- and trace element data in silicate and metal phases of chondrules, a metal-troilite spherule, and matrix from the enstatite chondrites Sahara 97072 (EH3) and Indarch (EH4) using laser ablation split stream -ICP-MS, which combines femto-second LA-MC-ICP-MS and Quadrupole-ICP-MS. Silicates in chondrules show variations in $\delta^{30}\text{Si}$ (‰ variations of $^{30}\text{Si}/^{28}\text{Si}$ relative to NBS-28) ranges from $-1.06 \pm 0.13\text{‰}$ (2 S.E.) to $-0.38 \pm 0.11\text{‰}$. $\delta^{30}\text{Si}$ in matrix silicates ranges from $-0.96 \pm 0.18\text{‰}$ to $-0.22 \pm 0.12\text{‰}$. The $\delta^{30}\text{Si}$ -value of silicate phases varies independently of Mg/Si, ruling out simple equilibrium condensation from nebular gas. Some silicates in both enstatite chondrites have $\delta^{30}\text{Si}$ -values like CI chondrites, whereas Si in other silicates is isotopically lighter, suggesting that the precursor materials of EH chondrites were already depleted in heavy Si isotopes.

The metal phases in the matrix show average $\delta^{30}\text{Si}$ of $-6.0 \pm 0.6\text{‰}$. In spite of different metamorphic grades, the fractionation of Si isotopes between matrix metal and silicates in Sahara 97072 and Indarch shows no systematic differences, and thus no re-equilibration of Si

isotopes occurred between silicates and metal at metamorphic temperatures below 900 K. The $\delta^{30}\text{Si}$ -value of metal from a metal-troilite spherule from Sahara 97072 ($-8.24 \pm 0.12\%$) is lower than that of matrix metals. These differences were likely inherited from different formation environments of matrix- and spherule metal. If metal formation occurred under equilibrium conditions, then matrix metal may have formed at higher temperatures than the MTS metal. or at similar temperatures but slightly lower oxygen fugacities, or the MTS metal equilibrated with gas or silicates which were not incorporated into EH chondrites because they were lost from the EH chondrite formation region. Alternatively, the differences in $\delta^{30}\text{Si}$ of different metals could also reflect variable kinetic isotope fractionation during the formation of metal and exsolution of perryite.

The considerably lower $\delta^{30}\text{Si}$ -values of bulk EH chondrites compared to CI- and other chondrites partly reflects the presence of Si bearing metal with isotopically light Si and partly silicates with isotopically light Si. The latter indicate loss of a heavy Si-rich silicate component from the EH3 formation region, presumably together with refractory elements. Although the Si isotopic composition of bulk EH chondrites precludes that these represent major building material of the Earth, the combination of complementary heavy Si isotope- and refractory element-enriched reduced materials and carbonaceous or ordinary chondrites could provide a match for the heavy Si isotopic composition of Earth.

1. Introduction

The Earth is isotopically identical to enstatite chondrites for many elements, notably major elements such as O, Fe, Mg and Ca (Clayton et al. 1984, Wang et al., 2014, Teng et al., 2010, Dauphas et al., 2014). However, because of the lighter Si isotope composition of enstatite chondrites compared to the Bulk Silicate Earth (BSE), it has been argued that enstatite chondrites cannot represent the predominant building material of the Earth (Fitoussi and Bourdon, 2012). Other chondrite classes also show lighter Si isotope compositions compared to BSE (Georg et al., 2007; Fitoussi et al., 2009; Savage et al., 2010; Chakrabarti and Jacobsen, 2010; Armytage et al., 2011; Zambardi and Poitrasson, 2011; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013; Pringle et al., 2014; Zambardi et al., 2013; Dauphas et al., 2015). Three different processes were proposed to account for the heavier Si isotopic composition of the BSE compared to chondrites. Some authors suggested that segregation of light silicon-bearing Fe-Ni metal into the Earth's core may have led to a heavier Si isotopic composition of the BSE (Georg et al., 2007; Fitoussi et al., 2009; Shahar et al., 2011; Armytage et al., 2011; Hin et al., 2014). Alternatively, nebular fractionation of Si isotopes between condensed solids, mainly forsterite, and gas phases such as $\text{SiO}_{(\text{g})}$ and $\text{SiS}_{(\text{g})}$ may have produced coupled variations of Si isotopes and Mg/Si of bulk planetary objects and meteorites (Fitoussi et al., 2009; Dauphas et al., 2015). Another hypothesis postulates the importance of mass loss and mass-dependent fractionation of Si and Mg by evaporation of large fractions of mass from mostly molten terrestrial planet precursors during planetary accretion (e.g., Pringle et al., 2014; Hin et al., 2017).

Metal-silicate isotopic fractionation and silicate-gas fractionation may also have played a role in setting the Si isotope composition of enstatite chondrites. The Fe-Ni metal in enstatite chondrites contains up to 5 wt-% Si (Horstmann et al., 2014 and references therein). Furthermore, in EH chondrites, Fe is enriched relative to Mg and refractory elements (e.g.,

Fe/Mg_{EH} > Fe/Mg_{CI}, Wasson and Kallemeyn, 1988), which appears to reflect enrichment of Fe-Ni metal in the formation region of enstatite chondrites (Wasson and Kallemeyn, 1988). Therefore, metal-silicate partitioning of Si during condensation of Fe-Ni metal could have had a significant influence on the Si isotopic composition (but perhaps not on Mg/Si) of enstatite chondrites. Mg/Si (Mg/Si_{atomic} = 0.79, Wasson and Kallemeyn, 1988) and $\delta^{30}\text{Si}$ (ranging from -0.77 to -0.59 ‰) of enstatite chondrites are the lowest amongst all meteorite groups and differentiated planetary bodies such as Vesta, Mars and Earth (Georg et al., 2007; Fitoussi et al., 2009; Armytage et al., 2011; Savage and Moynier, 2013; Dauphas et al., 2015). $\delta^i\text{Si}$ is the ‰-deviation of a Si isotope ratio in a sample relative to a reference material and is defined as

$$\delta^i\text{Si} (\text{‰}) = \left[\frac{\left(\frac{{}^i\text{Si}}{{}^{28}\text{Si}} \right)_{\text{Sample}}}{\left(\frac{{}^i\text{Si}}{{}^{28}\text{Si}} \right)_{\text{NBS-28}}} - 1 \right] \times 1000 \quad (1)$$

where i = 29 and 30.

Enstatite chondrites from the EH group (high-Fe) show lower silicon isotope ratios (Savage and Moynier, 2013) compared to EL chondrites (low-Fe), ordinary chondrites (OC) and carbonaceous chondrites (CC). Previous studies suggested that the lowest $\delta^{30}\text{Si}$ of EH chondrites may result from the high abundance of low- $\delta^{30}\text{Si}$ metal (Savage and Moynier, 2013). So far, no direct *in-situ* measurements of Si isotope ratios have been performed on EH chondrite metal and thus its contribution to the $\delta^{30}\text{Si}$ of bulk EH chondrites remains uncertain. The mass balance of Si isotopes in silicate and metal phases of equilibrated and unequilibrated EH chondrites potentially allows constraining Si isotope fractionation in nebular processes and during metal-silicate fractionation. Here we report the first *in-situ* Si-isotope data on such materials, combined with major- minor and trace element abundances in the silicate and metal phases of different components of the enstatite chondrites Sahara 97072 (EH3) and Indarch (EH4). This work places constraints on the formation conditions of EH chondrite components,

their precursor compositions in the solar nebula and the possible influence of later parent body heating processes.

2. Samples, preparation and methods

2.1 Description of samples

Both samples analyzed in this study belong to the EH chondrite group. Reflected light images of thick sections from both samples along with the laser analysis spots are shown in Supplementary Fig. S1 and S2. The average proportion of silicates and metal + sulfides in analyzed sections of both chondrites are $79 \pm 4 \%$ and $22 \pm 4 \%$, respectively. Sahara 97072 is an unequilibrated EH3 enstatite chondrite (EH_b, which have $> 2 \text{ wt\% Cr}$ in troilite based on a new classification scheme of Weyrauch et al., 2018) and is mainly composed of chondrules, silicate clasts, metal-troilite spherules (MTS), opaque clasts and matrix (Lehner et al., 2014)). The modal proportion of matrix in Sahara 97072 is approximately 22 % (Supplementary Fig. S1). Chondrules are mainly composed of silicate minerals such as enstatite, olivine, plagioclase and silica. Metal-troilite spherules are spherical nodules that are sometimes deformed. Major constituents of MTS are kamacite ($\alpha\text{-(Fe, Ni)}$) and troilite (FeS) with minor taenite ($\gamma\text{-(Ni, Fe)}$), different types of other sulfides characteristic of enstatite chondrites (e.g., niningerite) and enstatite. The matrix mainly contains fragments of chondrules and fine-grained metal-sulfide aggregates and fine-grained silicates. The matrix of Sahara 97072 hosts presolar carbon-bearing and silicate grains (Ebata et al., 2006, 2008) and is characterized by unique trace element compositions (Lehner et al., 2011, Kadlag and Becker, 2015). The metal-troilite spherules in Sahara 97072 were suggested to have a pre-accretionary origin (Lehner et al., 2010). For comparison, back scattered electron images of matrix metal grains and MTS metal are shown in Fig. 1. Matrix metal grains of Sahara 97072 and Indarch are irregular in shape and grain sizes are smaller compared to MTS metal (Fig. 1). Indarch is an EH4 (EH_a, $< 2 \text{ wt\% Cr}$ in troilite) meteorite, with a similar bulk composition as Sahara 97072. The matrix of Indarch hosts

presolar SiC grains with similar size as circumstellar grains (Huss and Lewis, 1995; Russell et al., 1997).

2.1 Sample preparation for in-situ LA-ICP-MS analysis

Thick sections (one-inch rounds) of Sahara 97072 and Indarch were prepared in epoxy resin. These sections were further polished and carbon coated to study their mineralogy. Chemical compositions of minerals in both samples were analyzed prior to laser ablation analysis using a JEOL JXA 8200 SuperProbe at Freie Universität Berlin using a beam current of 2 nA at 15 KV (see Supplementary Data for chemical composition).

2.2 Mass spectrometry

In-situ Si stable isotope- and the chemical composition of metal and silicate phases of chondrules, a metal-troilite spherule and matrix were determined using a laser ablation split stream (LASS) method (Glaus et al., 2013; Frick et al., 2016). A custom-built deep-UV (196 nm) femtosecond laser ablation system (GFZ fem2, a frequency-quadrupled Spectra Physics Solstice femtosecond laser, see Schuessler and Blanckenburg, 2014 for more details about the laser) was used to produce sample aerosol in a He gas stream. The aerosol was split between a multi-collector ICP-MS (Neptune, equipped with the Neptune Plus Jet Interface) for Si isotope analysis (~80 % of the volume) and a quadrupole ICP-MS (iCAPq) for determination of the chemical composition of ablated material (~20% of the volume). The laser was rastered over an area of 100-150 μm^2 with a laser spot diameter of ~20 μm to obtain the most precise $\delta^{30}\text{Si}$ -values by maintaining a stable signal for the duration of the analysis. Details of analytical parameters during laser ablation measurements are given in Table 1. To avoid cracks and analysis of mixed mineral phases, material was ablated along irregular paths (in the matrix). The relative abundances of masses ^{28}Si , ^{29}Si and ^{30}Si were determined in medium resolution mode with a mass resolving power ($m/\Delta m$) > 5000 in a clipped ion beam mode. It has been

140 shown that this method can resolve molecular interferences such as $^{14}\text{N}^{16}\text{O}^+$ on $^{30}\text{Si}^+$ or $^{12}\text{C}^{16}\text{O}$
 141 on ^{28}Si (Schuessler and Blanckenburg, 2014). In case of metal samples, interferences from
 142 doubly-charged species like $^{56}\text{Fe}^{++}$, $^{58}\text{Ni}^{++}$, $^{58}\text{Fe}^{++}$ and $^{60}\text{Ni}^{++}$ may affect signals at masses 28,
 143 29 and 30, respectively. The effect of doubly charged species on Si masses was evaluated using
 144 three different commercially available Ni and Fe metal wires (V2a-304, Nickel200 and
 145 NiFe48). V2a-304 is a stainless steel, Nickel200 is nearly pure nickel metal (99.5%) and NiFe48
 146 is a Ni-Fe alloy with nominally 52 wt % Ni and 48 wt% Fe. Samples of these metal wires were
 147 embedded in an epoxy mount, polished and analysed at similar conditions as the meteorite
 148 samples. A wide mass scan during the ablation of V2a-304 shows no signal on the half masses,
 149 indicating the absence of detectable doubly charged ^{57}Fe , ^{59}Co or ^{61}Ni . Intensities on ^{28}Si , ^{29}Si
 150 and ^{30}Si obtained during the analysis of Ni-Fe48 were $< 2\times$ background intensities. These results
 151 suggest that under the instrumental conditions used, the isotope ratios were not measurably
 152 affected by interferences from doubly charged ions. Another means to assess interferences from
 153 doubly charged ions is the $\Delta^{29}\text{Si}$ -value ($= \delta^{29}\text{Si} - 0.518 \times \delta^{30}\text{Si}$) (Ziegler et al, 2010) that deviates
 154 from zero beyond the analytical precision when interferences exceed a certain threshold. For
 155 kinetic and equilibrium Si isotope fractionation (KIF and EIF), the values of the triple isotope
 156 fractionation exponents β_{KIF} and β_{EIF} are 0.509 and 0.518, respectively (Young et al., 2002, note
 157 that β is also called θ in other literature, here we use notation β in the text for consistency with
 158 Young et al., 2002). Silicon isotope ratios were normalized to NBS-28 quartz sand (NIST
 159 SRM8546 alias NBS-28, $\delta^{29}\text{Si} \equiv 0$ and $\delta^{30}\text{Si} \equiv 0$) that was alternately measured, i.e. by standard-
 160 sample bracketing. The long-term reproducibility of this method is $< 0.23 \text{ ‰ } \delta^{30}\text{Si}$ (2s) for
 161 different matrices, as demonstrated by *in situ* analysis of various reference materials. To verify
 162 the accuracy of the analytical method, we have analyzed the *in-situ* silicon isotope ratios of the
 163 reference materials IRMM-17, BHVO-2G, NIST SRM610 and GOR132G by standard-sample
 164 bracketing against NBS-28. Average $\delta^{30}\text{Si}$ -values of IRMM-17, BHVO-2G, NIST SRM 610
 165 and GOR132G for two analytical sessions are $-1.20 \pm 0.14 \text{ ‰}$ (2s, $n= 12$), $-0.29 \pm 0.08\text{‰}$ ($n=$

10), $-0.09 \pm 0.11\%$ (n= 22) and $-0.42 \pm 0.11\%$ (n= 2), respectively. These values are identical within the analytical reproducibility to published values obtained by solution MC-ICP-MS, (Armytage et al., 2011, Savage et al., 2010, Zambardi and Poitrasson, 2011, Fitoussi et al., 2009, Tatzel et al. 2015). In the analytical session in which Indarch was analyzed, measured $\delta^{30}\text{Si}$ -values significantly deviate from mass fractionation lines, likely resulting from a loss in mass resolving power through the deterioration of the entrance slit during analysis causing interference on ^{30}Si from $^{14}\text{N}^{16}\text{O}^+$. Therefore, $\delta^{30}\text{Si}$ of Indarch was calculated from unbiased $\delta^{29}\text{Si}$ data using the mass dependent fractionation relation ($\delta^{30}\text{Si}^* = 1.93 \times \delta^{29}\text{Si}$) and is denoted $\delta^{30}\text{Si}^*$ in Table 3. The measured $\delta^{30}\text{Si}$ values in Sahara 97072 show no systematic difference to the $\delta^{30}\text{Si}^*$ values from Indarch (Table 2 and 3).

Major- and minor element abundances (Si, Mg, Fe, Al, Na, V, Cr and Ni) were quantified by 100 wt-% oxide normalization. Uncertainties on major element abundances were typically <10 % (1s), as determined by analysis of a range of reference materials. Data for the trace elements P, V, Cr, Co, Ni, Ga, Ge, Mo, Rh, Pd, Sb, W, Re, Pr, and Au are reported in the Supplementary Table S2. Quantification limits were up to tens of ng/g for these elements.

3. Results

Results of electron microprobe analysis are reported in Supplementary Table S1. The concentration of Si in Fe-Ni metal of both meteorites is $2.5 \pm 1.1\%$ (2s). The main host phases of Si are silicates (mainly orthopyroxene, plagioclase and glass) and Fe-Ni metal. In sulfides the concentration of Si is below the detection limit.

Silicon isotope ratios and major element concentration data of chondrule and matrix silicates (mainly enstatite and plagioclase) and of metal in metal-troilite spherules and matrix from Sahara 97072 and Indarch acquired by LASS method are reported in Table 2 and 3. The analysed spots on the sections are shown in Supplementary Fig. S1 and S2. Most analyses were

carried out on single mineral phases, typically enstatite, some analyses represent mixtures of intergrown mineral phases as indicated in cases where Al or Fe were > 1 wt%). An x-ray element map (obtained by electron microprobe) of a part of chondrule 1 of Sahara 97072 is shown in Supplementary Fig. S3. The dominant phase in this chondrule is enstatite, with (high concentrations of Al and Na) plagioclase and glass in interstitial space between enstatite grains.

3.1 Chondrules

Silicate phases (enstatite, plagioclase, and silica) in chondrules and chondrule fragments of Sahara 97072 and Indarch have $\delta^{30}\text{Si}$ -values between $-0.27 \pm 0.21\text{‰}$ and $-1.06 \pm 0.24\text{‰}$ (Table 2 and 3) and thus partly overlap $\delta^{30}\text{Si}$ -values of bulk ordinary and carbonaceous chondrites (Fitoussi et al., 2009; Armytage et al., 2011; Fitoussi and Bourdon, 2012; Pringle et al., 2014; Savage and Moynier, 2013; Zambardi et al., 2013; Dauphas et al., 2015), however, some silicates show considerably more negative $\delta^{30}\text{Si}$ -values. $\delta^{30}\text{Si}$ of chondrule silicates of Sahara 97072 ranges from $-0.81 \pm 0.16\text{‰}$ (2S.E.) to $-0.38 \pm 0.17\text{‰}$ (Table 2, Fig. 2) and in Indarch from $-1.06 \pm 0.24\text{‰}$ to $-0.27 \pm 0.21\text{‰}$ (Table 3). The variation of $\delta^{30}\text{Si}$ with Mg/Fe, Mg/Si and Mg/Al is shown in Fig. 3. Bulk rock data from enstatite, ordinary and carbonaceous chondrites from literature sources are given for comparison (Fig. 3).

3.2 Matrix silicates

Matrix silicates of Sahara 97072 have similar $\delta^{30}\text{Si}$ -values as chondrules and range from $-0.96 \pm 0.18\text{‰}$ to $-0.38 \pm 0.30\text{‰}$ (Table 2, Fig. 2). Matrix silicates of Indarch show variations in $\delta^{30}\text{Si}^*$ that range from $-0.67 \pm 0.23\text{‰}$ to $-0.21 \pm 0.24\text{‰}$ (Table 3, Fig. 2). The variation of $\delta^{30}\text{Si}$ ($\delta^{30}\text{Si}^*$ for Indarch) in matrix silicates with major element ratios is shown in Fig. 3. A weak correlation between $\delta^{30}\text{Si}$ and Mg/Fe appears to be present in matrix of Sahara 97072, however it cannot be well resolved due to relatively large uncertainties.

3.3 Metal in metal-troilite spherule

Silicon concentrations in metal of a metal-troilite spherule (MTS) from Sahara 97072 range from 2.7 to 3.6 wt.% (Table 2) with $\delta^{30}\text{Si}$ between $-8.24 \pm 0.12\text{‰}$ and $-7.09 \pm 0.19\text{‰}$. There is no systematic relationship between Si concentration and $\delta^{30}\text{Si}$ of MTS metal. The MTS metal has the lowest $\delta^{30}\text{Si}$ -value of all components of EH3 chondrites.

3.4 Matrix metal

The average Si concentration of matrix metal grains is 2.3 ± 0.3 wt.% (Table 2). Variations between Si concentrations and Si isotope compositions in matrix metal grains cannot be resolved, because most values overlap within uncertainties. In Sahara 97072, $\delta^{30}\text{Si}$ of the matrix metal is $-5.89 \pm 0.25\text{‰}$, significantly higher than in the MTS metal (Table 2). $\delta^{30}\text{Si}^*$ of matrix metal grains of Indarch range from $-5.95 \pm 0.26\text{‰}$ to $-5.53 \pm 0.24\text{‰}$ (Note: reported values are on metal phases without silicate contamination, see Table 3 for details).

4. Discussion

4.1 Zoning of $\delta^{30}\text{Si}$ in chondrules

No systematic relationship is observed between Si isotope ratios and the abundances and ratios of major elements such as Mg, Fe and Si in silicates of chondrules and chondrule fragments (Fig. 3). However, chondrules from Sahara 97072 show a weak systematic decrease of $\delta^{30}\text{Si}$ from chondrule core to rim, though differences cannot be well resolved on the 2 SE level (Fig. 4). The putative systematic decrease in $\delta^{30}\text{Si}$ with increasing distance from core to rim in Sahara 97072 might have resulted from the interaction of primary silicates in chondrule cores with ^{28}Si -rich SiS and/or SiO in the gas phase during chondrule crystallization and cooling (Fig. 4). The mineralogy and textures of the studied thick sections of Sahara 97072 and Indarch do not show visible evidence for shock melting (Supplementary Fig. S1, S2, and S3), suggesting that the Si isotope compositions of silicate phases were inherited from processes that occurred prior to accretion. Javoy et al. (2012) suggested that under the reducing conditions of enstatite

chondrites, the nebular gas was dominated by $\text{SiS}_{(\text{g})}$ and the $\delta^{30}\text{Si}$ of the $\text{SiS}_{(\text{g})}$ was -6 ‰. Interaction of such ^{28}Si -rich gas with enstatite during crystallization of the chondrules may have caused the slight decrease in $\delta^{30}\text{Si}$ from chondrule cores to rims. No systematic zoning of $\delta^{30}\text{Si}$ with distance from chondrule core to rim is observed in Indarch (Fig. 4b). A putative $\delta^{30}\text{Si}$ -zoning in chondrules from Indarch might have been erased either during heating in the solar nebula or during thermal metamorphism on parent body. Considering the low diffusion coefficients of Si in enstatite (Dohmen et al., 2002, Fei et al., 2012) the later explanation is less likely (this will be discussed in detail in section 4.3.2).

4.2 Variation of $\delta^{30}\text{Si}$ in matrix silicates

Matrix silicates show no systematic relationship between $\delta^{30}\text{Si}$ ($\delta^{30}\text{Si}^*$ in case of Indarch) and Mg/Si or Mg/Al (Fig. 3). Weak correlations between $\delta^{30}\text{Si}$ and Mg/Fe are observable in some matrix silicates of Sahara 97072 (Fig. 3). However, uncertainties are too large to clearly resolve the trend in the data. The decoupling of $\delta^{30}\text{Si}$ from major element ratios such as Mg/Si and Mg/Fe in matrix silicates suggests that equilibrium nebular fractionation during condensation likely did not control the variation of $\delta^{30}\text{Si}$ and major element ratios, at least not in a simple way. Previous work (Russell et al., 1997) showed that tiny SiC grains from Indarch show large mass independent variations in Si isotopes. Compared to the rastered area in our analysis ($\sim 100\mu\text{m}^2$) these grains are very small ($\ll 1\mu\text{m}$) and thus any effect on $\delta^{30}\text{Si}^*$ due to presence of such grains are within the analytical uncertainty of our data. In order to avoid ambiguities caused by the presence of presolar components, we have not considered data in the discussion that deviates from the mass fractionation line. Also, chondrule and matrix silicates of both chondrites show a similar range of Si isotope ratios, suggesting that chondrule and matrix silicates likely formed from the same reservoir or underwent similar Si isotope fractionation processes before accretion into the enstatite chondrite parent body. A detailed

discussion of the origin of Si isotope variations in silicates from EH chondrites will be given in later sections.

4.3 *Different origins of matrix metal and metal from metal-troilite spherules*

Despite the different metamorphic grades of Indarch and Sahara 97072, matrix metal grains in both meteorites have similar Si isotope ratios (Table 2 and 3, Fig. 2). The $\delta^{30}\text{Si}$ values of metal from the metal-troilite spherule are about 0.8 ‰ to 2.7 ‰ lower than matrix metal of Sahara 97072 and Indarch (Fig. 2). In the following sections we discuss processes that might have caused these variations.

4.3.1 *Contamination from neighboring silicates*

The difference in $\delta^{30}\text{Si}$ of MTS metal and matrix metal could result from contamination of ablated matrix metal with ablated nearby enstatite, which would increase $\delta^{30}\text{Si}$ of matrix metal in Sahara 97072 and Indarch. Assuming contamination is mainly from enstatite, concentrations of Si and Al in the ablated metals can be used to trace the effect of contamination. Silicon concentrations in matrix metal are not significantly higher than in MTS metal (if anything, the opposite is the case, Table 2). Assuming that the Al content of matrix metal (from 0.001 wt% to 0.06 wt.%) is derived from silicates and using the Al content of enstatite (Table 2 and 3), the Al-concentrations in analyses of metals suggests that the fraction of contamination by enstatite is ranging from zero to < 2%. Applying corrections for contamination (assuming an average Si concentration of 27.1 ± 1.3 wt% in silicates) yields a significant (up to 1.5 ‰ $\delta^{30}\text{Si}$) change in the $\delta^{30}\text{Si}$ values of a few matrix metal grains (see corrected values in Table 2 and 3). The uncertainty on corrected $\delta^{30}\text{Si}$ -values is relatively large in the case of analyses with the largest contamination. For instance, $\delta^{30}\text{Si}_{\text{matrix metal}}$ of Sahara 97072 changes from $-5.89\text{‰} \pm 0.25\text{‰}$ to $\delta^{30}\text{Si}_{\text{matrix metal, corrected}}$ of -6.5 ± 0.6 ‰ (1s). Due to the larger uncertainties associated with corrected values, it is hard to assess if corrected data are different from uncorrected $\delta^{30}\text{Si}_{\text{metal}}$ values. Electron microprobe analyses of matrix metal grains of Sahara 97072 yielded Si

concentrations of 3.3 wt. % (see Supplementary Table S1). The Si concentration of ablated metal is 2.58 wt.% (Table 2). In case of contamination with enstatite, the Si concentration of this metal grain measured by LA-ICP-MS should also increase with increased Al concentration. However, the data do not show this. All corrected $\delta^{30}\text{Si}$ values of contaminated metal from Indarch are similar with data on metal analyses that were not contaminated by enstatite, with an average value of $\delta^{30}\text{Si} = -6.0 \pm 0.6 \text{ ‰}$ (1s). Note that this measured average value is similar within uncertainty to the calculated $\delta^{30}\text{Si}$ ($-5.8 \pm 4.5 \text{ ‰}$, Savage and Moynier, 2013) of Indarch metal. This average value is still higher than the $\delta^{30}\text{Si}$ of the MTS metal. Therefore, we conclude that contamination from neighboring silicates alone cannot account for higher $\delta^{30}\text{Si}$ of matrix metal grains compared to MTS metal.

4.3.2 *Diffusion of Si during metamorphic heating*

Late diffusive exchange of Si from neighboring silicates due to metamorphic heating might have caused higher $\delta^{30}\text{Si}$ of matrix metal compared to MTS metal. The highest metamorphic temperatures of type 3 chondrites and Indarch were $\leq 900 \text{ K}$ (Huss and Lewis, 1994). At 900 K, the diffusion length of Si is $\sim 10^{-4}$ to $10^{-2} \text{ }\mu\text{m}$ in enstatite, assuming a time scale of 300 Ma (Dohmen et al., 2002, Fei et al., 2012). At these temperatures, solid state diffusion of Si between metal and enstatite at grain boundaries would require more than 4500 million years, to significantly change the $\delta^{30}\text{Si}$ of the metal. At lower temperatures (for instance 700 K) diffusion is even slower, and thus time scales will be much longer. However, these experimental diffusion coefficients of Si were determined at oxidizing conditions of $\Delta\log fO_2$ from IW+15 to IW+1 (IW = iron-wüstite buffer). There is a hint of a weak increase of the self-diffusion coefficient of Si in olivine at low fO_2 (Houlier et al., 1990), however, other studies have not confirmed this. Therefore, it is considered unlikely that diffusion of Si between enstatite and metal during metamorphic heating has caused significant change in the Si isotope composition of matrix metal.

Indarch (EH4) shows a higher metamorphic grade than Sahara 97072 (EH3). The metamorphic temperature calculated for Indarch using noble gas retention in presolar diamonds is 923 K, whereas for EH3 chondrites such as Qingzhen, metamorphic temperatures were ≤ 770 K (Huss and Lewis, 1994). Although equilibration temperatures differ for these EH chondrites, Si isotope fractionation between matrix metal and silicate phases in Sahara 97072 and Indarch is indistinguishable within analytical reproducibility. We note that if Si isotopic re-equilibration of silicates with metals occurred due to metamorphic heating, average Si isotopic compositions of Indarch silicates should be lighter than silicates of Sahara 97072, which is not observed (Table 2 and 3). Higher $\delta^{30}\text{Si}$ -values in some metal grains, such as M2, M4 and M6 may be attributed to contamination from neighboring silicates. After correction for contamination, these grains show similar $\delta^{30}\text{Si}$ -values as uncontaminated metal grains, with an average $\delta^{30}\text{Si}$ of all metal grains of -6.0 ± 0.6 (1s). Work by Ziegler et al., (2011) shows that the $\delta^{30}\text{Si}$ of aubrite metal is -6.4 ± 0.4 (1s), which overlaps within analytical reproducibility with matrix metals analyzed in this study. The $\delta^{30}\text{Si}$ data suggest insignificant effects of metamorphic heating on the diffusion of silicon isotopes between metal and silicates at the range of relevant metamorphic temperatures e.g. from ~ 770 K in EH3 chondrites to 1270 K for aubrites (Huss and Lewis, 1994; Ziegler et al., 2010).

4.3.3 *Differences in the formation temperatures of matrix metal and MTS metal*

The very low $\delta^{30}\text{Si}$ of metal grains (ranging from $-5.53 \pm 0.24\text{‰}$ to $-8.24 \pm 0.12\text{‰}$) may have been inherited from equilibrium isotope fractionation or kinetic isotope fractionation during their formation. The $\delta^{30}\text{Si}$ of metal from metal-troilite spherule are about 0.8 ‰ to 2.7 ‰ lower than matrix metal of Sahara 97072. We will discuss the likelihood of both possibilities (kinetic and equilibrium isotope fractionation) in detail. The effect of kinetic isotope fractionation on $\delta^{30}\text{Si}$ is discussed in later sections. In this section we discuss two scenarios of equilibrium isotope fractionation: the Si isotope composition of metal grains analysed in this study might

reflect equilibrium isotope fractionation, either with silicate dust or with nebular gas. For this, the Si isotopes of the fine-grained metal grains and silicate dust or fine-grained metal grains and remaining nebular gas need to be in chemical equilibrium with each other during the formation of the metal grains. However, metal-silicate equilibrium may not be feasible in a dynamically evolving solar nebula, as it requires fine grained silicate dust and metal grains to remain in equilibrium with each other. The second scenario involves equilibrium isotope fractionation of Si between Fe-Ni metal and SiS or SiO gas. If we assume that the matrix metal and MTS metal were formed by equilibrium condensation in the solar nebula, and matrix metal formed at ~ 1350 K (Larimer and Bartholomay, 1979, Lodders, 2003), then the $\delta^{30}\text{Si}$ observed in matrix metal (i.e. -6.0 ‰) suggest that $\delta^{30}\text{Si}_{\text{SiO(gas)}}$ was -5 ± 1 ‰ (calculated using the fractionation factor between Fe_{15}Si and $\text{SiO}_{\text{(gas)}}$ from Javoy et al., 2012 at $T = 1350$ K). If similar $\delta^{30}\text{Si}_{\text{SiO(gas)}}$ are assumed, then a similar calculation for MTS metal ($\delta^{30}\text{Si} \sim -8$ ‰) yields a formation temperature of $800 + 100$ K. Thus, $\delta^{30}\text{Si}$ of MTS metal could reflect low temperature nebular processing under equilibrium conditions.

In summary, the difference in the $\delta^{30}\text{Si}$ of matrix metal and MTS metal is likely due to variable pre-accretionary formation conditions (such as temperature, $f\text{O}_2$, chemical composition) which, in terms of Si concentration and $\delta^{30}\text{Si}$, produced variable compositions of the precursors of the metal grains in these objects.

In the next section we will discuss different physicochemical boundary conditions that might be an alternative way to explain the different Si isotopic compositions in the metals.

4.3.4 The influence of oxygen fugacity on the Si isotope composition

The mineralogy of enstatite chondrites and the presence of Si as a major element in Fe-Ni metal of EH chondrites indicate formation under extremely reducing conditions, consistent with a C/O of 0.83 (Mason, 1966; Keil 1968; Kallemeyn and Wasson, 1986; Fleet and MacRae,

1987; Keil, 1989; Grossman et al., 2008). The predicted onset of condensation calculated by Grossman et al. (2008) at $P_{\text{total}} = 10^{-4}$ atm occurs at $\Delta \log fO_2$ of about IW-8.9 and $\Delta \log fO_2$ decreases during the removal of high temperature condensates (such as forsterite, spinel, melilite, diopside and refractory metal alloys) from IW-10.1 at 1200 K to IW-13 at 900 K (Grossman et al., 2008). Assuming C/O of 0.83 at the time of formation of metal grains with a Si concentration of 2.5 ± 1.1 wt.%, suggests formation temperatures of the metal grains between 1200 K and 1300 K (Grossman et al., 2008). If a similar scenario is applied to MTS metal and MTS metal formed at lower temperatures under equilibrium conditions ($T = 800 \pm 100$ K), this would imply lower fO_2 (because of the T-dependence of fO_2 , i.e. at 800 K, $\Delta \log fO_2$ is IW-13). In that case, Si contents of MTS metal should be higher than Si contents of matrix metals. We observe variations in Si concentrations in MTS metal, ranging from values similar to matrix metal of Sahara 97072, to about 1 wt.% higher than matrix metal of Indarch (Table 2, Supplementary Table S1). The heterogeneity in Si concentrations in MTS metal grains suggests that changes in fO_2 and the C/O ratio occurred during solidification of metal grains. Alternatively, the moderate Si concentration variations reflect ablation of Si-rich and Si-poor mineral phases (such as perryite, schreibersite, troilite) along with the metal.

An alternative formation process of MTS metal may involve formation in a different nebular domain than matrix metal. For instance, if high temperature condensates were removed from a nebular region prior to the formation of MTS metal, remaining nebular gas would have $\Delta \log fO_2 < \text{IW-8.9}$ (Grossman et al., 2008). If MTS metal formed from this remaining gas at C/O ~ 0.83 , condensation calculations suggest that under these conditions and at $P_{\text{total}} = 10^{-3}$ bar, MTS metal should contain ~ 6.5 wt.% to 8.8 wt.% Si (Grossman et al., 2008), which is not observed (Table 2). Therefore, the $\delta^{30}\text{Si}$ and Si concentrations of the metals permit that MTS metal and matrix metal reflect formation at either somewhat different temperatures, or at different fO_2 and C/O ratios (see additional discussion of evidence from Cr/V ratios in metal and silicates in the

Supplementary Text and Supplementary Fig. S5). The relatively homogenous $\delta^{30}\text{Si}$ compositions of matrix metal may have been set by the last pre-accretionary heating event (chondrule formation).

Note that the variation of Si concentrations of matrix metal and MTS metal is $\leq 1\text{wt.}\%$, and that values of 2-3 wt. % Si in metal imply formation temperatures between 1200 K and 1300 K at $\text{C/O} > 0.81$ (Grossman et al., 2008). The lower $\delta^{30}\text{Si}$ of MTS metal suggests that MTS metal grains equilibrated with nebular gas or silicates with $\delta^{30}\text{Si}$ of $-1.5 \pm 1.0\text{‰}$. Very few analyses of EH chondrite silicates show $\delta^{30}\text{Si}$ -values as low as -1‰ (Table 2). Either these silicate phases with lower $\delta^{30}\text{Si}$ were lost from the EH chondrite formation region, or MTS formed separately in a different EC reservoir and were later incorporated into EH chondrites. In conclusion, MTS metal may have formed either at lower temperatures or from a different, already fractionated and ^{30}Si -depleted reservoir at lower $f\text{O}_2$

4.3.5 Kinetic isotope fractionation of Si during formation of metal or exsolution of Si-bearing minerals

Fractionation laws for equilibrium- and kinetic isotope fractionation predict that triple isotope fractionation exponents β for silicon are 0.518 and 0.509, respectively (Young et al., 2002). A best fit linear regression line of all our metal and silicate data from Sahara 97072 yields $\beta = 0.503 \pm 0.008$ (2s, see Supplementary Fig. S5). Kinetic fractionation of isotopologues is predicted to yield lower triple isotope fractionation exponents due to the decreasing relative mass difference with increasing isotopologues mass. Fe-Si and Ni-Si isotopologues fractionation yields a theoretical β -value of 0.5034 to 0.5035, identical to the slope of the regression line through our Sahara 97072 data. This result thus would suggest that kinetic isotope fractionation between the analysed metal and silicate phases or gas could have been the predominant isotope fractionation process. We note that because of the limited isotopic variation between similar components (e.g. silicates only), kinetic and equilibrium isotope

fractionation are indistinguishable at the component scale and the best fit line is strongly affected by the metal data. Moreover, we note that the differences in beta between atomic and isotopologue fractionation are small (approx. 0.005 in this example), making the distinction between these fractionation mechanisms still difficult using current analytical techniques.

If the estimated β value from the analysed components is correct, then the kinetic isotope fractionation of Si isotopes in MTS metal must have occurred during high temperature processes prior to accretion. Assuming incorporation of Si into the MTS metal from a gas of CI chondrite-like $\delta^{30}\text{Si}$ and for equal condensation coefficients for ^{28}Si and ^{30}Si , kinetic isotope fractionation during condensation of Si into the Fe metal yields $\Delta^{30}\text{Si}_{\text{Kinetic}}^{\text{Si metal/Si gas}} = -34$ for pure Si as a gas species. Taking into account that the nebular gas is mainly dominated by SiO and SiS, $\Delta^{30}\text{Si}_{\text{Kinetic}}^{\text{Si metal/SiO gas}} = -22$ ‰ and $\Delta^{30}\text{Si}_{\text{Kinetic}}^{\text{Si metal/SiS gas}} = -16$ ‰. All these values are very low and are not observed in metal. However, kinetic isotope fractionation due to Rayleigh distillation during progressive evaporation of Si from MTS metal with initial $\delta^{30}\text{Si} = -22$ ‰ leads to $\delta^{30}\text{Si}$ of -6.6 to -8.3‰ for 80-82% loss of initial Si from the metal. We note that a simple kinetic fractionation effect is not observed in other stable isotope systems, e.g. Fe (Wang et al. 2014) and KIF does not explain the decoupling of $\delta^{30}\text{Si}$ from major elements in the silicates (Fig.3).

Processes that led to kinetic Si isotope fractionation in MTS metal might be related to the final thermal processing during chondrule formation or during the formation of perryite ((Ni, Fe)₈(Si, P)₃). If correct, this would render temperature estimates for MTS metal from Sahara 97072 from equilibrium isotope fractionation meaningless. A best fit linear regression line of $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ data of silicates and metals from Sahara 97072, excluding MTS data, yields $\beta = 0.5031 \pm 0.0192$ (2s). The mean value is lower than β for equilibrium isotope fractionation, however, the uncertainty is too high to clearly resolve equilibrium or kinetic fractionation process within the 95% confidence interval. Although the β value for Si in Sahara 97072

suggests that kinetic isotope fractionation may have played a role, the relatively large uncertainties of the data shows that it is difficult to unequivocally resolve the specific isotope fractionation process. Therefore, we conclude that in case of MTS metal, the variation in $\delta^{30}\text{Si}$ might be an effect of a late process, such as kamacite-perryite exsolution. However, we cannot quantify this process with the spatial resolution of our method.

4.4 Constraints on metal formation from siderophile element abundances

Bulk EH chondrites show a depletion of refractory lithophile and siderophile elements in CI normalized abundance diagrams compared to Fe, Mg and more volatile elements such as Si, K or Au (Kallemeyn and Wasson, 1986). If the formation of MTS metal and matrix metal occurred in different nebular settings, the different formation conditions could be reflected in their siderophile element patterns. Siderophile element abundances of matrix and MTS metal grains analyzed in this study show fractionated patterns with respect to CI chondrites (Fig. 5). CI normalized abundances of Re, Pt and Pd are depleted compared to CI normalized abundances of W, Mo, Rh, Au, Ni, Co and Fe. Fractionations of Re, Pt, Pd, W and Au in both types of metal grains are likely inherited from the solar nebula as these approximately reflect fractionations observed in bulk EH chondrites (Fig. 5, bulk rock data from Crocket et al., 1967, Morgan and Lovering, 1967, Wiik, 1969, Michaelis et al., 1969, Schmitt et al., 1972, Hintenberger et al., 1973, Baedeker and Wasson, 1975, Ehmann et al., 1979, Bhandari et al., 1980, Kallemeyn and Wasson 1986, Morgan et al., 1990, Kong et al., 1997, McDonald and Russell, 2001, Kadlag and Becker, 2015). During partial melting of metal grains on reduced parent bodies, elements such as Pd and Au show similar partition coefficients between solid metal and liquid, sulfur-rich metal. Furthermore, Re, W and Pt also show comparable solid metal-liquid metal partitioning (Chabot and Jones, 2003; Chabot et al., 2003, 2006). The normalized siderophile element patterns show a depletion of Pd relative to Au and scatter in Re and Pt, however, W displays no changes in relative abundances. Thus, no complementary pattern with W depletion is observed

that could be diagnostic of local solid metal-liquid metal partitioning, for instance during impact melting (Fig. 5). The correlation of Mo and P abundances in matrix metal of Indarch indicate preferential incorporation of Mo into schreibersite $[(\text{Fe}, \text{Ni})_3\text{P}]$, whereas other elements are mainly residing in kamacite. The heterogeneity of Mo and P in MTS metal and matrix metal grains of Sahara 97072 suggests that schreibersite and adjacent kamacite were not in equilibrium with each other. The absence of systematic variations between P and siderophile elements (except Mo) in all metal grains indicates negligible diffusive re-equilibration between schreibersite and kamacite on the parent body (Fig. 5). Hence, the observed patterns are inconsistent with fractionation during solid metal-liquid metal partitioning, metal-sulfide partitioning or metal-silicate partitioning (Chabot and Jones, 2003; Chabot et al., 2003, 2006) on the parent body, which indicates that the major process controlling the siderophile element abundances in metals and bulk EH chondrites is heterogeneous mixing of different metal precursors from the solar nebula. Partitioning of Mo might have occurred during the formation of schreibersite during cooling of the metal. As schreibersite and sulfides do not contain Si, the contamination from these minerals during the analysis of metal does not affect $\delta^{30}\text{Si}$ of kamacite. In conclusion, the difference in siderophile element abundance patterns and $\delta^{30}\text{Si}$ of metal were likely inherited from already fractionated metal precursors in the solar nebula, as the metals overall show similarities with the siderophile element patterns of bulk rocks of EH chondrites. It can be concluded that the homogeneous Si concentration and Si isotope composition of matrix metal (section 4.3) and siderophile element abundances in the metals of this study yield no evidence for the metamorphic heating or local melting caused by late impacts as proposed for some E chondrite impact breccias (e.g., Horstmann et al., 2014).

4.5 *Silicon isotope composition of bulk enstatite chondrites*

Bulk enstatite chondrites show lower $\delta^{30}\text{Si}$ -values compared to CI chondrites (Fig. 2, $\delta^{30}\text{Si}_{\text{IEH}} = -0.69 \pm 0.05 \text{ ‰}$, $\delta^{30}\text{Si}_{\text{IEL}} = -0.581 \pm 0.033 \text{ ‰}$, $\delta^{30}\text{Si}_{\text{CI chondrites}} = -0.448 \pm 0.143 \text{ ‰}$, 2s; Georg et

486 al., 2007; Fitoussi et al., 2009; Chakrabarti and Jacobson, 2010; Armytage et al., 2011; Fitoussi
 487 and Bourdon, 2012; Savage and Moynier, 2013; Zambardi et al., 2013). The average $\delta^{30}\text{Si}$ -value
 488 of bulk Indarch is $-0.66 \pm 0.07 \text{ ‰}$ (1s) and that of conventionally analyzed silicate fractions of
 489 Indarch is $-0.61 \pm 0.06 \text{ ‰}$ (Chakrabarti and Jacobson, 2010; Ziegler et al., 2010; Fitoussi and
 490 Bourdon, 2012; Savage and Moynier, 2013).

491 If we assume that the initial $\delta^{30}\text{Si}$ of EH chondrite precursors was similar to average CI
 492 chondrites, and the average $\delta^{30}\text{Si}$ of EH metal is -6.0 ‰ , then, according to mass balance (3 %
 493 g/g of the Si in EH chondrites is in the metal, 97 % g/g in silicates), $\delta^{30}\text{Si}$ of silicates should be
 494 -0.28 ‰ . However, the average $\delta^{30}\text{Si}$ of silicates analyzed in this study is $-0.58 \pm 0.10 \text{ (2s) } 08$
 495 ‰ (note that the average $\delta^{30}\text{Si}$ of EH silicates from literature data = $-0.56 \pm 0.18 \text{ (2s)}$, Ziegler
 496 et al., 2010; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013) which is 0.3‰ lower than
 497 expected from metal-silicate partitioning of Si isotopes of CI chondrite-like precursors. These
 498 results indicate that simple closed system equilibrium condensation from a CI-like reservoir
 499 cannot explain the $\delta^{30}\text{Si}$ of silicates in EH chondrites.

500 The $\delta^{30}\text{Si}$ of silicate phases in EH and EL chondrites analyzed by Savage and Moynier (2013)
 501 overlap with $\delta^{30}\text{Si}$ of bulk ordinary and carbonaceous chondrites within uncertainties. Because
 502 $\delta^{30}\text{Si}$ and Mg/Si and Al/Si in silicate phases did not correlate, Savage and Moynier (2013) ruled
 503 out that loss of refractory element-enriched material with higher $\delta^{30}\text{Si}$ was the main process
 504 responsible for the low $\delta^{30}\text{Si}$ of enstatite chondrites. They suggested that the presence of ^{28}Si -
 505 rich metal caused the light Si isotopic composition of bulk enstatite chondrites. We note that
 506 the average $\delta^{30}\text{Si}$ of silicates in this study ($-0.61 \pm 0.13 \text{ ‰}$ (1s) and $-0.55 \pm 0.19 \text{ ‰}$ for Sahara
 507 97072 and Indarch, respectively) are lower than $\delta^{30}\text{Si}$ of CI chondrites (Table 2 and 3, Fig. 2).
 508 None of the silicate phases from our study and bulk silicate data from previous studies show
 509 higher $\delta^{30}\text{Si}$ -values than CI chondrites (Ziegler et al., 2010; Fitoussi and Bourdon, 2012; Savage
 510 and Moynier, 2013). This observation suggests that all silicate precursors of EH chondrites had

either lower or similar $\delta^{30}\text{Si}$ as CI chondrites. The bulk rock $\delta^{30}\text{Si}$ of Sahara 97072 and Indarch
 calculated from mass balance of silicates and metal in this study ($-0.74 \pm 0.08 \text{ ‰}$) are identical
 to the average $\delta^{30}\text{Si}$ of bulk rocks of EH chondrites (Georg et al., 2007; Fitoussi et al., 2009;
 Chakrabarti and Jacobson, 2010; Armytage et al., 2011; Fitoussi and Bourdon, 2012; Savage et
 al., 2010; Savage and Moynier, 2013). The metal phases of enstatite chondrites show the lowest
 $\delta^{30}\text{Si}$ analyzed so far among chondrite components. The difference in average $\delta^{30}\text{Si}$ of
 calculated bulk rocks with and without metal phases is $\sim 0.2 \text{ ‰}$. Thus, the contribution from light
 Si in metal shifts $\delta^{30}\text{Si}$ of bulk rocks towards more negative values because the silicate phases
 show similar $\delta^{30}\text{Si}$ as the bulk rocks within uncertainty (this work and Savage and Moynier,
 2013). However, consideration of the effect of isotopically light Si in metal does not remedy
 the absence of silicate phases with higher $\delta^{30}\text{Si}$ than CI-chondrite and the effects that a loss of
 refractory phases would have on Si isotope fractionation in EH chondrites.

The silicate and metal compositions in these EH chondrites and bulk EH compositions can
 be explained by a formation scenario (Fig. 6) which starts with a gas of CI chondrite-like
 composition (Step I, Fig. 6). Equilibrium fractionation between condensing silicates and SiO_{gas}
 yields refractory silicates (e.g. forsterite) with higher $\delta^{30}\text{Si}$ and Mg/Si than CI chondrites (Javoy
 et al., 2012, Méheut et al., 2009, Dauphas et al., 2015). The condensation of isotopically heavy
 silicate phases (notably forsterite with $\delta^{30}\text{Si}_{\text{LRS}} = 0.70 \text{ ‰}$ and atomic $\text{Mg/Si}_{\text{LRS}} = 2$) and
 separation/loss of $15 \pm 4 \text{ ‰}$ of the total Si originally present (i.e. $\sim 30 \text{ ‰}$ Si condensed in
 refractory phases) occurred in the second step (for details of the calculations see supplementary
 text). This “lost refractory silicate” (LRS) component may have accreted to form as yet
 unsampled objects in the formation region of EH (presumably the innermost solar system) or
 accreted to planetesimals that quickly accreted into larger planetary bodies (as discussed in
 section 4.6). Thus, the heavy Si isotopes may have been lost simultaneously with refractory
 elements from the EH chondrite formation region, which may have taken place before the

accretion of volatile elements and the late modification of EH chondrite components by
 chondrule formation. Major silicate minerals lost from the EH chondrite formation regions are
 possibly, Ca-Ti-Al rich silicates and forsterite (assuming the condensation sequence of Larimer
 and Bartholomay, 1979 is valid). The separation of refractory silicates left behind residual gas
 with $\delta^{30}\text{Si}_{\text{RGD}} = -0.75 \pm 0.08$ (1s) ‰ and $\text{Mg}/\text{Si}_{\text{RGD}} \sim 0.74 \pm 0.06$ (calculated using mass fractions
 of Si in the solid phase and gas phase see supplementary information). Separation of refractory
 silicates and oxides also would have resulted in further increase of C/O (> 0.5) of the remaining
 nebular gas. Based on the results of this study, we assume that the average $\delta^{30}\text{Si}$ of matrix metal
 in EH chondrites is -6.0 ‰, and that the formation of metal with 3% Si with $\delta^{30}\text{Si}_{\text{Met}} = -6.0$ ‰
 and $\text{Mg}/\text{Si}_{\text{Met}} < 0.01$ occurred at ~ 1350 K (Larimer and Bartholomay, 1979, Lodders, 2003).
 The observed $\delta^{30}\text{Si}$ of matrix metal in this study requires partial ($> 80\%$) gas-solid equilibrium.
 Thus, the measured $\delta^{30}\text{Si}$ of matrix metal was affected by both KIF and EIF of Si isotopes in
 the matrix metal grains from SiO and SiS gas. The main assumptions used in the isotopic mass
 balance are that equilibrium isotope fractionation occurred between Fe_{15}Si and SiO and SiS gas
 (values from Javoy et al., 2012) and that kinetic isotope fractionation occurred between Fe-Ni
 metal and SiO and SiS gas. The remaining 82% of the gas + solid had $\delta^{30}\text{Si}$ of -0.59 ± 0.23 ‰
 (1s) and a Mg/Si of 0.76 (Step III, Fig. 6). In step IV, the variation of $\delta^{30}\text{Si}$ and Mg/Si in silicates
 which formed from the remaining 82 % of gas + solids may have been affected by both kinetic
 and equilibrium isotope fractionation (for details see Fig. 6). Kinetic isotope fractionation in a
 gas with an initial composition of $\delta^{30}\text{Si} \sim -0.59 \pm 0.2$ ‰ (1 σ) and $\text{Mg}/\text{Si} \sim 0.76$ (see above)
 resulted in formation of silicates with $\delta^{30}\text{Si}_{\text{Sil}} < -0.59\text{‰}$ and $\text{Mg}/\text{Si}_{\text{Sil}} > 0.76$. Some of these
 silicates may have preserved $\delta^{30}\text{Si}$ and Mg/Si values from the time of their formation by the
 shielding effect of mineral rims which could have prevented reaction with remaining nebular
 gas. Because the equilibrium fractionation factor between enstatite and SiO or SiS gas is
 positive (Javoy et al., 2012), equilibrium isotope fractionation (EIF) would have led to the
 formation of silicates with $\delta^{30}\text{Si}_{\text{Sil}} > -0.59\text{‰}$ and $\text{Mg}/\text{Si}_{\text{Sil}} > 0.76$. Which of these processes was

dominant may have been influenced by the timescale of the formation and growth of mineral grains and time-dependent changes in ambient gas pressure. Kinetic fractionation is favored when mineral growth is faster than the reaction timescale of gas and already formed solids.

Several authors favored KIF during the formation of enstatite and metal (Fitoussi et al., 2009; Armytage et al., 2011; Dauphas et al., 2015), however, equilibrium isotope exchange may also account for the Si isotope data of some EH metals and silicates. The Si isotope composition of SiS and SiO in the remaining nebular gas is lighter than in CI chondrites. The following reactions could be plausible mechanisms in the nebular source regions of EH chondrites.

Assuming heavy Si and refractory element-rich phases (such as ^{30}Si enriched Mg_2SiO_4 and Ca-Al-rich silicates) were lost before accretion of the lighter Si-rich phases in enstatite chondrites, then equilibrium isotope fractionation might explain the lighter Si isotope composition of bulk silicates (average $\delta^{30}\text{Si} \sim -0.56 \pm 0.18$, 2s, data from this study and Ziegler et al., 2010; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013) of EH chondrites compared to other chondrites and planetary objects. Formation of enstatite and other minor silicate phases ($T_{\text{condensation}} < 1400$ K) in EH chondrites may involve interaction of leftover material of earlier formed silicates with remaining SiO and SiS gas in the solar nebula (Eq. 4). The variation of $\delta^{30}\text{Si}$ in second-generation silicate mineral phases and metal (right hand side of Eqs. 2, 3 and 4) depends on the composition of primary solid phases and remaining gas (left hand side of Eqs. 2, 3 and 4). In such an environment, the enrichment of ^{28}Si in metal can be explained by both equilibrium and kinetic fractionation during the formation of metal grains.

To conclude, because of the low Si concentration in metal and low $\delta^{30}\text{Si}$ -values in a significant fraction of silicates in EH chondrites (this study, Ziegler et al., 2010; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013), the low $\delta^{30}\text{Si}$ -value of bulk EH chondrites (this study, Georg et al., 2007; Fitoussi et al., 2009; Chakrabarti and Jacobson, 2010; Armytage et al., 2011; Fitoussi and Bourdon, 2012; Savage et al., 2010; Savage and Moynier, 2013) compared to CI chondrites cannot be attributed exclusively to the presence of metal with very low $\delta^{30}\text{Si}$. If the metal and silicate phases of EH chondrites were formed from a common reservoir, then the initial $\delta^{30}\text{Si}$ of this reservoir was already lower than $\delta^{30}\text{Si}$ of CI chondrites. Alternatively, metal and silicate phases formed independently in highly reduced domains ($\Delta\log fO_2$ from IW-8.9 to IW-13) in the solar nebula and accreted later to form EH chondrites. In either case, isotopically heavy silicates must have been removed from the EH reservoir prior to condensation or accretion of metal and silicates (step II, Fig. 6). This isotopically heavy component most likely resided in the missing refractory silicates from EH chondrites, which is indicated by their low $\text{Al}/\text{Si}_{\text{atomic}}$ (0.60 x CI chondrites) and $\text{Mg}/\text{Si}_{\text{atomic}}$ (0.73 x CI chondrites, Wasson and Kallemeyn, 1988). The value of the triple isotope fractionation exponent β and the absence of systematic variations of $\delta^{30}\text{Si}$ with Mg/Si of silicates suggest that KIF and perhaps EIF have affected the EH chondrites during later stages of their evolution.

4.6 *Implications for the silicon isotope composition of the Earth*

Bulk rocks, most silicates and metal of enstatite chondrites show lower $\delta^{30}\text{Si}$ compared to BSE (Georg et al., 2007; Fitoussi et al., 2009; Shahar et al., 2011; Armytage et al., 2011; Hin et al., 2014; Savage et al., 2010; Savage and Moynier, 2013, this study). Previous studies concluded that the heavy Si isotope composition of the BSE might have been caused by equilibrium isotope fractionation between metal and silicate melt during formation of Earth's core, which requires a lower $\delta^{30}\text{Si}$ of the Earth's core compared to the mantle and bulk Earth (Georg et al., 2007; Fitoussi et al., 2009; Shahar et al., 2011; Armytage et al., 2011; Hin et al.,

2014). Using EH chondrites as a precursor material for the Earth yields ~ 35 wt% Si_{core} , (calculated from equations and parameters described in Armytage et al., 2011, section 3.5; final values of wt % Si_{core} obtained from their eq. 5, $M_{\text{BSE}}/M_{\text{core}} = 2.33$, Si fraction of BSE = 0.212 and a Si isotope fractionation factor between silicate and metal of 0.89 ‰ at a mean temperature of metal-silicate segregation of 3000 K). Clearly, such a high Si_{core} is inconsistent with other geophysical and geochemical constraints (Birch, 1964; Allègre et al., 1995; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013; Badro et al., 2015). Bulk values obtained from the mass balance of average silicate and metal Si isotope composition of Sahara 97072 and Indarch from the present study would yield ~ 39 -60 wt% Si_{core} . Whereas the silicate fractions only from both meteorites would yield ~ 22 wt% Si_{core} (Savage and Moynier, 2013; Ziegler et al., 2010). These values are very high and rule out that bulk enstatite chondrites (or their components) represent a major building material of the proto-Earth (e.g., Fitoussi and Bourdon, 2012). We note that between 40% to 70% of the analyzed silicate phases of Indarch and Sahara 97072 show $\delta^{30}\text{Si}$ overlapping with BSE values (Table 2 and 3, Fig. 2). If a component similar to EC silicates with $\delta^{30}\text{Si}$ similar to CI chondrites and BSE was a major constituent of the proto-Earth, then the heavier $\delta^{30}\text{Si}$ of BSE can be explained without requiring significant Si isotope fractionation during high-temperature core formation. However, such a model fails to explain the higher Mg/Si of bulk Earth ($\text{Mg}/\text{Si}_{\text{BSE}} = 1.23 \pm 0.025$, Palme and O'Neill, 2014) compared to the low mean Mg/Si of all EH silicates ($\sim 0.74 \pm 0.06$ (1σ), this study).

A plausible hypothesis for the $\delta^{30}\text{Si}$ value of the BSE is the accretion of chemically and isotopically heterogeneous precursors to the proto-Earth. For instance, Fitoussi and Bourdon (2012) used such a model to point out that a mix of different types of carbonaceous and ordinary chondrites might account for the $\delta^{30}\text{Si}$, $\Delta^{17}\text{O}$ and nucleosynthetic isotope variations of elements such as Cr and Ni in the Earth. Recent data and models of terrestrial planet formation suggest rapid accretion of planetesimals and embryo precursors of the proto-Earth within 1 Ma of the

solar system (Schiller et al., 2011, 2015; Lambrechts and Johansen, 2012; Kruijer et al., 2014; Johansen et al., 2015). Physical accretion disk models (Dullemond et al., 2006 and references therein) combined with chemical accretion models of the terrestrial planets (e.g. Rubie et al. 2015) predict initial accretion of highly reducing material similar to EC from the innermost disk to the forming proto-Earth. Consequently, it is likely that the processing of the EH chondrite precursors described in previous sections occurred in the early feeding zones of the growing terrestrial planets, proximal to the young sun. Here, we use aspects of the model presented in the previous chapter to elaborate on the role of refractory, volatile-depleted material as one of the building materials of the terrestrial planets. As shown in Fig. 6, we assume that 15 % of the Si from EH chondrite precursors with CI chondrite-like Mg/Si and $\delta^{30}\text{Si}$ was condensed into refractory silicates with Mg/Si = 2 and $\delta^{30}\text{Si} = 0.70$ (see supplementary text details). We assume this material contributed to the proto-Earth in variable proportions together with variable proportions of chondritic material, to account for ≤ 8 wt. % (Fig. 7). The latter assumption is broadly in agreement with recent studies of the concentrations of other light elements (e.g. O and S) in the Earth's core (Badro et al., 2015; Mahan et al., 2017) and with estimates of the Si content in Earth's core obtained from forward models of accretion and core formation (e.g., Wade and Wood, 2005; Javoy et al., 2010; Rubie et al., 2011). In Fig. 7, we use the average values of Mg/Si_{BSE} and $\delta^{30}\text{Si}_{\text{BSE}}$ from the literature (1.23 ± 0.05 and -0.29 ± 0.08 ‰, respectively, Savage et al., 2010; Palme and O'Neill, 2014) and $\Delta^{30}\text{Si}$ from experiments to calculate Mg/Si and $\delta^{30}\text{Si}$ of the bulk Earth for 0 and 8 wt. % Si in the core. The possible compositional range of bulk Earth is best explained by a mixture of 10-20 % lost refractory silicates (LRS) and 80-90 % carbonaceous chondrite like composition (Fig. 7a) or by 30-70% high temperature equilibrium condensates with 70-30% carbonaceous chondrites (Fig. 7b). The alternative model in Fig. 7b assumes that refractory silicates continued to react with surrounding gas until they reach a composition (Mg/Si = 1.32, $\delta^{30}\text{Si} = -0.11$) that would be complementary to bulk EH chondrites. Considering other chemical and isotopic evidence (e.g., Schönbachler

et al., 2010; Clay et al., 2017; Budde et al., 2019), a lower fraction of carbonaceous material in Earth may be more plausible. Additional contributions from other types of chondrites are possible (Fitoussi and Bourdon, 2012), in particular if the effect of Si isotope fractionation at the high temperatures of terrestrial core formation is smaller than the extrapolations from experiments suggest.

The low $\delta^{30}\text{Si}$ and Mg/Si of bulk EH chondrites and their silicates and the missing isotopically heavy complement (a fraction of which may now reside in the terrestrial planets and perhaps in some achondrite parent bodies) may provide information on the dynamics of the early innermost solar system. Critically, there is no evidence among the EC silicates for admixture of ^{30}Si enriched material, suggesting efficient separation of the EC reservoir from other reservoirs. A schematic of the timing and conditions of the processes during the formation of the EC chondrite precursors and the proto-Earth is presented in Fig. 8. Infall of dust enriched in neutron rich isotopes, formation of CAIs and their transport to the outer disk (Fig. 8a) must have predated formation of EC precursors, because the latter rarely contain CAIs, are depleted in neutron rich isotopes and because EC seem to have formed at least 3 Ma after CAIs (Shukolyukov and Lugmair, 2004). Early formed refractory silicates with high $\delta^{30}\text{Si}$ and Mg/Si (Fig. 6) rapidly accreted into planetesimals due to runaway growth (Fig. 8b). The fast-growing mass of planetesimals effectively separated these from the remaining gas due to density separation limiting further interaction of these bodies with remaining gas and dust (Fig. 8c). After further condensation and subsequent thermal processing, the remaining gas + dust (with lower $\delta^{30}\text{Si}$ and Mg/Si than CI chondrites) finally accreted as E chondrite parent bodies (Fig. 8c, d). Migration of the giant planets (e.g., Walsh et al., 2011) or other types of instabilities may have disturbed the inner solar system, which may have ejected enstatite meteorite parent bodies into feeding zones of growing terrestrial planets and into the early asteroid belt (Fig. 8d).

Previously, some authors have proposed that the Earth is somewhat enriched in refractory elements, however, similarities to volatile-element depleted carbonaceous chondrite-like material were indicated (Palme and O'Neill, 2014). Here, we argue that the starting material likely was much more reduced than carbonaceous chondrites and chemically unlike known chondrites but similar to the lost refractory silicate condensates of EH chondrite precursors.

5. Conclusions

We have studied the *in-situ* $\delta^{30}\text{Si}$ -values along with major, minor and trace element abundances of silicate and metal phases of chondrules, matrix and metal-troilite spherules in the enstatite chondrites Sahara 97072 (EH3) and Indarch (EH4). The data shows large differences of $\delta^{30}\text{Si}$ of up to 8 ‰ between silicate and metal phases of enstatite chondrites. A comparison of the $\delta^{30}\text{Si}$ -values of metals and silicates and siderophile element abundance patterns of metal grains in EH3 and EH4 meteorites suggests that the Si isotopic compositions of the minerals in these EH chondrites were not modified by heating during thermal metamorphism at 700-900 K, consistent with the notion that the diffusion of Si isotopes from silicates into metal is negligible at metamorphic temperatures ≤ 1270 K and reasonable heating time scales.

$\delta^{30}\text{Si}$ -values of silicates from matrix and chondrules of these EH chondrites are indistinguishable within analytical uncertainties. In contrast, Fe-Ni metal from the matrix and MTS metal show a difference in $\delta^{30}\text{Si}$ of ~ 2 ‰, suggestive of different formation conditions for these different types of metal. Either the formation temperature of matrix metal was higher compared to MTS metal or the different metals were affected differently by kinetic and equilibrium isotope fractionation in nebular environments. Alternatively, the difference in $\delta^{30}\text{Si}$ of MTS metal grains of Sahara 97072 stem from variable magnitudes of kinetic isotope fractionation during the formation of perryite from kamacite. Few matrix metal grains show contamination from neighboring silicates. After correction for contamination by silicates,

matrix metal grains of Indarch display a homogeneous average $\delta^{30}\text{Si}$ -value of -6.0 ± 0.6 (1s) ‰.

The $\delta^{30}\text{Si}$ of the silicates and metal from different components and mass balance indicate that most precursor materials of silicates and metal in EH chondrites were formed from a reservoir enriched in ^{28}Si compared to CI chondrites. The complementary, refractory element-rich and isotopically heavy reservoir appears to have been lost from the precursors of EH chondrites. About 15 % of the original Si inventory (i.e. ~30% Si from refractory phases) must have been lost from EH chondrite precursors to account for the difference in $\delta^{30}\text{Si}$ compared to CI chondrite values. From the standpoint of $\delta^{30}\text{Si}$ -values and mass balance it is clear that neither bulk rocks, nor silicates or metal of EH chondrites can represent major building materials of the proto-Earth. In the light of these conclusions, the heavy Si isotope composition of the BSE and the requirements for a significant fraction of reduced building materials postulated from models of terrestrial accretion and core formation pose a particular challenge. Although metal-silicate segregation and large-scale evaporation of Si from planet precursors have been offered as processes that can explain the heavy Si isotopic composition of the BSE compared to chondrites, the heavy Si isotope composition of BSE may also have been, at least partly, inherited from nebular condensation processes. A combination of the refractory element- and heavy Si isotope-enriched component lost from EH chondrite precursors and carbonaceous and other chondrite-like materials may explain the composition of the Earth.

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Table 1a : Operating instrument conditions for the LA-MC-ICP-MS analysis, gas flows are typically within 0.1 L min ⁻¹ for the different measurement sessions.	
Parameter	Condition
RF power (W)	1250
Extraction (V)	-2000
Focus (V)	-594
Sample cone	Ni, Jet
Skimmer cone	Ni, H
Slit resolution	Medium Resolution
Resolving power	> 5500
Faraday cup configuration	Al27 Si28 Si29 Si30 L4 L2 C H2
Measurement mode	1.04 s integration time, 1 block, 200 cycles
Sample gas (He)	1.65 (L min ⁻¹)
Cool gas (Ar)	14 (L min ⁻¹)
Auxiliary gas (Ar)	0.6 (L min ⁻¹)
Nebuliser gas (Ar)	0.547 (L min ⁻¹)
PFA Nebuliser, MiliQ Water	50 uL/min
Background acquisition time (s)	100
Settle time (s)	3
measurement time	200

Table 1b : Operating settings of the laser beam	
Parameter	Condition
Raster diameter of laser spot	100-150 µm
Repetition Rate for silicates	35 Hz
Repetition Rate for metal	91 Hz
Scan velocity	40 µm/s
Output energy	11 mW
Wavelength	196 nm
Passes	up to 10

Table 1c : Operating instrument conditions for the iCAP-Q ICP-MS, gas flows are typically within 0.1 L min ⁻¹ for the different measurement sessions.	
Parameter	Condition
RF power (W)	1525
Extraction (V)	-175.2
Cool Gas Flow (L min ⁻¹)	14
Auxiliary Gas Flow (L min ⁻¹)	0.8363
Nebuliser Gas Flow (L min ⁻¹)	0.804
CCT Focus (V)	0.25

Table 1 Silicon isotope composition, major element concentrations and Cr/V ratios of silicates in matrix and chondrules and metal of Sahara 97072. Relative distance of analysed spots from rim to core is given in case of chondrules. Mcorrected is the corrected $\delta^{30}\text{Si}$ values for silicate contamination.

Sample	Mineral composition of analysed spot	Distance from rim [mm]	$\delta^{29}\text{Si}$	2SE	$\delta^{30}\text{Si}$	2SE	Mg (wt%)	Al (wt%)	Si (wt%)	Fe (wt%)	Na (wt%)	Cr/V
Sahara 97072												
Ch 1_1	Enst + sul	0.1	-0.42	0.12	-0.80	0.23	48	0.7	<i>bdl</i>	12.9	0.2	44
Ch 1_5	87% Enst + 13% plag	0.2	-0.36	0.13	-0.53	0.18	18	1.7	29.1	2.7	1.1	43
Ch 1_6	85% Enst + 15% plag	0.1	-0.42	0.10	-0.77	0.16	18	1.9	29.2	1.4	1.2	46
Ch 1_7	90% Enst + 10% plag	0.2	-0.33	0.15	-0.54	0.16	15	1.3	32.0	1.7	0.8	39
Ch 1_8	79% Enst + 21% plag	0.3	-0.36	0.15	-0.53	0.16	15	2.8	30.7	0.6	1.8	45
Ch 1_10	Enst + sul	0.07	-0.27	0.15	-0.67	0.20	46	2.1	<i>bdl</i>	13.3	1.1	50
Ch 2_5	92% Enst + 8% plag	0.3	-0.33	0.11	-0.58	0.15	16	1.0	31.9	2.0	0.6	65
Ch 2_6	91% Enst + 9% plag	0.09	-0.45	0.12	-0.71	0.17	13	1.1	34.8	0.7	0.7	48
Ch 2_7	89% Enst + 11% plag	0.07	-0.48	0.11	-0.81	0.16	18	1.4	28.9	3.1	0.9	54
Ch 2_8	91% Enst + 9% plag	0.2	-0.38	0.11	-0.59	0.17	13	1.1	34.4	1.5	0.7	58
Ch 2_9	86% Enst + 14% plag	0.2	-0.33	0.10	-0.50	0.17	19	1.9	27.9	1.6	1.2	56
Ch 2_10	90% Enst + 10% plag	0.07	-0.34	0.10	-0.71	0.14	19	1.1	27.6	3.9	0.8	52
Ch 3_1	88% Enst + 12% plag	0.2	-0.37	0.16	-0.73	0.13	12	1.6	33.9	1.3	1.0	31
Ch 3_2	Enst + sul	0.3	-0.25	0.16	-0.38	0.17	47	5.1	<i>bdl</i>	3.5	3.1	36
Ch 3_3	Enst + sul	0.3	-0.34	0.13	-0.51	0.16	47	4.3	<i>bdl</i>	6.0	2.3	47
Ch 3_4	84% Enst + 12% plag +4% met/sul	0.07	-0.48	0.17	-0.76	0.16	10	1.5	30.4	9.5	1.0	55
Ch 3_5	90% Enst + 10% plag	0.09	-0.37	0.12	-0.64	0.15	13	1.5	34.2	0.8	0.9	39
Ch 3_6	88% Enst + 12% plag	0.3	-0.31	0.12	-0.51	0.18	13	1.7	34.0	0.8	1.0	35
Ch 3_7	88% Enst + 12% plag	0.2	-0.38	0.12	-0.66	0.17	15	1.8	31.0	2.5	1.0	58
CF_1	94% Enst + 6% plag		-0.13	0.21	-0.38	0.30	12	0.7	35.9	1.0	0.5	76
CF_2	87% Enst + 13% plag		-0.27	0.10	-0.40	0.13	19	1.4	28.2	2.2	1.0	88
M1	98% Fe, Ni met + 2% sil/sul		-3.01	0.25	-5.89	0.25	0.5	0.04	2.6	65.0	0.09	72
M1 _{corrected}					-6.5	1.2						
MTS_1	100% Fe, Ni met		-3.61	0.14	-7.09	0.19	0.07	0.01	3.2	68.4	0.01	41
MTS_2	100% Fe, Ni met		-3.94	0.11	-7.65	0.14	0.1	0.01	3.6	63.7	0.03	38
MTS_3	100% Fe, Ni met		-4.16	0.10	-8.24	0.12	0.07	0.004	2.7	66.4	0.01	52
Mat_1	80% Enst + 11% plag +8% met/sul		-0.48	0.18	-0.75	0.24	16	1.5	23.2	13.8	1.0	49
Mat_2	96% Enst + 4% plag		-0.22	0.11	-0.55	0.13	23	0.3	27.0	2.3	0.3	35
Mat_3	72% Enst + 28% plag		-0.44	0.12	-0.76	0.15	17	3.4	27.6	2.4	2.3	44
Mat_5	82% Enst + 14% plag +4% met/sul		-0.47	0.15	-0.96	0.18	15	1.5	25.6	10.3	1.1	79
Mat_6	77% Enst + 15% plag + 8% met/sul		-0.27	0.14	-0.49	0.19	18	1.8	24.1	8.6	1.2	70

Abbreviations are as, Ch = chondrules, CF= chondrule fragments, Mat = matrix, M = metal and MTS = metal-troilite spherule. Enst = Enstatite, Plag = Plagioclase, met = Metal sul = sulfides, sil = silicates and *bdl* = below detection limit.

Table 2 Measured Silicon isotope composition $\delta^{29}\text{Si}$ and corrected Si isotope composition is $\delta^{30}\text{Si}^*$, major and minor element concentrations and Cr/V ratios of silicates in chondrules (Ch), chondrule fragments (CF), metal (M) and matrix of Indarch. Relative distance of analysed spots from rim to core is given in case of chondrules and chondrule fragments. Mcorrected are the corrected $^{30}\text{Si}^*$ values for silicate contamination. Abbreviations are same as Table 1.

Sample	Mineral composition of analysed spot	Distance from rim [mm]	$\delta^{29}\text{Si}$	2SE	$\delta^{30}\text{Si}^*$	2SE	Mg (wt%)	Al (wt%)	Si (wt%)	Fe (wt%)	Na (wt%)	Cr/V
Indarch												
Ch 1_1	91% Enst + 7% plag + 2% met/sul	0.05	-0.54	0.13	-1.04	0.24	20	1	26	6	0.6	71
Ch 1_2	99% Enst + 1% plag	0.09	-0.29	0.10	-0.55	0.20	23	0.4	28	1	0.1	39
Ch 1_3	96% Enst + 4% plag	0.2	-0.46	0.12	-0.89	0.23	21	0.4	27	3	0.3	59
Ch 1_4	82% Enst + 18% plag	0.28	-0.47	0.13	-0.91	0.25	18	2	26	5	1.5	79
Ch 2	91% Enst + 9% plag	0.06	-0.31	0.10	-0.59	0.20	19	1	27	4	0.7	47
Ch 3_1	92% Enst + 8% plag	0.06	-0.24	0.10	-0.46	0.20	20	1	28	4	0.7	61
Ch 3_2	90% Enst + 10% plag	0.07	-0.14	0.11	-0.27	0.21	19	1	26	7	0.8	58
Ch 4	91% Enst + 9% plag	0.12	-0.38	0.11	-0.73	0.21	20	2	27	1	0.8	45
Ch 5_1	89% Enst + 11% plag	0.08	-0.30	0.12	-0.58	0.23	19	1	28	2	0.9	66
Ch 5_2	85% Enst + 15% plag	0.18	-0.29	0.12	-0.57	0.23	19	2	29	1	1.2	69
Ch 5_3	86% Enst + 14% plag	0.18	-0.37	0.11	-0.71	0.21	18	1	26	6	1.2	71
Ch 5_4	83% Enst + 17% plag	0.08	-0.33	0.12	-0.63	0.22	16	2	27	7	1.4	60
Ch 5_5	87% Enst + 13% plag	0.11	-0.33	0.11	-0.64	0.22	19	1	28	2	1.1	73
Ch 5_6	83% Enst + 17% plag	0.11	-0.31	0.09	-0.60	0.17	18	2	28	2	1.4	70
Ch 6_1	93% Enst + 7% plag	0.06	-0.23	0.20	-0.45	0.39	21	1	27	2	0.6	40
Ch 6_2	92% Enst + 8% plag	0.08	-0.23	0.26	-0.44	0.50	20	2	27	2	0.7	43
Ch 7_1	89% Enst + 11% plag	0.06	-0.22	0.12	-0.42	0.23	18	2	28	3	0.9	38
Ch 7_2	91% Enst + 9% plag	0.22	-0.20	0.11	-0.39	0.22	20	2	28	2	0.7	38
Ch 7_3	86% Enst + 14% plag	0.07	-0.23	0.11	-0.45	0.22	18	2	28	2	1.2	37
CF 1	90% Enst + 10% plag	0.12	-0.30	0.11	-0.57	0.22	20	2	27	2	0.9	45
CF 2	89% Enst + 10% plag	0.06	-0.40	0.13	-0.76	0.24	20	1	28	2	0.9	33
CF 3	97% Enst + 2% plag +1% met/sul	0.05	-0.28	0.11	-0.53	0.22	19	1	27	6	0.1	44
CF 4	92% Enst + 7% plag + 1% met/sul	0.06	-0.44	0.12	-0.85	0.22	19	2	28	2	0.6	39
CF 5	93% Enst + 7% plag	0.13	-0.37	0.13	-0.71	0.24	21	1	28	1	0.6	38
CF 6_1	93% Enst + 6% plag	0.13	-0.18	0.10	-0.35	0.20	17	1	26	8	0.5	50
CF 6_2	94% Enst + 5% plag	0.08	-0.24	0.09	-0.46	0.18	18	1	25	9	0.4	50
CF 7	99% Enst + 1% plag	0.05	-0.38	0.11	-0.73	0.20	21	0.1	28	3	0.1	48
CF 8_1	88% Enst + 12% plag	0.14	-0.27	0.18	-0.52	0.34	17	1	26	9	1.0	62
CF 8_2	88% Enst + 12% plag	0.11	-0.20	0.18	-0.38	0.35	18	1	27	6	1.0	62
CF 9	79% Enst + 18% plag + 3% met/sul	0.05	-0.28	0.10	-0.54	0.20	18	2	28	3	1.5	42
CF 10	88% Enst + 12% plag	0.06	-0.22	0.11	-0.43	0.20	19	2	27	2	1.0	35
CF 11	87% Enst + 12% plag + 2% met/sul	0.19	-0.31	0.11	-0.60	0.20	20	1	27	4	1.0	39
CF 12	92% Enst + 6% plag + 1% met/sul	0.05	-0.26	0.11	-0.51	0.22	20	1	27	4	0.5	42
CF 13	94% Enst + 6% plag	0.06	-0.19	0.11	-0.37	0.21	20	1	27	3	0.5	37
CF 14	83% Enst + 17% plag	0.06	-0.23	0.11	-0.44	0.22	19	2	28	2	1.4	38
CF 15	95% Enst + 5% plag	0.06	-0.25	0.10	-0.48	0.20	21	1	25	6	0.4	61
M1	100 % Fe,Ni met		-2.90	0.15	-5.60	0.30	0.03	0.003	2.3	68	0.003	45
M2	99% Fe, Ni met + 1% sil/sul		-2.30	0.23	-4.43	0.45	0.36	0.04	2.5	67	0.04	58
M2corrected					-5.5	1.2						
M3	100% Fe,Ni met		-3.08	0.13	-5.95	0.26	0.004	0.004	2.1	68	0.009	<i>bdl</i>
M4	99.5% Fe, Ni met + 0.5% sil/sul		-2.53	0.17	-4.88	0.32	0.12	0.06	2.3	66	0.07	62
M4corrected					-5.2	1.0						
M5	100% Fe,Ni met		-2.86	0.13	-5.53	0.24	0.004	0.01	2.2	69	0.02	74
M6	99% Fe, Ni met + 1% sil/sul		-2.66	0.14	-5.13	0.27	0.3	0.05	2.2	67	0.05	61
M6corrected					-6.2	1.2						
M7	98% Fe, Ni metal + 2% silicate/sul		-2.91	0.14	-5.63	0.26	0.4	0.02	2.5	68	0.02	50
M7corrected					-7.1	1.4						
M8	100% Fe,Ni metal		-2.91	0.14	-5.62	0.27	0.04	0.01	2.1	69	0.01	53
Mat-1	92% Enst + 7% plag + 1% met/sul		-0.21	0.12	-0.40	0.23	19	2	26	5	0.6	36
Mat-2	98% Enst + 2% plag		-0.16	0.13	-0.31	0.25	22	0.4	27	2	0.2	43
Mat-3	87% Enst + 6% plag + 7% met/sul		-0.35	0.12	-0.67	0.23	17	1	26	9	0.5	45
Mat-4	91% Enst + 9% plag		-0.33	0.10	-0.64	0.20	18	2	27	4	0.8	53

Fig. 1 Backscattered electron images of metal-troilite spherule (MTS) metal and matrix metal grains from Sahara 97072 and Indarch. a) and b) are images of MTS from Sahara 97072 before and after the laser ablation, respectively. The MTS is mainly comprised of kamacite, silicate inclusions and troilite. Schreibersite and perryite mainly occur at the boundary of the troilite grains and sometimes as enclosed phases in the troilite. c) Matrix metal grain from Sahara 97072. d), e) f) and g) are the matrix metal grains M1, M5, M3 and M8 from Indarch. $\delta^{30}\text{Si}$ values of Indarch metal grains are shown in the figure. Average $\delta^{30}\text{Si}$ of MTS metal grains and matrix metal grains are -7.7 ± 0.6 (1s) ‰ and -6.0 ± 0.6 (1s) ‰, respectively.

Fig. 2 a) $\delta^{30}\text{Si}$ or $\delta^{30}\text{Si}^*$ (see text for definition) of analyzed metal and silicate phases of Sahara 97072 and Indarch. $\delta^{30}\text{Si}$ of bulk rocks and silicate phases of enstatite chondrites (Georg et al., 2007; Fitoussi et al., 2009; Chakrabarti and Jacobson, 2010; Armytage et al., 2011; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013) are included for reference. Yellow circles indicate conventionally obtained $\delta^{30}\text{Si}$ data on silicates from the literature. b) Enlarged version of silicate and bulk rock data. BSE value shown by the grey shaded bar is from Savage et al., (2010). Within uncertainties, both chondrule and matrix silicates show indistinguishable silicon isotope compositions compared to bulk EH chondrites. MTS metal is lighter than matrix metal and aubrite metal (Ziegler et al., 2010). Most silicates show lighter Si isotope compositions compared to BSE and CI chondrites, which indicates that incorporation of isotopically light Si into metal (~3% Si) is not the only reason for the lighter Si isotope composition of bulk enstatite chondrites compared to CI chondrites (Savage and Moynier, 2013, see Discussion).

Fig. 3 a) $\delta^{30}\text{Si}$ -Mg/Fe, b) $\delta^{30}\text{Si}$ -Mg/Si, c) $\delta^{30}\text{Si}$ -Mg/Al variation of silicates from chondrules and matrix in Sahara 97072, and d) $\delta^{30}\text{Si}^*$ -Mg/Fe, e) $\delta^{30}\text{Si}^*$ -Mg/Si, f) $\delta^{30}\text{Si}^*$ -Mg/Al variation of silicates from chondrules and matrix in Indarch. Bulk rock data of ordinary and carbonaceous chondrites from literature sources are shown by the brown dashed ellipse and bulk rock enstatite chondrite data is shown by the green ellipse. Some matrix silicates show slightly increasing $\delta^{30}\text{Si}$ with increasing Mg/Fe ratio, whereas no systematic variation is observed between $\delta^{30}\text{Si}$ and Mg/Si or the Mg/Al ratio of silicates in chondrules and matrix. The absence of systematic variations in $\delta^{30}\text{Si}$ with Mg/Al and Mg/Si, suggests that the heterogeneity in the silicon isotope composition of silicates is independent of variations in the chemical composition of minerals, which likely reflect stoichiometric controls and inter-mineral element partitioning during the formation and cooling of chondrules.

Fig. 4 $\delta^{30}\text{Si}$ vs. distance from rim to core in chondrules from Sahara 97072 (a) and Indarch (b). Chondrules in Sahara 97072 show a systematic increase in $\delta^{30}\text{Si}$ from rim to core, possibly reflecting reaction and diffusion of gas with isotopically light Si into chondrules during cooling (see text for details). Chondrules from Indarch display no systematic spatial variation in $\delta^{30}\text{Si}^*$.

Fig. 5 CI normalized abundances of siderophile elements in a) Sahara 97072 and b) Indarch metal, respectively. Bulk rock data is plotted for reference. Bulk rock data for all elements except W in Indarch from Baedeker and Wasson, (1975), Horan et al., 2003, Kallemeyn and Wasson (1986), Morgan et al., (1990), Michaelis et al., (1969), McDonald and Russell (2001). For comparison, W data of the Abee (EH4) meteorite from Hintenberger et al., (1973) is shown. Values of Re, Pt, Rh, Rh, Ni, Co, Fe, Pd, Au in bulk Sahara 97072 are from Kadlag and Becker,

(2015) and W, P, Sb, Ga and Ge data are from other EH3 chondrites (Yanai et al., 1995; Kong et al., 1997; Kallemeyn and Wasson, 1986). Elements are ordered according to decreasing condensation temperatures in gas with a solar composition (Lodders, 2003). Depletions in Re and Pt with respect to W were likely inherited from fractionated nebular precursors of metal. The correlation between Mo and P reflects preferential incorporation of Mo into schreibersite compared to kamacite. No systematic relationships between abundances of siderophile elements and $\delta^{30}\text{Si}$ are observed.

Fig. 6 Evolution of molar Mg/Si and Si isotope compositions of EH chondrite precursors that can explain the EH chondrite data. The starting composition of the nebular gas is assumed to be CI-chondrite-like (I). Early separation of condensed refractory silicates (including forsterite) leave a residual gas enriched in Si and Fe and depleted in refractory elements and Mg (II). Fe-Ni metal is the first phase to condense from the residual gas (III), followed by enstatite (IV) as the dominant silicate phase incorporating Si and Mg. For step II, Si isotopes of gas and solids are assumed to be in equilibrium. In step III and IV (the last step before accretion of the EH parent body) gas and solids may have partially equilibrated and may reflect multiple heating and cooling events (e.g., chondrule formation). The details of mass balance calculations are given in the supplementary text. The final $\delta^{30}\text{Si}$ and Mg/Si values of the bulk EH chondrites, silicates and metal are from this study and from the literature (Georg et al., 2007; Fitoussi et al., 2009; Chakrabarti and Jacobson, 2010; Armytage et al., 2011; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013; Zambardi et al., 2013).

Step I: Nebular gas with CI chondrite-like $\delta^{30}\text{Si}$ and Mg/Si and the full Si inventory (100% Si_{CI} indicating the initial gas mass).

Step II: Formation of refractory solids with $\delta^{30}\text{Si} = 0.70$ and Mg/Si = 2 (e.g. forsterite). These silicates (15 % of the total mass of Si_{CI}) were lost from the enstatite chondrite formation region.

Step III: Formation of Fe-Ni metal in equilibrium with silicate dust. $\delta^{30}\text{Si}$ of Fe-Ni metal is ~ -6.0 (this study and calculated values from Savage and Moynier, 2013) and Mg/Si < 0.01 at T = 1350 K. In this case, 3% of the mass of Si is in the metal phase and 97% in the nebular gas and silicates out of total 85% Si_{CI} .

Step IV: Formation of silicates from remaining nebular gas having $\delta^{30}\text{Si} = -0.59 \pm 0.23$ and Mg/Si = 0.76 ± 0.20 (for details, see Supplementary text). The variation of $\delta^{30}\text{Si}$ and Mg/Si observed in the EH3 silicates may be due to two fractionation processes operating simultaneously before or during chondrule formation: Kinetic isotope fractionation (KIF) leads to silicates with $\delta^{30}\text{Si} < -0.59$ for Mg/Si > 0.76 and $\delta^{30}\text{Si} > -0.59$ for Mg/Si < 0.76. Equilibrium isotope fractionation (EIF) results in $\delta^{30}\text{Si} > -0.59$ for Mg/Si > 0.76 and $\delta^{30}\text{Si} < -0.59$ for Mg/Si < 0.76. MTS metal may have inherited its variable $\delta^{30}\text{Si}$ values due to formation at different $f\text{O}_2$, formation at lower temperatures or due to gas at different Si isotope compositions or due to kinetic isotope fractionation during Si diffusion in larger metal grains and exsolution products (e.g. perryite).

Step V: Accretion of silicates and metal in enstatite chondrite parent body which remain unequilibrated with each other.

Fig. 7 Evolution of $\delta^{30}\text{Si}$ -Mg/Si_{atomic} of bulk Earth for mixing of early condensed refractory material with chondrites. Two cases are shown, a) Earth = 10-20% Lost Refractory Silicates (LRS) + chondrites and b) Earth = 30-70% refractory equilibrium condensates + 70-30 %

chondrites. The likely abundance of Si in Earth's core is assumed to range from 0 to 8 wt. % (e.g. Wade and Wood, 2005; Rubie et al., 2011; Badro et al., 2015). The gray field represents the possible range of bulk Earth compositions using 1σ (i.e. 68.3 % confidence interval) of the $\delta^{30}\text{Si}$ value of the bulk Earth. For 0 % Si in the core, $\delta^{30}\text{Si}$ and $\text{Mg}/\text{Si}_{\text{atomic}}$ of bulk Earth is similar to the values of BSE (Savage et al., 2010; Palme and O'Neill, 2014). For 8% Si in the core, $\delta^{30}\text{Si}$ and $\text{Mg}/\text{Si}_{\text{atomic}}$ of bulk Earth can be calculated from the BSE values and metal-silicate partitioning of Si at the conditions of core formation (see text for details).

The basic assumptions for the composition of the refractory component are: the initial composition of the nebular gas from which early refractory material condensed was similar to CI chondrites ($\delta^{30}\text{Si} = -0.448\text{‰}$ and $\text{Mg}/\text{Si} = 1.04$) and refractory silicates (LRS) lost from EC precursors might have contributed to the proto-Earth together with chondritic material. To calculate the composition of LRS, the $\delta^{30}\text{Si}$ value of precursors of EH3 chondrites is assumed to be -0.78‰ and corresponding $\text{Mg}/\text{Si} = 0.76$ (calculated from $\text{Mg}/\text{Si} = 1.1943 \times \delta^{30}\text{Si} - 1.6885$, this equation was derived from linear regression of the values of Mg/Si and $\delta^{30}\text{Si}$ of forsterite and nebular gas). The composition of lost solids calculated from equilibrium fractionation of gas and solids (for details see supplementary information) are: $\delta^{30}\text{Si} = -0.11\text{‰}$ and $\text{Mg}/\text{Si} = 1.32$. These values and also the $\delta^{30}\text{Si}$ - Mg/Si evolution of LRS for variable proportions of Si in the core (black symbols) are much higher than the measured BSE values. It indicates that the LRS (and simple high temperature equilibrium condensates from the solar gas) alone cannot account for the observed $\delta^{30}\text{Si}$ and Mg/Si of the bulk Earth. Accordingly, we have calculated three different trends for mixing between LRS and carbonaceous (CC), ordinary (OC) and enstatite (EC) chondrites. Mixing lines between CC and LRS, EC and LRS and OC and LRS are shown in yellow, green and blue color, respectively. Each Symbol on the lines represents different proportions of chondrites and LRS (e.g. 10% CC indicates a mixture of 10% CC with 90% LRS). The different trends suggest that if Earth's core contains ≤ 8 mass % Si, the composition of bulk Earth is best explained either by a mixture of 90-80% CC + 10-20% LRS (a) or by 30-70% equilibrium condensates + 30-70% of CC (b). Considering constraints from volatile element abundances in Earth, the latter model is more viable (Schönbächler et al., 2010; Palme and O'Neill, 2014).

Fig. 8 Schematic representation of the sequence of events during the formation of the EH chondrites in the solar nebula in the context of evolution of the solar system. a) Formation of CAIs near the Sun and subsequent transport of the CAIs in the out solar system occurs at $t = 0$. The infill of supernovae dust may still continue throughout the disk, some of which may transported from inner solar system to the outer solar system along with the CAIs. b) Formation of smaller planetesimals due to accretion of condensed refractory solids starts and continues, likely between 0 to 3 Ma after CAIs (assuming the enstatite chondrites are at least 3 Ma younger than CAIs, Shukolyukov and Lugmair, 2004). Enlarged window shows the region of enstatite chondrites and developing planetesimals (which later may become proto-Earth or nucleus of terrestrial planet). The Earlier formed refractory silicates (with higher $\delta^{30}\text{Si}$ and Mg/Si than CI chondrites) were likely accreted to the small planetesimals. c) The growing mass of the solids was effectively separated from the remaining gas due to density separation and also would resulted in minimum solid-gas interaction. d) The remaining gas + fine dust (with lower $\delta^{30}\text{Si}$ and Mg/Si than CI chondrites) finally accreted as a EH chondrite parent body /bodies. The migration of giant planets was likely causes instability in the terrestrial planet formation region, which resulted in transportation of the EH chondrite parent bodies to asteroid belt and some EH

chondrite like material may also have accreted to planetary embryos or proto-planets at this stage.

Supplementary Fig. S1) Reflected light image of the studied section of Sahara 97072. Chondrule cores tend to show heavier $\delta^{30}\text{Si}$ compared to chondrule rims. The average proportion of silicates and metal + sulfides in the analyzed sections of Sahara 97072 and Indarch are in both cases $79 \pm 4 \%$ and $22 \pm 4 \%$, respectively. Average wt. % of Si in Fe-Ni metal of both meteorites is $2.5 \pm 1.1 \%$ (2s). Metal troilite spherule (MTS) metal shows the lightest $\delta^{30}\text{Si}$ (-8.24‰).

Supplementary Fig. S2) Reflected light image of the studied section of Indarch. No systematic variation is observed in $\delta^{30}\text{Si}$ with chondrule size, composition or core to rim distance. $\delta^{30}\text{Si}$ in metal grains are ranging from $-4.43 \pm 0.45 \text{‰}$ to $-5.95 \pm 0.26 \text{‰}$. Heavier values are likely due to the contamination from neighboring silicates (after correction, average $\delta^{30}\text{Si}$ of all metal grains are $-6.0 \pm 0.6 \text{‰}$).

Supplementary Fig. S3) X-ray map of part of a chondrule 1 for Mg, Si, Na, Al and Ca. The main mineral phase is Mg-rich enstatite. Plagioclase and glass are present in the mesostasis.

Supplementary Fig. S4) $\delta^{29}\text{Si}$ - $\delta^{30}\text{Si}$ diagram showing data of analyzed silicate and metal grains. Grey and red lines indicate equilibrium ($\beta = 0.518$) and kinetic ($\beta = 0.509$) isotope fractionation, respectively, calculated from theoretical fractionation factors (Young et al., 2002). The best fit linear regression line of all analyzed samples yields β of 0.503 ± 0.008 (2s), suggesting predominance of kinetic isotope fractionation in the analyzed samples. However, because of the restricted isotopic variations (e.g. silicates only), kinetic or equilibrium isotope fractionation effects cannot be resolved among specific phases.

Supplementary Fig. S5) Variation of Cr vs. V in silicates in chondrules, MTS, matrix and in metal. We do not observe systematic variations of Cr/V in different mineral phases. Because the change in $D(\text{Cr})/D(\text{V})$ between orthopyroxene and silicate melt is sensitive to changes in redox conditions (Cartier et al., 2014), the deviation of Cr/V from $\text{Cr}/\text{V}_{\text{CI}}$ in enstatites from chondrules and matrix may indicate the formation under variable $f\text{O}_2$ ($\log f\text{O}_2 < \text{IW}-4$). Most metal analyses show CI chondrite like Cr/V ratios. Matrix metal of Sahara 97072 shows higher Cr/V than CI chondrites, which is likely due to contamination by neighboring sulfides with higher Cr/V ratios. The relative partitioning of Cr and V between orthopyroxene and silicate melt ($D_{\text{Cr}/\text{Dv}}$) is a sensitive indicator of changes in $f\text{O}_2$ and is independent of P, T, and chemical composition (Cartier et al., 2014). The data show a correlation of Cr and V for most components, with Cr/V scattering around the CI chondrite ratio. Most metal grains show the CI chondritic Cr/V ratio. Cr/V in metal and silicates range from $0.56 \times \text{CI}$ to $2.2 \times \text{CI}$. Chondrules show variations in Cr/V, where lower Cr/V (< 40) are associated with analyses on $> 99\%$ pure enstatite and the highest Cr/V (> 70) are found in mixed analyses near grain boundaries of orthopyroxenes with silica and plagioclase, indicating relative oxygen fugacities of IW-6 to IW-7 (Cartier et al., 2014) during the formation of orthopyroxene, if these minerals were in equilibrium with each other. MTS metal also shows variable Cr/V in different spots analyzed and heterogeneity of $\delta^{30}\text{Si}$ in

individual nodules. However, no clear relationship between Cr/V, $\delta^{30}\text{Si}$ and Si concentration of metal grains or silicates is observed (Table 2 and 3). Therefore, we suggest that differences in fO_2 may have led to the different concentration of Si in metal grains (Grossman et al., 2008), without significantly changing their Si isotope composition.

Sulfides in EH chondrites typically contain 0.3-3.6% Cr (Weyrauch et al., 2018 and references therein, this study). Thus, it cannot be excluded that the suprachondritic Cr/V reflect contributions from small sulfide grains in mixed silicate analyses. The absence of correlations between $\delta^{30}\text{Si}$, Cr/V and Si concentration in MTS metal grains (Table 2) indicates that either $\delta^{30}\text{Si}$ variations are independent of changes in fO_2 , or that contamination by sulfides make it difficult to use the Cr/V ratio in orthopyroxenes as an indicator of variation in fO_2 .

Step I

Step II

Step III

Fe-Ni condensation
($T \sim 1350 \text{ K}$)

$\delta^{30}\text{Si}_{\text{Fe-Ni metal}} \sim -6.0$,
 $\text{Mg/Si}_{\text{Fe-Ni metal}} < 0.01$
3% Si

Both EIF ($>80\%$) and KIF ($<15\%$) of Si isotopes between Fe-Ni metal and $\text{SiS/SiO}_{\text{gas}}$ are required to explain the observed $\delta^{30}\text{Si}_{\text{Fe-Ni matrix metal}}$

Step IV

Formation of silicates
($T < 1100 \text{ K}$)

KIF: $\delta^{30}\text{Si} < -0.59$, $\text{Mg/Si} > 0.76$ and $\delta^{30}\text{Si} > -0.59$, $\text{Mg/Si} < 0.76$

EIF: $\delta^{30}\text{Si} > -0.59$, $\text{Mg/Si} > 0.76$ and $\delta^{30}\text{Si} < -0.59$, $\text{Mg/Si} > 0.76$

Step V

Color terminology

CAIs

Supernovae dust

$\delta^{30}\text{Si} = \text{CI chondrites}$

$\delta^{30}\text{Si} > \text{CI chondrites}$

$\delta^{30}\text{Si} < \text{CI chondrites}$

Supplementary information

1) Isotopic mass balance evolution model of the composition of bulk EH chondrites

The goal is to determine the amount of refractory silicates (mainly forsterite) and Si that must be removed from solar gas to obtain the Mg/Si and $\delta^{30}\text{Si}$ of bulk EH chondrites and their metals and silicates.

Main assumption: initial gas with solar composition (H, He etc.) and CI chondrite like Mg/Si and $\delta^{30}\text{Si}$.

$\delta^{30}\text{Si}_{\text{CI}} = -0.448 \pm 0.071$ (2SE, Armytage et al., 2011; Fitoussi et al., 2009; Zambardi et al., 2013)

$\text{Mg/Si}_{\text{CI}} = 1.04$ (Lodders, 2003)

The condensation temperature of Forsterite is 1354 K (Lodders, 2003).

Because the atomic Mg/Si of CI like gas is about 1, condensation of all Mg into forsterite removes nearly half of the Si. Thus at 1354 K, equilibrium condensation between gas and forsterite requires that 50% Si (by atomic proportion) enters the solid phase and 50% Si remains in the gaseous phase

The equilibrium fractionation factor between forsterite and SiO_{gas} at $T = 1354$ K can be calculated from (e.g., Dauphas et al. 2015)

$$\Delta^{30}\text{Si}_{\text{Forsterite-SiOgas}} = 4.2 \times 10^6 / T^2 \quad (1)$$

and yields $\Delta^{30}\text{Si}_{\text{Forsterite-SiOgas}} (T = 1354 \text{ K}) = 2.3 \text{ ‰}$.

Note that the equilibrium fractionation factor between enstatite and SiO_{gas} is almost same as between forsterite and SiO_{gas} (Javoy et al., 2012).

Thus $\delta^{30}\text{Si}_{\text{forsterite}}$ is $= -0.448 \text{ ‰} + 2.3 \text{ ‰} \times 0.5 = 0.70 \text{ ‰}$ with atomic $\text{Mg/Si}_{\text{forsterite}} = 2$ and $\delta^{30}\text{Si}_{\text{RG}}$ of the remaining nebular gas is $= -0.448 - 2.3 \times 0.5 = -1.59 \text{ ‰}$ with $\text{Mg/Si}_{\text{RG}} \sim 0.08$. These calculations were given in detail by Dauphas et al. (2015).

We assume that the EH chondrite precursors have lost early-condensed silicates along with other refractory elements ("Lost refractory silicates", LRS). The remaining gas + remaining refractory silicate dust (RGD) should match bulk compositions of EH chondrites. Remaining refractory condensates may react with the changed gas composition (higher C/O) to form sulfides and enstatite.

The average $\delta^{30}\text{Si}$ and Mg/Si of bulk EH chondrites are from the present study (average $\delta^{30}\text{Si}_{\text{EH}} = -0.74 \pm 0.08 \text{ ‰}$ and $\text{Mg/Si}_{\text{EH}} = 0.74 \pm 0.06$. These values overlap with literature values within uncertainties.

In order to match EH chondrite compositions, the mass balance of refractory solids and remaining nebular gas requires that $30 \pm 8\%$ of the Si from refractory solids, i.e. $15 \pm 4\%$ Si ($30\% \text{ Si of } 50\% \text{ Si} = 30 \times 0.5 = 15\%$ initial/total Si (Si_{CI}) from the total Si_{CI} inventory, must have been lost from the precursors of EH chondrites to obtain average $\delta^{30}\text{Si}_{\text{EH}} = -0.74$ and $\text{Mg/Si}_{\text{EH}} = 0.74$. Thus, the fraction of Si_{CI} remaining in the residual gas is $= 100\% - 15\% = 85\%$.

In the model 70% of the condensed forsterite (comprising 35 % of Si_{CI}) remains with the residual gas, yielding a total $\text{Si}_{\text{CI}} = 85\%$ in EH chondrites. In EH chondrites (= the final product of the residual gas + remaining forsterite, assuming subsequent closed system processing of Si and Mg) $\text{Si}_{\text{EH}} = \text{Si}_{\text{RGD}}$ is distributed to yield 3% Si in metal and 97% Si in silicates.

Thus, the fraction of original Si_{Cl} in the metal = $3 \times 0.85 = 2.55\%$ and the fraction of Si_{Cl} in EH silicates = $97 \times 0.85 = 82.45\%$.

2) Composition of the bulk Earth

Basic parameters:

Mg/Si ratio of the bulk silicate Earth ($\text{Mg}/\text{Si}_{\text{BSE}}$) = 1.23 ± 0.05 (Ringwood, 1979; Jagoutz et al., 1979; Wänke et al., 1984; Hart and Zindler 1986; McDonough and Sun, 1995; Allegre et al., 1995; Palme and O'Neill, 2014)

$\delta^{30}\text{Si}_{\text{BSE}} = -0.29 \pm 0.08 \text{ ‰}$ (Savage et al., 2010)

Two end-member cases are considered:

Case I: If the Earth has 0 % Si in the core then $\text{Mg}/\text{Si}_{\text{BSE}} = \text{Mg}/\text{Si}_{\text{bulk Earth}}$ and $\delta^{30}\text{Si}_{\text{BSE}} = \delta^{30}\text{Si}_{\text{Bulk Earth}}$

Case II: If the Earth has 8 % Si in the core and assuming an isotopic fractionation factor of $\Delta^{30}\text{Si}_{\text{silicate-metal}} = 0.89$ at 3000 K (Armstrong et al., 2011) then from mass balance at core formation conditions (for details see text) $\text{Mg}/\text{Si}_{\text{bulk Earth}} = 1.13 \pm 0.05$ and $\delta^{30}\text{Si}_{\text{Bulk Earth}} = -0.36 \pm 0.08 \text{ ‰}$.

Figure 7 illustrates two scenarios

a) If the Earth comprises 10-20 % the lost refractory silicates (LRS) of EH chondrite precursors, (i.e. $\text{Mg}/\text{Si}_{\text{LRC}} = 2$ and $\delta^{30}\text{Si}_{\text{LRC}} = 0.70$), then addition of 80 to 90% of a carbonaceous chondrite like composition can explain $\text{Mg}/\text{Si}_{\text{Bulk Earth}}$ and $\delta^{30}\text{Si}_{\text{Bulk Earth}}$ for a compositional range of 0 to 8 % of Si in the core.

b) If the starting composition is CI chondrite-like then equilibrium condensation of Si in solids and gas produce Mg/Si and $\delta^{30}\text{Si}$ values of forsterite and gas as mentioned before. If mixing between solids and remaining gas occur and an EH chondrite like gas composition ($\text{Mg}/\text{Si}_{\text{EH}} = 0.76$ and $\delta^{30}\text{Si}_{\text{EH}} = -0.82$) separates from condensates in the nebular region, then remaining reacted equilibrium condensates have $\text{Mg}/\text{Si} = 1.32$ and $\delta^{30}\text{Si} = -0.11$. If 30-70% of the proto-Earth was derived from reacted equilibrium condensates ($\text{Mg}/\text{Si} = 1.32$ and $\delta^{30}\text{Si} = -0.11$) then addition of 70-30% of the carbonaceous chondrite-like composition can explain the $\text{Mg}/\text{Si}_{\text{bulk Earth}}$ and $\delta^{30}\text{Si}_{\text{Bulk Earth}}$ for 0 to 8 % of Si in the core.

b) Indarch

Legend
 $\delta^{54}\text{Sr}$
 Component name

Map Display

Sample

Realtime

Operation

Exit

Mg — 50 um

Si — 50 um

Na — 50 um

CP — 50 um

Al — 50 um

Ca — 50 um

Mg	Lv	%	Si	Lv	%	Na	Lv	%
167	0.0		79	0.0		43	0.0	
	0.4			0.0			0.0	
146			69			37		
13.7				0.2			0.2	
125			59			32		
41.3				0.5			1.2	
104			49			26		
15.8				4.2			3.1	
83			39			21		
5.4				37.5			4.1	
62			29			16		
3.9				45.4			4.0	
41			19			10		
3.7				7.7			3.3	
20			9			5		
15.8				4.4			84.1	
0			0			0		
Ave	89.0		Ave	27.0		Ave	3.0	
CP	Lv	%	Al	Lv	%	Ca	Lv	%
2040	0.0		199	0.0		88	0.0	
	1.9			0.0			0.0	
1886			174			77		
0.6				0.0			0.0	
1733			149			66		
0.4				0.0			0.1	
1580			124			55		
0.5				0.1			0.2	
1427			99			44		
1.1				0.2			0.2	
1274			74			33		
87.5				5.5			0.2	
1121			49			22		
6.9				8.9			0.9	
968			24			11		
1.1				85.2			98.4	
815			0			0		
Ave	1195.0		Ave	9.0		Ave	1.0