Earth's accretion inferred from iron isotopic anomalies of supernova nuclear statistical equilibrium origin

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Nucleosynthetic Fe isotopic anomalies in meteorites may be used to learn about the early evolution of the solar system and to identify the origin and nature of the material that built the terrestrial planets. Using high-precision iron isotopic data of 23 iron meteorites from nine major chemical groups we show that all iron meteorites define the same dichotomy between non-carbonaceous (NC) and a carbonaceous (CC) meteorites previously observed for other elements. The Fe isotopic anomalies are predominantly produced by variations in $^{54}$Fe, where all CC iron meteorites are characterized by an excess in $^{54}$Fe relative to NC iron meteorites. This excess in $^{54}$Fe is accompanied by an excess in $^{58}$Ni observed in the same CC meteorite groups. Together, these overabundances of $^{54}$Fe and $^{58}$Ni are explained by nuclear statistical equilibrium either in type Ia supernovae or in the Si/S shell of core-collapse supernovae. The Fe isotopic composition of Earth's mantle plots on or close to correlations defined by Fe, Mo, and Ru isotopic anomalies in iron meteorites, indicating that throughout Earth's accretion, the isotopic composition of its building blocks did not drastically change. While Earth's mantle has a similar Fe isotopic composition to CI chondrites, the latter are clearly distinct from Earth's mantle for other elements (e.g., Cr and Ni) whose delivery to Earth coincided with Fe. The fact that CI chondrites exhibit large Cr and Ni isotopic anomalies relative to Earth's mantle, therefore, demonstrates that CI chondrites are unlikely to have contributed significant Fe to Earth and are not its main building blocks.

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1. Introduction

Meteorites and planets carry isotopic anomalies of nucleosynthetic origin that were produced in stars that lived before the Sun was born, and escaped homogenization in the interstellar medium and protoplanetary disk (Dauphas and Schauble, 2016). This isotopic heterogeneity may have been inherited from the solar system’s parental molecular cloud core (Burkhardt et al., 2019; Dauphas and Schauble, 2016; Jacquet et al., 2019; Nanne et al., 2019) or reflects physical and thermal processing of isotopically anomalous dust in the solar system (e.g., Burkhardt et al., 2011; Dauphas et al., 2002b; Trinquier et al., 2009). Regardless of their cause, nucleosynthetic isotopic anomalies provide a powerful tool for reconstructing the evolution of the protoplanetary disk and for establishing genetic ties between terrestrial planets and meteorite parent bodies.

The isotopic compositions of several elements in meteorites display a fundamental dichotomy between carbonaceous (CC) and non-carbonaceous (NC) materials (for reviews see Bermingham et al., 2020; Kleine et al., 2020; Kruijer et al., 2020). While it was known for some time that carbonaceous chondrites are isotopically distinct from most other meteorites (e.g., Leya et al., 2008; Niederer et al., 1981; Niemeyer, 1988; Rotaru et al., 1992), the first indication of what is now recognized as the NC-CC dichotomy was given by Trinquier et al. (2007), who showed that carbonaceous chondrites have systematically distinct Cr and O isotopic compositions compared to some differentiated meteorites, enstatite chondrites, and ordinary chondrites. Subsequently, Warren (2011) showed that for O, Ti, Cr, and Ni, meteorites always define two isotopically distinct clusters and introduced the term carbonaceous and non-carbonaceous to distinguish between these two groups. More recent work demonstrated that the NC-CC dichotomy extends to several other elements (e.g., Mo; Buddé et al., 2016; Poole et al., 2017; Worsham et al., 2017) and is present in early- and late-formed planetesimals (as represented by iron meteorites and...
chondrites, respectively) in both reservoirs (Budde et al., 2016; Kruijer et al., 2017). Together, these observations imply that the NC and CC reservoirs were established early in the evolution of the protoplanetary disk, in less than ~1 Ma after the condensation of the first solids in the solar system (refractory CaAl-rich inclusions; CAIs), and that they remained spatially isolated at least until accretion of NC chondrite parent bodies at ~2 Ma post CAI formation (Budde et al., 2016; Kruijer et al., 2017). The prolonged spatial separation of the NC and CC reservoirs requires limited mixing and homogenization between the two reservoirs, which may have been accomplished by the early formation of proto-Jupiter (Kruijer et al., 2017) or pressure maxima near the location where Jupiter later formed (Brasser and Mojsis, 2020). In addition, the initial separation of the NC and CC reservoirs may also reflect the migration of the snow line that led to two distinct bursts of planetesimal formation at distinct locations in the disk (Lichtenberg et al., 2021).

Despite widespread nucleosynthetic isotopic variations among meteorites and planets, for most elements Earth is isotopically most similar to enstatite chondrites (Dauphas, 2017). This has been interpreted to indicate that Earth’s building material was characterized by an enstatite chondrite-like isotopic composition during most of Earth’s growth, with only little contribution from CC material (Dauphas, 2017). However, a recent study found that the Fe isotopic composition of CI chondrites is similar to the Earth’s mantle, and on this basis argued that the majority of Fe in Earth’s mantle derived from CI-like material (Schiller et al., 2020). Moreover, although the same study found two distinct clusters of Fe isotopic anomalies for NC (groups IC and IIA-B) and CC (groups IIC and IVB) iron meteorites, the Fe isotopic composition of CI chondrites appears to be distinct from both, and more similar to NC than CC iron meteorites. Taken at face value, these observations seem to challenge the idea that an isotopic dichotomy for Fe persisted in the protoplanetary disk for millions of years.

In order to better constrain the extent of Fe isotopic variations in the early solar system when the first planetesimals formed, and to evaluate the significance of Fe isotopes for constraining the nature and origin of Earth’s building material, we have measured the Fe isotopic compositions of 23 iron meteorites from nine chemical groups belonging to NC (IAB, IC, IIAB, IIIAB, IVA) and CC (IIC, IID, IIIF, IVB) groups. We first evaluate to what extent exposure to galactic-cosmic rays (GCR) during the long residence of iron meteorites in space compromises the quantification of nucleosynthetic Fe isotopic anomalies (Cook et al., 2020). We then use the data to test whether there is an Fe isotopic dichotomy for iron meteorites and to identify the stellar environment from which these nucleosynthetic Fe isotopic anomalies initially originated. Finally, we compare the Fe isotopic data with isotopic anomalies of other elements (i.e., Cr, Ni, Mo, Ru) in meteorites and discuss their implications for the evolution of the protoplanetary disk and the identification of Earth’s building blocks.

2. Samples and analytical methods

2.1. Samples and preparation

In this study 23 iron meteorites from nine chemical groups were selected for Fe isotope analyses. Five groups of iron meteorites were previously classified as non-carbonaceous (IAB, IC, IIAB, IIIAB, IVA) and four as carbonaceous (IIC, IID, IIIF, IVB) based on their Mo and Ni isotope systematics (Budde et al., 2016; Kruijer et al., 2017; Nanne et al., 2019; Worsham et al., 2019). For 18 iron meteorite samples, the Fe isotopic compositions were analyzed on solution aliquots (~1-2 mg Fe) of digestions that were previously analyzed for their Pt, Mo, Ni, and/or W isotopic compositions (Kruijer et al., 2017; Nanne et al., 2019; Spitzer et al., 2020; Worsham et al., 2019). For five other iron meteorite samples (Toluca, Gibeon, Duchesne, Skookum, Tlacotepec) ~50 mg pieces were cut using a diamond saw, polished with SiC abrasive paper, and cleaned in ethanol. These pieces were then digested in aqua regia (3:1 HCl-HNO₃) at 120 °C for 24 hours on a hot plate. Aliquots of these digestions (~1-2 mg Fe) were processed through iron purification chemistry. Prior to chemical purification, all sample solutions were converted to chloride form and redissolved in 0.25 ml 10 M HCl.

We also analyzed geostandards BHVO-2 and BCR-2 (basalts from Hawaii and Oregon) to assess whether the terrestrial reference material used for reporting Fe isotopic anomalies (IRMMS-524a) is an appropriate proxy of the composition of the silicate Earth, as industrial processes used for preparing chemically pure materials can induce spurious isotopic effects (Steele et al., 2011). The basalt samples were digested using HF-HNO₃ (2:1) at 150 °C on a hot plate for 48 hours followed by several steps of aqua regia, converted and dissolved in 0.25 ml 10 M HCl, and then processed alongside the iron meteorite samples.

2.2. Chemical purification

A procedure to purify Fe for measurements of mass-independent isotopic variations that allows efficient separation of Fe from Cu, Ni, Co, and Cr is described by Tang and Dauphas (2012). The sample aliquots are loaded in 0.25 ml 10 M HCl onto 10.5 cm long PFA columns (0.62 cm inner diameter) filled with 3 ml pre-cleaned AGI-X8 (200-400 mesh) anion resin. Iron is fixed on the resin while Ni and other major elements are eluted in 5 ml 10 M HCl. Other possible contaminants (e.g., Cu, Cr) are rinsed off the resin using 30 ml 4 M HCl. Finally, Fe is eluted using 9 ml 0.4 M HCl, dried down, re-dissolved in 10 M HCl, and the chemical purification is repeated using new resin. Finally, the purified Fe is dried down and dissolved in 0.3 M HNO₃ for concentration and isotopic measurements. The overall Fe yield is >99% and the total procedural blank is ~70 ng and thus negligible considering that 1-2 mg Fe was purified for each sample. After purification, the interfering elements Cr (54Cr on 54Fe) and Ni (58Ni on 58Fe) were present at low enough levels (Cr/Fe ≤ 1.7 × 10⁻⁶ and Ni/Fe ≤ 2 × 10⁻⁶) to allow accurate Fe isotopic ratio measurements (see Supplementary Material S1; Fig. S1).

2.3. Isotopic analyses

Iron isotopic measurements were performed at the University of Chicago using a Thermo Scientific Neptune multicolonlector inductively coupled plasma mass spectrometer (MC-ICP-MS) that was upgraded to Neptune Plus specifications. Ion beams of 54Fe⁺, 56Fe⁺, 57Fe⁺, and 58Fe⁺ were analyzed in static mode on Faraday collectors using a 10¹⁰ Ω amplifier for 56Fe⁺ and 10¹¹ Ω amplifiers for the other Fe isotopes. Possible isobaric interferences from 54Cr⁺ and 58Ni⁺ were measured simultaneously by monitoring 54Cr⁺ and 58Ni⁺ using 10¹² Ω amplifiers. All Fe ion beams may be affected by molecular interferences from argide ions (54Ar²⁺, 54Ar³⁺, 54Ar⁴⁺, 54Ar⁵⁺, 54Ar⁶⁺, 54Ar⁷⁺, 54Ar⁸⁺), which need to be resolved for precise isotopic measurements. Therefore, the measurements were made on the flat-topped peak shoulder in either medium-resolution (MR) or high-resolution (HR) mode. We used Ni or Pt sampler and H skimmer cones. Even with Ni cones, little Ni was present and 58Ni⁺ interferences on 58Fe⁺ remained negligible. The main motivation for using Pt cones was an increase in sensitivity and a decrease in the frequency of cone cleaning because the intensity remained more stable.

The purified Fe solutions (10 μg/g in 0.3 M HNO₃) were introduced into the MC-ICP-MS at an uptake rate of ~100 μl/min using
either a cyclonic glass spray chamber (wet plasma, MR-mode, Pt cones) or an ESI Apex Ω desolvating nebulizer system (dry plasma, HR-mode, Ni cones) with no auxiliary N₂ flow. Typical $^{56}\text{Fe}^{+}$ ion signal intensities were 1.4 nA (wet plasma; MR-mode) to 2 nA (dry plasma; HR-mode), respectively. Each measurement consisted of 25 (HR-mode) or 50 (MR-mode) cycles of 8.369 s each. Sample analyses were bracketed by measurements of the reference material IRMM-524a that has an identical isotopic composition to IRMM-014 (Craddock and Dauphas, 2010). All sample and standard solutions were prepared with the same 0.3 M HNO₃ solution. The concentrations of the samples and standards were matched to ≤2%, which allows accurate and precise Fe isotopic measurements (see Supplementary Material S1; Fig. S2). On peak zero intensities from a blank solution measured at the beginning of each sequence were subtracted from all individual measurements and a washout time of 210 s was used between all measurements.

Measurements were corrected for instrumental and natural mass fractionation using the exponential law (Dauphas and Schäuble, 2016), and internal normalization to either $^{57}\text{Fe}/^{56}\text{Fe} = 0.023095$ or $^{57}\text{Fe}/^{54}\text{Fe} = 0.362549$, the certified ratios of IRMM-014. Mass-independent variations of the isotopic ratios in the samples are expected to be small and we use the $\mu$-notation, which provides the parts-per-million deviation of an isotopic ratio of a sample relative to the mean value of the two bracketing standards,

$$\mu^{1}\text{Fe}(k/j) = \left[\frac{(^{1}\text{Fe}/^{2}\text{Fe})(k/j)_{\text{sample}}}{(^{1}\text{Fe}/^{2}\text{Fe})(k/j)_{\text{IRMM-524a}}} - 1\right] \times 10^{6},$$

(1)

where the subscript $(k/j)$ indicates the ratio used for internal normalization, in our case either $^{57}\text{Fe}/^{56}\text{Fe}$ or $^{57}\text{Fe}/^{54}\text{Fe}$. Previous studies used the $\varepsilon$-notation (Cook et al., 2020; Cook and Schönbräucher, 2017; Dauphas et al., 2008; Völkken and Papanastassiou, 1989) that can easily be converted into $\mu$ by multiplying by 100 ($1\varepsilon = 100 \mu$). [see Supplementary Material S2 for a derivation to renormalize published $\varepsilon^{56}\text{Fe}(7/4)$ values to $\mu^{54}\text{Fe}(7/6)$]. The purified solutions are measured $N$ times in a sample-standard bracketing (SSB) scheme and the average $\mu$ values are reported in Table 1. Uncertainties for individual samples are based on repeat measurements ($N = 10$ to 35) of each sample solution using the average value and Student’s $t$-value for a two-sided 95% confidence interval (95% c.i.).

We also report mass-dependent isotopic variations, which are given in the $\delta$-notation,

$$\delta^{56}\text{Fe}(\%o) = \left[\frac{^{56}\text{Fe}^{54}\text{Fe}}{(^{56}\text{Fe}^{54}\text{Fe})_{\text{sample}}}}\right]_{\text{IRMM-524a}} - 1\] \times 10^{3},$$

(2)

allowing us to monitor possible spurious effects on internally normalized isotope ratios introduced by natural mass fractionation (Tang and Dauphas, 2012).

3. Results

The Fe isotopic data, together with previously reported Pt isotopic data ($\varepsilon^{186}\text{Pt}(8/5)$; $^{198}\text{Pt}/^{195}\text{Pt}$ ratio internally normalized to a constant $^{198}\text{Pt}/^{195}\text{Pt}$ in parts per 10,000 deviation from a standard) for the same sample digestion or meteorites, are reported in Table 1 and plotted in Figs. 1 and 2. The basaltic geostandards BHVO-2 and BCR-2 give average $\mu^{54}\text{Fe}(7/6) = 2 \pm 2$ (95% c.i.) and $\mu^{58}\text{Fe}(7/6) = 4 \pm 6$ (95% c.i.), which are normal within uncertainties and agree with previously reported values for terrestrial geostandards (Schiller et al., 2020) (see Supplementary Material S3; Table S1; Fig. S3). We take this value as representative of Earth’s mantle because the silicate Earth is thought to be homogeneous from the point of view of isotopic anomalies, and the degree of mass-dependent fractionation in mafic igneous rocks is small (Dauphas et al., 2017 and references therein).

Mass-dependent fractionations in the iron meteorites are small and similar to basalts with $\varepsilon^{56}\text{Fe}$ values ranging from ~0.03 to 0.14 (Table 1). Thus, any spurious isotope effects from non-exponential mass-dependent fractionation should be lower than ~1 ppm for both $\mu^{54}\text{Fe}(7/6)$ and $\mu^{58}\text{Fe}(7/6)$ (Dauphas and Schäuble, 2016; Tang and Dauphas, 2012), which is within the uncertainties of the measurements. The Fe isotopic data of iron meteorites reveal mass-independent variations in $\mu^{54}\text{Fe}(7/6)$ but no resolvable variations in $\mu^{58}\text{Fe}(7/6)$. Samples from the four CC iron meteorite groups (IIC, IID, IIIF, IVB) have $\mu^{54}\text{Fe}(7/6)$ values ranging from +24 to +42. Samples from the NC groups (IAB, IC, IIAB, IIIAB, IVB) have more variable $\mu^{58}\text{Fe}(7/6)$ values ranging from ~5 to ~30 (Fig. 1). These results are in good agreement with previously reported data for iron meteorites (see Supplementary Material S3; Table S1; Fig. S3) (Cook et al., 2020; Dauphas et al., 2008; Schiller et al., 2020). For most chemical groups with several measurements (IIC, IID, IIAB, IVB, IVA), $\chi^{2}$ tests of homogeneity indicate the individual samples have indistinguishable Fe isotopic compositions (the null hypothesis is that they are indiscernible, and all p-values are much higher than 0.05). However, we can resolve small variations within the IC and IIAB iron meteorites when $\mu^{54}\text{Fe}(7/6)$ is plotted against $\mu^{58}\text{Fe}(7/6)$ (Fig. 1).

The isotopic composition of several samples are affected by GCR exposure as monitored by their Pt isotopic compositions (i.e., $\varepsilon^{186}\text{Pt}(8/5)$) (Table 1). The IC and IIAB iron meteorites samples with the largest within-group $\mu^{54}\text{Fe}(7/6)$ variations (i.e., Arispe, Bendego, Sikhote Alin, Ainsworth) are also the samples with the longest GCR exposure time and display the largest Pt isotopic anomalies (transparent symbols in Fig. 1). This suggests that GCR-exposure is responsible for at least some of the observed within-group Fe isotopic variations.
Table 1
Fe and Pt isotopic data of iron meteorites and geostandards.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu^{56}$Fe/$\mu^{54}$Fe</th>
<th>$\Delta^{56}$Fe/$\Delta^{54}$Fe</th>
<th>$\mu^{56}$Fe/$\mu^{54}$Pt</th>
<th>$\Delta^{56}$Fe/$\Delta^{54}$Pt</th>
<th>$\epsilon^{195}$Pt/$\mu^{195}$Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHVO-2 (HR)²</td>
<td>20 4 ± 5</td>
<td>1 ± 11</td>
<td>−1 ± 2</td>
<td>2 ± 11</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>Replicate</td>
<td>15 3 ± 5</td>
<td>5 ± 7</td>
<td>−1 ± 2</td>
<td>6 ± 6</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td>RCR-2 (HR)²</td>
<td>10 3 ± 8</td>
<td>1 ± 15</td>
<td>−1 ± 3</td>
<td>2 ± 14</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>Replicate</td>
<td>15 0 ± 8</td>
<td>10 ± 14</td>
<td>0 ± 3</td>
<td>10 ± 16</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>Average</td>
<td>2 ± 2</td>
<td>4 ± 6</td>
<td>−1 ± 1</td>
<td>5 ± 5</td>
<td></td>
</tr>
<tr>
<td>IAB</td>
<td>14 −5 ± 5</td>
<td>1 ± 11</td>
<td>2 ± 2</td>
<td>−1 ± 10</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Toluca</td>
<td>15 16 ± 6</td>
<td>−8 ± 16</td>
<td>−5 ± 2</td>
<td>−2 ± 15</td>
<td>0.07 ± 0.03</td>
</tr>
<tr>
<td>Bendego</td>
<td>14 20 ± 8</td>
<td>−20 ± 7</td>
<td>−7 ± 3</td>
<td>−14 ± 8</td>
<td>0.14 ± 0.08</td>
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<tr>
<td>Chihuahua City</td>
<td>25 12 ± 7</td>
<td>2 ± 22</td>
<td>−4 ± 2</td>
<td>−1 ± 13</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>Mt. Dooling</td>
<td>15 12 ± 7</td>
<td>−10 ± 12</td>
<td>−5 ± 12</td>
<td>−2 ± 15</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>Low exposure weighted average²</td>
<td>10 ± 5</td>
<td>−7 ± 11</td>
<td>−3 ± 1</td>
<td>0 ± 11</td>
<td></td>
</tr>
<tr>
<td>Intercept of Fe-Pt correlation²</td>
<td>9 ± 5</td>
<td>−7 ± 11</td>
<td>−3 ± 2</td>
<td>2 ± 11</td>
<td></td>
</tr>
<tr>
<td>IAB</td>
<td>15 30 ± 6</td>
<td>−20 ± 9</td>
<td>−10 ± 2</td>
<td>−11 ± 8</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>Ainsworth (HR)</td>
<td>15 18 ± 6</td>
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<td>−6 ± 2</td>
<td>1 ± 14</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>Braunau</td>
<td>19 15 ± 5</td>
<td>−13 ± 13</td>
<td>−5 ± 2</td>
<td>−7 ± 12</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>North Chile</td>
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<td>−11 ± 13</td>
<td>−7 ± 2</td>
<td>−5 ± 12</td>
<td>0.01 ± 0.01</td>
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<tr>
<td>Sihkote Aliin</td>
<td>15 12 ± 7</td>
<td>12 ± 16</td>
<td>−12 ± 2</td>
<td>24 ± 15</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>Low exposure weighted average²</td>
<td>16 ± 4</td>
<td>−9 ± 10</td>
<td>−6 ± 1</td>
<td>−4 ± 9</td>
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<td>−9 ± 9</td>
<td>−6 ± 1</td>
<td>−3 ± 8</td>
<td></td>
</tr>
<tr>
<td>IIC</td>
<td>15 42 ± 5</td>
<td>−3 ± 15</td>
<td>−14 ± 2</td>
<td>10 ± 15</td>
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</tr>
<tr>
<td>Perriville</td>
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<td>−12 ± 2</td>
<td>24 ± 15</td>
<td>0.06 ± 0.02</td>
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<tr>
<td>Kumerina</td>
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<td>−11 ± 2</td>
<td>23 ± 11</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Wiley (an.)</td>
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<td>−12 ± 1</td>
<td>20 ± 8</td>
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<tr>
<td>Weighted average</td>
<td>27 ± 3</td>
<td>7 ± 7</td>
<td>−9 ± 1</td>
<td>13 ± 7</td>
<td></td>
</tr>
<tr>
<td>IIB</td>
<td>14 11 ± 8</td>
<td>7 ± 17</td>
<td>−3 ± 3</td>
<td>11 ± 17</td>
<td>0.03 ± 0.03</td>
</tr>
<tr>
<td>Cape York (HR)</td>
<td>10 9 ± 7</td>
<td>8 ± 13</td>
<td>−3 ± 2</td>
<td>16 ± 12</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>Low exposure weighted average²</td>
<td>9 ± 5</td>
<td>8 ± 10</td>
<td>−3 ± 2</td>
<td>11 ± 10</td>
<td></td>
</tr>
<tr>
<td>IIIF</td>
<td>10 27 ± 7</td>
<td>0 ± 14</td>
<td>−9 ± 2</td>
<td>7 ± 14</td>
<td>0.03 ± 0.04</td>
</tr>
<tr>
<td>Clark County (HR)</td>
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<td>−4 ± 3</td>
<td>10 ± 15</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>Dachenes²</td>
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<td>−1 ± 7</td>
<td>−2 ± 2</td>
<td>1 ± 7</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>Weighted average</td>
<td>8 ± 4</td>
<td>−1 ± 6</td>
<td>−3 ± 2</td>
<td>1 ± 6</td>
<td>0.04 ± 0.04</td>
</tr>
<tr>
<td>IVB</td>
<td>15 25 ± 6</td>
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<td>−8 ± 2</td>
<td>13 ± 11</td>
<td>0.03 ± 0.02</td>
</tr>
<tr>
<td>Skoomkum</td>
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<td>0.02 ± 0.02</td>
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<tr>
<td>Weighted average</td>
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<td>8 ± 8</td>
<td>−9 ± 1</td>
<td>16 ± 8</td>
<td>0.02 ± 0.02</td>
</tr>
</tbody>
</table>

² Number of individual analyses.
³ Fe isotopic composition internally normalized to either $^{56}$Fe/$^{54}$Fe = 0.223095 or $^{56}$Fe/$^{54}$Fe = 0.362549 and expressed as $\mu$-notation defined as the parts-per-million deviation of the $^{56}$Fe/$^{54}$Fe ratio in the sample relative to the two IRMM-524a standard solution bracketing measurements.
⁴ Mass-dependent Fe isotopic composition calculated by sample-standard bracketing and given as $\delta$-notation defined parts-per-thousand deviation of the $^{56}$Fe/$^{54}$Fe ratio of the sample relative to the IRMM-524a standard solution.
⁵ Pt isotopic composition expressed as the $\epsilon$-notation (parts-per-10,000 deviation of the $^{195}$Pt/$^{195}$Pt ratio of the sample relative to the standard, internally normalized to $^{195}$Pt/$^{195}$Pt. For all but five samples (Toluca, Duchesne, Gibeon, Skoomkum, Tlacotepec) the Fe and Pt isotopic composition was analyzed from the same digestion solution. Data from Hunt et al. (2018), Kruijer et al. (2017, 2013), Spitzer et al. (2020), Worsham et al. (2019).
⁶ Measurements using the high-resolution mode (HR) setup and all other measurements were made using medium-resolution mode setup as described in section 2.3.
⁷ Pt isotopic data for these samples were not measured on the same digestion or known to be from adjacent pieces. The data can be used as a qualitative indicator of GCR exposure. Toluca, Gibeon, and Skoomkum can be expected to have negligible or low GCR exposure effects whereas Tlacotepec is known to have high GCR exposure effects in its Pt isotopic composition but shows no variation in measured Fe isotopic anomalies of IVB iron meteorites.
⁸ Calculated weighted averages (±95% c.l.) using samples with low galactic cosmic ray exposure ($\epsilon^{195}$Pt/$\mu^{195}$Pt ≤ 0.16) if significant within group variations are observed.
⁹ Pre-exposure Fe isotopic composition of IC and IIAB iron meteorites defined by the intercept of the $\mu^{56}$Fe- $\epsilon^{195}$Pt correlations. Regression were calculated using the York method.
¹⁰ No Pt isotopic data is available for this sample. The weighted average of the two IVA iron meteorites is similar to the value of the unirradiated sample Gibeon and therefore can be assumed to represent the nucleosynthetic isotopic anomaly of the IVA parent body.

4. Discussion

4.1. Galactic cosmic ray effects and the Fe isotopic dichotomy in iron meteorites

GCR-induced stable isotope effects in meteorites complicate the use of nucleosynthetic anomalies as genetic tracers. Iron meteorites display longer cosmic ray exposure ages than stony meteorites because they are more likely to survive transit through space due to their material strength (e.g., Herzog and Caffee, 2014). As such, GCR-induced neutron capture effects are more pronounced in iron meteorites and have been reported for various elements, most notably W, Os, and Pt (e.g., Kruijer et al., 2013; Qin et al., 2015). Cook et al. (2020) used model calculations to evaluate the combined GCR exposure effects on Fe, Ni, and Pt isotopes in IAB iron
cosmogenic effects on Fe isotopes. Neutron capture induces net losses of $^{54}\text{Fe}$ and $^{56}\text{Fe}$, and net gains of $^{57}\text{Fe}$ and $^{58}\text{Fe}$. Spallation induces a net gain of $^{54}\text{Fe}$ and net losses of $^{56}\text{Fe}$, $^{57}\text{Fe}$, and $^{58}\text{Fe}$, but the effects are significantly smaller than those induced by neutron capture (Cook et al., 2020). The calculations of Cook et al. (2020) show that at depth (e.g., 40–100 cm), combined neutron capture and spallation reactions on Fe isotopes in IAB iron meteorites lead to an increase in $\mu^{54}\text{Fe}_{(7/6)}$ and a decrease in $\mu^{58}\text{Fe}_{(7/4)}$. These authors also argued that (i) pre-atmospheric size had little influence on the correlation between GCR-induced shifts in $\mu^{54}\text{Fe}_{(7/6)}$ and $\mu^{58}\text{Fe}_{(7/4)}$, and (ii) because these shifts are mostly induced by neutron capture on Fe itself, the Fe/Ni ratio is not expected to have a significant influence. The predicted overall effects are small and Cook et al. (2020) did not detect any isotopic shift in the IAB iron meteorite dataset outside of the ±12 ppm uncertainty on $\mu^{54}\text{Fe}_{(7/6)}$ (see Supplementary Material S3; Table S1).

The data of this study may be used to more completely assess the significance of GCR effects on Fe isotopes in iron meteorites, because several iron meteorites having large GCR effects in the neutron capture dosimeter $\epsilon^{196}\text{Pt}_{(8/5)}$ were analyzed. For instance, the samples of this study include Ainsworth (IIAB), which is one of the most strongly irradiated magmatic iron meteorites known. Fig. 2 shows that Fe isotopic anomalies in group IC and IIAB iron meteorites are correlated with their Pt isotopic anomalies. However, the predicted GCR effects are of the same scale as the precision of the isotopic analyses, meaning that these effects can be difficult to resolve. Nevertheless, the correlations between $\mu^{54}\text{Fe}_{(7/6)}$ and $\epsilon^{196}\text{Pt}_{(8/5)}$ among IC and IIAB iron meteorites are significant, defining slopes of 20 ± 18 and 12 ± 7, respectively, which agree with the GCR model slope for IABs (~13) from Cook et al. (2020) (Fig. 2a,b). By contrast, no significant correlation is observed for IID iron meteorites, but the slope of a linear regression between the IID sample with the lowest $\mu^{54}\text{Fe}_{(7/6)}$ (N’Kandhia) and the most irradiated sample (Carbo) of 7 ± 9 is also consistent within error with the expected slope of ~13 and the data plots on the calculated model line (Fig. 2c). As such, these data are not inconsistent with small GCR effects on Fe isotopes in IID iron meteorites.

Assessing the magnitude and extent of nucleosynthetic Fe isotopic variations among iron meteorites requires either correction of GCR effects or exclusion of samples affected by GCR exposure from the dataset. Most of the samples of this study display no significant GCR-effects in $\epsilon^{196}\text{Pt}_{(8/5)}$ and based on the GCR-model and the uncertainties of the Fe isotopic data, we, therefore, excluded four samples that have $\epsilon^{196}\text{Pt}_{(8/5)} > 0.16$ to calculate low-exposure averages of Fe isotopic anomalies for the different iron meteorite groups (Table 1). The reliability of this criterion was tested by comparing the low-exposure values of IC and IIAB iron meteorites with the pre-exposure value defined by the intercept of the $\epsilon^{196}\text{Pt}_{(8/5)}$-$\mu^{54}\text{Fe}_{(7/6)}$ Correlations (Fig. 2a; Table 1). Recently, Spitzer et al. (2021) showed that some ungrouped iron meteorites have small nucleosynthetic Pt isotopic anomalies ($\epsilon^{196}\text{Pt}_{(8/5)} = -0.06 ± 0.01$), but this only minimally affects the GCR-correction on $\mu^{54}\text{Fe}_{(7/6)}$ values (<0.7 ppm). The good agreement of the low-exposure averages and the intercept-derived pre-exposure $\mu^{54}\text{Fe}_{(7/6)}$ of the IC and IIAB iron meteorites show that both methods provide reliable and accurate pre-exposure Fe isotopic compositions (Table 1). Additionally, correction of individual samples using the $\epsilon^{196}\text{Pt}_{(8/5)}$-$\mu^{54}\text{Fe}_{(7/6)}$ slope defined by IABs (which is similar to the IAB model) results in similar pre-exposure values but larger uncertainties due to the uncertainty on the slope (see Supplementary Material S4; Table S2). Five samples of this study were not analyzed for their Pt isotopic compositions on the same digestion aliquot, and the absolute GCR effects for these samples are therefore not well constrained. In those cases, we use $\epsilon^{196}\text{Pt}_{(8/5)}$ data for other samples of the same meteorite but be-

**Fig. 2.** Plots of $\mu^{54}\text{Fe}_{(7/6)}$ versus $\epsilon^{196}\text{Pt}_{(8/5)}$ for (a) IC, (b) IIAB, and (c) IID iron meteorites. The $\mu^{54}\text{Fe}_{(7/6)}$ values of samples within the IC and IIAB iron meteorite groups correlate with $\epsilon^{196}\text{Pt}_{(8/5)}$ (a,b) and reveal that exposure to galactic-cosmic rays modified the Fe isotopic composition of some samples. The best fits (solid grey line) and corresponding uncertainties (95% c.i.; dashed grey lines) were calculated using the York method. The correlations agree well with the GCR model calculated for IAB iron meteorites by Cook et al. (2020) (black dashed line). The light grey areas represent the low-exposure average of $\mu^{54}\text{Fe}_{(7/6)}$ and corresponding 95% c.i. calculated from the intercepts. (c) IID iron meteorites do not show a clear correlation of $\mu^{54}\text{Fe}_{(7/6)}$ with $\epsilon^{196}\text{Pt}_{(8/5)}$. The light grey area represent the low-exposure average of $\mu^{54}\text{Fe}_{(7/6)}$ and corresponding 95% c.i. The irradiated sample (Carbo) agrees within uncertainties with the model of Cook et al. (2020) calculated using the unirradiated IID iron meteorite with the lowest $\mu^{54}\text{Fe}_{(7/6)}$ (N’Kandhia) as pre-exposure value (grey dashed line). The Pt isotopic compositions are from Spitzer et al. (2020) and compiled in Table 1.
cause these effects are expected to be influenced by the depth in the pre-atmospheric body, the actual GCR effects in different pieces of these samples may be variable. However, the Fe isotopic composition of these samples (i) agree well with other samples from the same group, displaying no significant within-group variations (IVAs, IVBs; Table 1), (ii) are in very good agreement with literature values (IABs, IVBs; Table S3) (Cook et al., 2020; Schiller et al., 2020), and (iii) show similar signatures as other samples from the same group, i.e. CC meteorites (IVBs). These samples are, therefore, also included in the discussion.

Fig. 3 displays the average pre-exposure Fe isotopic anomalies of nine iron meteorite groups together with Ni isotopic data for the same groups (compiled in Table S3; all Ni isotopic data relative to NIST SRM986) (Cook et al., 2020; Nanne et al., 2019; Steele et al., 2011; Tang and Dauphas, 2014, 2012). The average pre-exposure $\mu^{54}\text{Fe}(7/6)$ values of NC and CC iron meteorites are distinct from each other (Fig. 3a), where a $x^2$ test of homogenity indicates a statistically significant difference between the NC and CC populations (the null hypothesis is that they are indiscernible, and the $p$-value is $\ll 0.05$). Furthermore, the iron meteorite groups define two distinct NC-CC clusters in $\mu^{54}\text{Fe}(7/6)-\mu^{58}\text{Ni}(2/1)$ space (Fig. 3b), indicating that the NC-CC dichotomy previously identified for several elements in meteorites extents to the Fe isotopic anomalies of (at least) major iron meteorite groups. The inferred accretion ages for these iron meteorites are $\sim 1$ Ma after CAI formation (Kruijer et al., 2017; Spitzer et al., 2021), indicating that, like for other elements, the Fe isotopic compositions of the NC and CC reservoirs were established within the first $\sim 1$ Ma of solar system formation.

4.2. Stellar origin of neutron-poor $^{54}\text{Fe}$ and $^{58}\text{Ni}$ isotopic anomalies

Isotopic anomalies in meteorites and their constituents can help constrain the stellar environments that contributed material to the solar system’s parental molecular cloud core. However, identifying which isotopes of an element vary is often non-trivial because the small magnitude of isotopic anomalies in bulk meteorites requires internal normalization to a fixed isotope ratio to correct for instrumental and natural mass-dependent fractionation. For example, variation in an internally normalized isotope ratio, such as $\mu^{54}\text{Fe}(7/6)$, can arise from variation of one or several of the isotopes involved (e.g., $^{54}\text{Fe}$, $^{56}\text{Fe}$, or $^{57}\text{Fe}$).

The data of this study reveal resolvable isotopic anomalies in the pre-exposure $\mu^{54}\text{Fe}(7/6)$ values, but not in the pre-exposure $\mu^{58}\text{Fe}(7/6)$ values, which are normal within uncertainties of $\sim \pm 15$ ppm (Fig. 3; Table 1). If the culprit for the variations in $\mu^{54}\text{Fe}(7/6)$ was solely $^{56}\text{Fe}$, then variations in $\mu^{58}\text{Fe}(7/6)$ of $\sim -10$ would be expected in CC iron meteorites by way of normalization. In contrast, if the variations in $\mu^{54}\text{Fe}(7/6)$ were solely caused by $^{57}\text{Fe}$, then variations in $\mu^{58}\text{Fe}(7/6)$ of $\sim -30$ would be expected (Fig. 4). The absence of significant variations in $\mu^{58}\text{Fe}(7/6)$, therefore, suggests that $^{56}\text{Fe}$, $^{57}\text{Fe}$, and $^{58}\text{Fe}$ are within uncertainty present in proportions that correspond to the terrestrial standard composition. Although we cannot exclude that nucleosynthetic isotopic variations would mimic mass-dependent fractionation on $^{56}\text{Fe}$, $^{57}\text{Fe}$, and $^{58}\text{Fe}$, the most straightforward explanation is that the observed Fe isotopic variations predominantly reflect anomalies in $^{58}\text{Ni}$ (Fig. 4). The observation that the neutron-poor nuclide $^{54}\text{Fe}$ is responsible for the Fe isotopic heterogeneity is consistent with the view that the primary driver for the Ni isotopic variations among bulk meteorite is the neutron-poor nuclide $^{58}\text{Ni}$ (Steele et al., 2012). Thus, for both, Fe and Ni, CC meteorites reveal excesses in the neutron-poor isotopes (Fig. 3).

Iron and Ni isotopes are primarily produced in massive stars, either during quiescent burning stages or during supernovae explosions of core-collapse (cc-SN; the end point of a massive star when core neutronization is unable the sustain the pressure of the overlying layers) and type Ia (SNia; explosion of a white dwarf near the Chandrasekar mass by accretion from a companion star). The high Fe/O ratio of the solar system points to $1/3-1/2$ of Fe in galactic matter being produced by cc-SN, while the remaining comes from SNIa (Heger et al., 2014). Both $^{54}\text{Fe}$ and $^{58}\text{Ni}$ are produced in large amounts in (i) SNia with low density at ignition ($\rho_{\text{ig.,}}$) (e.g., Iwamoto et al., 1999) and (ii) the inner regions of cc-SN. In both cases, explosive Si burning approaches nuclear statistical equilibrium (Nomoto et al., 1984), which favors the production of isotopes with near-equal numbers of protons and neutrons ($Z = 26$ and $N = 28$ for $^{54}\text{Fe}$; $Z = 28$ and $N = 30$ for $^{58}\text{Ni}$). Radioactive $^{56}\text{Ni}$ ($Z = N = 28$) and $^{60}\text{Zn}$ ($Z = N = 30$) are also produced in large amounts during explosive Si burning, and they subsequently decay to $^{56}\text{Fe}$ and $^{60}\text{Ni}$, explaining their high cosmic abundances. Many presolar grain types were produced in Asymptotic Giant Branch (AGB) stars but as discussed by Dauphas et al. (2008), addition of material from AGB stars would create large collateral effects on $^{57}\text{Fe}$ and $^{58}\text{Fe}$, which is not observed. Thus, the most likely origin of the observed $^{54}\text{Fe}$ variations are SNia and/or cc-SN.
Further constraints on the origin of the $^{54}$Fe and $^{58}$Ni variations can be gained by testing whether the bulk addition of supernovae (SNe) material or the selective admixture of material from different shells of cc-SNe to material of solar composition can reproduce the $^{58}$Ni and $^{54}$Fe variations among meteorites. The slope of a correlation of isotopic anomalies of two elements $A$ and $B$ caused by mixing of stellar material to material with solar composition is given by Dauphas et al. (2014),

$$\mu_{j/i}^{A/B} \propto \frac{\rho_{A}}{\rho_{j/i}} \times \frac{\rho_{B}}{\rho_{i/p}} \times \frac{\rho_{i/p}}{\rho_{B}} \times \frac{\rho_{j/i}}{\rho_{A}} \times \frac{\mu_{j/i}}{\mu_{A/B}},$$

where superscript and subscripts i, j, k, p, q, and r are isotopes of elements $A$ and $B$, respectively, $\mu_{j/i}^{A/B} = (j/E^i/E)^{\rm{star}}/(j/E^i/E)^{\rm{sun}} - 1$ is the isotopic composition of a stellar source of an element $E$ (i.e., $A$ or $B$) normalized to the terrestrial composition, $\rho_{j/i}$ denotes the mass of the isotopes of element $E$, and $c_{j/i}^j = (A/P)^{\rm{star}}/(A/P)^{\rm{sun}}$ is the curvature coefficient of the mixing relationship between the isotopic anomalies of elements $A$ and $B$ (Dauphas et al., 2014, 2004). Fig. 5 summarizes the calculated $m^{54}$Fe/$m^{56}$Fe and $m^{64}$Ni/$m^{62}$Ni slopes produced by addition of the bulk ejecta from different SNe and cc-SN nucleosynthesis models to material with solar composition. Steele et al. (2012) argued that only one model output of a SN can explain the $m^{64}$Ni/$m^{62}$Ni slope defined by meteorites. A more recent set of SNi calculations contains several models that can reproduce the $m^{64}$Ni/$m^{62}$Ni by addition of bulk SNi ejecta (Seitenzahl et al., 2013) (Fig. 5). Moreover, bulk addition of several SNi and cc-SN bulk ejecta can also produce a $m^{54}$Fe/$m^{56}$Fe slope of $0.29 \pm 0.48$ (Fig. 5; calculated from iron meteorite data). However, none of the models considered here can simultaneously produce the slopes of $m^{54}$Fe/$m^{56}$Fe and $m^{64}$Ni/$m^{62}$Ni observed among meteorites (Fig. 5).

The calculations highlighted above were performed using bulk SNe ejecta, but many studies have shown that isotopic anomalies are often carried by presolar grains that can sample distinct regions of stars. The inner Si/S zone of cc-SNe can produce $^{58}$Ni in large amounts and addition of such material can explain the Ni isotopic anomalies observed in meteorites (Steele et al., 2012). Fig. 6 shows profiles of Fe and Ni isotopes abundances as a function of interior mass for a 25 M$_\odot$ cc-SN progenitor (Rauscher et al., 2002). As expected, the Si/S shell is characterized by overproduction of the neutron-poor $^{54}$Fe and $^{58}$Ni isotopes, but it also produces significant amounts of $^{56}$Fe and $^{60}$Ni (Fig. 6a,c). We calculated the slopes of $m^{54}$Fe/$m^{56}$Fe and $m^{64}$Ni/$m^{62}$Ni produced by admixture of material from specific cc-SN zones to material with solar composition and compare them to the slopes expected for $^{54}$Fe and $^{58}$Ni variations in meteorites (Fig. 6b,d). The addition of material from the Si/S shells satisfies the predicted $m^{54}$Fe/$m^{56}$Fe and $m^{64}$Ni/$m^{62}$Ni slopes (Fig. 6b,d). While the $m^{64}$Ni/$m^{62}$Ni slope is independent of the stellar masses (15 M$_\odot$ to 40 M$_\odot$) (Rauscher et al., 2002; Steele et al., 2012), the $m^{54}$Fe/$m^{56}$Fe slope is only reproduced in the Si/S zone of cc-SN with M$_\odot \approx 25$ because yields of $^{54}$Fe decrease and $^{58}$Fe increase in the inner zones of cc-SNe with higher stellar masses.
In summary, addition of cc-SNe material from the inner Si/S zone can explain the observed \(^{54}\text{Fe}\) and \(^{58}\text{Ni}\) variations in meteorites. In contrast, none of the SNII and cc-SN bulk addition models considered here can simultaneously explain the Fe and Ni isotopic variations among meteorites. However, further work is needed to evaluate the viability of SNII models, as models of ejecta show considerable heterogeneity that is best captured by performing nucleosynthesis calculations on tracked particles in three-dimensional models (e.g., Seitenzahl et al., 2013). A difficulty with SNII models is that dust may not condense in ejecta, but that the atoms ejected could still condense on preexisting grains present in the interstellar medium. Further work is therefore needed to assess the contribution of SNII material to the Fe and Ni isotopic anomalies.

### 4.3. Possible origins of the Fe isotopic heterogeneity in the protoplanetary disk

Possible scenarios for the origin of the isotopic heterogeneity in the protoplanetary disk documented here for Fe are (i) selective thermal processing of isotopically distinct phases in an initially homogenized protoplanetary disk (Burkhardt et al., 2012; Dauphas et al., 2002a; Trinquier et al., 2009), (ii) unmixing of isotopically distinct components in the protoplanetary disk through physical processes such as size sorting (Dauphas et al., 2010; Dauphas et al., 2002b; Regelous et al., 2008) or (iii) the projection and subsequent processing of the isotopic heterogeneity of the solar system’s parental molecular cloud core onto the protoplanetary disk during collapse (Burkhardt et al., 2019; Dauphas and Schauble, 2016; Jacquet et al., 2019; Nanne et al., 2019).

Burkhardt et al. (2019) and Nanne et al. (2019) argued that CAIs represent the isotopic composition of the material responsible for the NC-CC isotopic dichotomy, because the isotopic anomalies of a large number of elements in CC meteorites are offset from NC meteorites towards the isotopic composition of CAIs. If true, CAIs would be expected to have large excesses of \(^{54}\text{Fe}\) (e.g., \(\sim 90\) for \(\mu^{54}\text{Fe}_{\text{CC}}\)) if we assume a simplified linear correlation between \(\mu^{54}\text{Fe}_{\text{CC}}\) and \(\varepsilon^{54}\text{Cr}\) among NC, CC, and CAIs). Völkering and Papanastassiou (1989) found large excesses in neutron-rich \(^{54}\text{Fe}\) in FUN-CAIs but no resolvable variations in normal CAIs. Shollenberger et al. (2019) found large negative \(\mu^{54}\text{Fe}_{\text{CC}}\) values in mineral separates from a type B CAI but non-FUN bulk CAIs revealed no resolvable variations of individual bulk CAIs relative to CC chondrites. The average \(\mu^{54}\text{Fe}_{\text{CC}}\) of 25 bulk CAIs measured by Shollenberger et al. (2019) is \(43 \pm 17\) (95% c.l.), which overlaps with values expected for their host CV and CK chondrites (Schiller et al., 2020). This suggests that the Fe isotopic composition of bulk CAIs is fully or partially overprinted by parent-body aqueous alteration (Shollenberger et al., 2019). Thus, it is currently not possible to evaluate whether material with CAI-like isotopic composition is responsible for the NC-CC Fe isotopic dichotomy observed among iron meteorites.
The Fe isotopic anomalies in iron meteorites do not only display a NC-CC dichotomy but also correlate with isotopic anomalies of Mo and Ru (Fig. 7). The Fe isotopic variations within the NC and/or CC clusters are not well resolved but the clear correlations with the isotopic anomalies of Mo and Ru provide strong evidence that the small $\mu^{54}\text{Fe}_{7(2)}$ variations among NC and CC iron meteorites are significant. All NC and some CC chondrites plot on the multi-element isotopic correlations defined by iron meteorites (Fig. 7), and only CI and CO chondrites seem to fall off these correlations (Fig. 7). This and the observation that the majority of chondrite groups plot in the NC-CC clusters defined by iron meteorites (Fig. 8a) suggests that the NC-CC Fe isotopic dichotomy observed for iron meteorites was maintained in the disk at least until the formation time of most chondrite parent bodies.

Earth’s mantle plots towards the end of the correlations defined by Fe, Mo, and Ru isotopic anomalies, and furthest away from most CC meteorites (Fig. 7). This contrasts with isotopic anomalies of other iron peak elements (e.g., Cr, Ti) for which Earth’s mantle does not have an endmember composition (Warren, 2011). The isotopic variations of Mo and Ru predominantly reflect variations in $s$- and/or $r$-process nuclides (e.g., Burkhardt et al., 2011; Dauphas et al., 2004; Fischer-Gödde et al., 2015; Stephan and Davis, 2021), whose carriers derive from different stellar environments than the carriers of $^{54}\text{Fe}$ anomalies (Section 4.2). Thus, the observed correlations of Fe, Mo, and Ru isotopic anomalies reveal correlated heterogeneities in material of different stellar origins that are likely hosted in distinct presolar carriers. As such, these correlations are consistent with the view that the large-scale dichotomy and the smaller scale variations within the NC and CC reservoirs represent heterogeneous mixing of two isotopically distinct components with broadly chondritic compositions (Burkhardt et al., 2019; Nanne et al., 2019; Spitzer et al., 2020). These observations are more difficult to account for by thermal processing and/or physical sorting of presolar dust in the nebula, because the isotopic correlations exist for elements across a range of volatilities and of distinct stellar origins.
4.4. Implications for the accretion of Earth

The nucleosynthetic isotopic anomalies and the distinct geochemical behavior of elements make it possible to reconstruct the isotopic evolution of the Earth and its building blocks through time (Dauphas, 2017). Based on the observation that CI chondrites have similar Fe isotopic composition to Earth’s mantle, Schiller et al. (2020) argued that most of the Fe in Earth’s mantle derives from CI-like dust that drifted sunwards through the gaseous disk and was accreted to proto-Earth within the first ~5 Ma of solar system history. Interestingly, CI chondrites also display smaller Mo and Ru s-process deficits than other CC groups (Fig. 7) (Burkart et al., 2011; Dauphas et al., 2002b; Fischer-Gödde and Kleine, 2017). However, while CI chondrites appear to overlap with NC meteorites for Fe and Ru isotopic anomalies, they have (i) distinct $\mu^{58}\text{Ni}_{2\text{D}}(1)$ values (Fig. 8a) (Steele et al., 2012; Tang and Dauphas, 2014), (ii) distinct $\varepsilon^{54}\text{Cr}_{2\text{D}}(0)$ (Fig. 8b) (Trinquier et al., 2007), and (iii) the same characteristic excess in r-process Mo nuclides of CC over NC meteorites (expressed as $\Delta^{95}\text{Mo}$) that is responsible for the Mo isotopic dichotomy (Busde et al., 2019, 2016).

Iron is a moderately siderophile element, and so the Fe isotopic composition of Earth’s mantle predominantly represents material accreted during later stages of Earth’s accretion. The Fe concentration of Earth’s mantle is 6.26 wt.% whereas the core contains 78.0 to 87.5 wt.% Fe (McDonough and Sun, 1995). This corresponds to an effective metal–silicate partition coefficient $D(\text{Fe})_{\text{M-S}}$ of 12.5 to 14. Iron in Earth is intermediate in its siderophile behavior between Cr (DM-SCr ~ 3) and Ni (DM-SNi ~ 26). Following the approach of Dauphas (2017) we calculated the cumulative density functions (CDFs) for the delivery of Cr, Fe, and Ni atoms during Earth’s accretion and their incorporation into Earth’s mantle through time (Fig. 9). The CDFs show that ~70% of Cr in Earth’s mantle was delivered together with all Fe, and ~70% of Fe was delivered together with all Ni. Thus, the Fe in Earth’s mantle inherited a majority of its isotopic signature from the same material that also delivered Cr and Ni. While CI chondrites have similar Fe isotopic compositions to Earth’s mantle, they display the largest $\varepsilon^{54}\text{Cr}_{2\text{D}}(0)$ and $\mu^{58}\text{Ni}_{2\text{D}}(1)$ isotopic anomalies of all carbonaceous chondrites, which are very different from the Earth’s mantle value (Fig. 8b) (Steele et al., 2011; Tang and Dauphas, 2014, 2012; Trinquier et al., 2007). Thus, CI chondrites are unlikely to resemble the majority of the material that delivered Fe, Cr, and Ni to Earth’s mantle during the accretion of Earth. The similarity of the Fe isotopic composition of CI chondrites with NC meteorites and Earth’s mantle, therefore, more likely represents isotopic variability within the CC reservoir, which was subject to admixture of different nucleosynthetic components that coincidently brought the isotopic composition of CI chondrites in the field of NC meteorites for some elements.

Earth’s mantle plots on or close to the correlations of Fe, Mo, and Ru isotopic anomalies in meteorites (Fig. 7). Ruthenium is a highly siderophile element and its budget in Earth’s mantle only represents the last ~0.5% of Earth’s accretion whereas Mo records the last ~12% of Earth’s growth (Dauphas, 2017). Thus, the fact that the Earth’s mantle plots on or close to the correlation lines in $\mu^{54}\text{Fe}_{7\text{D}}(3000)\text{Ru}_{9\text{D}1}$ and $\mu^{54}\text{Fe}_{7\text{D}}(3)\text{Mo}_{8\text{D}6}$ space suggests that the material accreted during the last ~60% of accretion of Earth did not significantly change in its isotopic composition (Fig. 7). It was previously shown that the Mo isotopic composition of Earth’s mantle is intermediate between those of the NC and CC reservoirs, indicating that some addition of CC material during the late stages of Earth accretion is required (Buède et al., 2019; Hopp et al., 2020). However, this minor addition of CC material did not contribute significantly to Earth’s mantle Fe budget, which is therefore dominated by NC material. These observations and the predominantly NC-like isotopic composition of Earth are, therefore, consistent with heterogeneous accretion models which proposed that Earth accreted some volatile-rich and most likely CI-like material towards the end of its growth (Rubie et al., 2011; Schönbächler et al., 2010).

Dauphas (2017) has shown that modeling of the multi–element isotopic evolution of the Earth’s mantle during different stages of Earth’s accretion suggests that the accreted material always contained large fractions of material with on average enstatite chondrite-like composition, but only minor fractions of carbonaceous chondrite-like material. If the small difference of $\mu^{54}\text{Fe}_{7\text{D}}(3)$ in enstatite chondrites and the Earth’s mantle measured by Schiller et al. (2020) is confirmed, it would call for the presence of an additional component that contributed Fe to Earth that is not yet sampled in meteorites. However, the similarity in Fe isotopic composition between CI and Earth’s mantle does not necessarily imply that a significant fraction of Earth’s Fe inventory was delivered by CI-like material as in this case collateral isotopic anomalies would have to exist for several other elements.

5. Conclusions

High precision Fe isotopic measurements of iron meteorites reveal the presence of isotopic anomalies of both nucleosynthetic and cosmogenic origins. After correction for CCR effects, the nucleosynthetic Fe isotopic anomalies in NC and CC iron meteorites plot in two distinct clusters corresponding to the NC-CC isotopic dichotomy previously observed for other elements. The Fe isotopic anomalies are produced predominantly by variability in the neutron-poor nuclide $^{54}\text{Fe}$, consistent with prior observations of variations in the neutron-poor nuclide $^{58}\text{Ni}$ among bulk meteorites. For both elements CC iron meteorites are characterized by excesses in neutron-poor isotopes (i.e., $^{54}\text{Fe}$ and $^{58}\text{Ni}$) relative to NC meteorites and Earth’s mantle. These excesses in $^{54}\text{Fe}$ and $^{58}\text{Ni}$ are best accounted for by the heterogeneous distribution of material produced by nuclear statistical equilibrium in the inner regions of cc-SN or possibly SNIa.

The Fe isotopic anomalies of iron meteorites and most chondrite groups correlate with s- and/or r-process variations in Mo and Ru, providing further evidence that isotopic anomalies in bulk meteorites correlate for elements produced in different stellar en-
virements and having a range of geo- and cosmochemical properties. Earth’s mantle plots close to the correlations between Fe, Mo, and Ru isotopic anomalies suggesting that the average isotopic composition of Earth’s building blocks did not drastically change throughout the last ~60% of its accretion. A previous study showed that CI chondrites have Fe isotopic compositions similar to Earth’s mantle and argued that the majority of Fe in Earth’s mantle derives from inward-drifting CI-like dust. However, during accretion and core segregation on Earth, Fe is intermediate in metal affinity between Cr and Ni. Thus, a large fraction of Fe in Earth’s mantle was delivered by the same material that delivered Cr and Ni. However, for these two elements CI chondrites are among the isotopically most anomalous meteorites relative to Earth, ruling out significant contributions of Cr, Fe, and Ni by accretion of CI-like material.

CRediT authorship contribution statement

Timo Hopp: Conceptualization, Investigation, Methodology, Validation, Visualization, Writing – original draft. Nicolas Dauphas: Conceptualization, Funding acquisition, Resources, Supervision, Writing – review & editing. Fridolin Spitzer: Resources, Writing – review & editing. Christoph Burkhardt: Funding acquisition, Resources, Writing – review & editing. Thorsten Kleine: Funding acquisition, Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data statement

All data generated or analyzed during this study are included in this published article (and its supplementary information file).

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Appendix A. Supplementary material

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