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The absence of nickel effect on iron isotope fractionation during core formation

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Abstract

The mantellic Fe isotope compositions from differentiated inner solar system bodies are similar to, or heavier than chondritic meteorites. Core–mantle differentiation is a likely contributor to planetary isotopic fractionation. However, previous metal–silicate experiments provide only equivocal evidence for such fractionation, in which it has been argued that the Ni content of core-forming metal influences the extent of Fe isotopic fractionation. Here, we complement existing data with twenty-two novel metal–silicate equilibrium experiments with

25 varying Ni content to better quantify its effect on the vector and magnitude of Fe isotope
26 fractionation during core formation. We find no statistically resolvable effect of the Ni content
27 in the metallic phase on the Fe isotopic fractionation factor over a wide range of Ni
28 concentrations (0 to 70 wt.% in the metal). In particular, the Fe isotopic composition of alloys
29 from two experiments performed with 70 wt.% of Ni ($\delta^{56}\text{Fe}_{\text{metal}}=0.27\pm 0.01$ and 0.32 ± 0.01) are
30 identical to the bulk experimental starting material (0.27 ± 0.10). Our data across all experiments
31 yield an average isotopic fractionation factor $\Delta^{56}\text{Fe}_{\text{met-sil}}=0.05\pm 0.11$ (2σ) at 1873 K and 1–2
32 GPa, suggesting that little to no isotopic fractionation of Fe is expected to occur during core
33 formation at low pressures. As such, our data does not support core formation as the main
34 mechanism causing the observed variability in Fe isotope ratios between the silicate Earth,
35 Moon, Vesta and other differentiated asteroids. A combination of multiple accretion-related
36 processes—including condensation from the solar nebula, volatile-depleting events such as
37 giant impacts, and disproportionation of ferrous iron to ferric iron and iron metal in larger
38 bodies—as well as deep mantle and recycling processes could explain the heavier signatures in
39 the silicate Earth and Moon. Furthermore, our results support the ideality of mixing among Fe–
40 Ni alloys, previously demonstrated for physical properties but less conclusively evidenced for
41 chemical properties.

42 **Introduction**

43 Experimental determination of isotopic fractionation of siderophile elements between
44 metal and silicate has been used to investigate core formation on planetary bodies (e.g. [Georg
45 et al., 2007](#); [Bourdon et al., 2018](#)). Recorded experimental isotopic fractionations can be
46 compared to natural isotope signatures, providing a powerful tool for interpretation of planetary
47 isotope signatures and refining our knowledge of the history of solar system planetary bodies.
48 In principle, a melted silicate and a melted metal are equilibrated at high pressure and high

49 temperature until elemental and isotopic equilibrium between the two phases is reached. The
50 silicate glass and metal grains from each quenched experiment are physically separated and
51 their isotope compositions are determined. Such studies on various siderophile elements can be
52 used to trace the conditions of planetary differentiation—its temperature (Hin et al., 2014), its
53 pressure (Labidi et al., 2016), redox conditions (Dalou et al., 2019), subsequent
54 rehomogenisation mechanisms (Kempl et al., 2013), and the composition of the core (Savage
55 et al., 2015; Mahan et al., 2017; Xia et al., 2019). Applied to elements presenting a volatile
56 behaviour, they open the possibility to trace the timing and origin of planetary volatile delivery
57 (Kubik et al., 2021). Such results allow the isotopic characterisation of the building blocks that
58 accreted into planetary bodies (Hin et al., 2014), permitting assessment of whether core
59 formation is the main planetary process controlling the abundances and isotope compositions
60 of certain elements in the accessible mantle of the body. Alternatively, other possible
61 mechanisms such as magmatic differentiation (Bonnand et al., 2016) or volatilisation processes
62 (Xia et al., 2019) may be required. Numerous key questions may thus be addressed through
63 experimental evidence. However, experimentally determined isotopic fractionation factors are
64 often in disaccord with one another, namely, Zn (Bridgestock et al., 2014; Mahan et al., 2017;
65 Xia et al., 2019), Si (Shahar et al., 2009,2011; Hin et al., 2014; Kempl et al., 2013), Ni (Lazar
66 et al., 2012; Guignard et al., 2020), Cu (Savage et al., 2015; Xia et al., 2019). These
67 discrepancies are partially attributable to differences in the experimental approach. In this
68 respect, replication of such experiments combined with independent, non-experimental
69 determination of the isotopic consequences of core formation (e.g. Georg et al., 2007; Moynier
70 et al., 2011) can only be beneficial to the general understanding of planetary differentiation.

71 Planetary materials show significant variability in Fe isotopic compositions. Ordinary,
72 enstatite and carbonaceous chondrites have an average $\delta^{56}\text{Fe}$ (per mil variation of the $^{56}\text{Fe}/^{54}\text{Fe}$
73 ratio relative to IRMM-014) of $0.00\pm 0.01\text{‰}$ (2σ) (Craddock and Dauphas, 2011; Schoenberg

74 and von Blanckenburg, 2006; Wang et al., 2013, 2014). The terrestrial mantle is estimated to
75 have a $\delta^{56}\text{Fe}=0.03\pm 0.02\text{‰}$ (Craddock et al., 2013; Sossi et al., 2016a; Weyer and Ionov, 2007)
76 while mid-ocean ridge basalts (MORB) are isotopically heavier with average
77 $\delta^{56}\text{Fe}=0.10\pm 0.01\text{‰}$ (Teng et al., 2013; Craddock et al., 2013; Craddock and Dauphas, 2011;
78 Nebel et al., 2018; Weyer and Ionov, 2007). Even accounting for the effect of olivine
79 crystallisation and correcting their Fe isotopic composition back to that of a primary melt in
80 equilibrium with mantle peridotite, MORBs define an average $\delta^{56}\text{Fe}=0.07\pm 0.01\text{‰}$ (Sossi et al.,
81 2016a; Nebel et al. 2018), heavier than chondritic meteorites. By contrast, primary melts of the
82 martian and vestan mantles, determined respectively from the SNC (shergottite-nakhite-
83 chassignite) and HED (howardite-eucrite-diogenite) groups of meteorites, have near-chondritic
84 isotopic signatures (Poitrasson et al., 2004; Schoenberg and von Blackenburg, 2006; Wang et
85 al., 2012; Sossi et al., 2016b) whereas angrites are markedly heavier ($\delta^{56}\text{Fe}=0.12\pm 0.04\text{‰}$, $n=7$,
86 Wang et al., 2012). Lunar basalts yield a range of isotopic compositions from near-chondritic
87 to 0.3‰ (Weyer et al., 2005; Poitrasson et al., 2004; Liu et al., 2010; Wang et al., 2015; Sossi
88 and Moynier, 2017; Poitrasson et al., 2019), but ferroan anorthosites and Mg suite rocks from
89 the lunar highlands define an estimated bulk lunar Fe isotope composition similar to that of the
90 Earth's mantle ($\delta^{56}\text{Fe}=0.05\pm 0.03\text{‰}$, Sossi and Moynier, 2017; Poitrasson et al., 2019).

91 Several processes have been proposed to account for this Fe isotopic variability
92 including (1) volatile loss by vaporisation during the Moon-forming giant impact (Poitrasson
93 et al., 2004; Poitrasson 2007; Liu et al., 2010), (2) accretion from the solar nebula associated
94 with various degrees of nebular or post-nebular Fe loss in planetary building blocks (Sossi et
95 al., 2016b), (3) disproportionation of ferrous iron (Fe^{2+}) into Fe^{3+} and metallic iron by
96 bridgmanite crystallisation during accretion in bigger planetary bodies such as the Earth
97 (Williams et al., 2012; Frost and McCammon, 2008), (4) core–mantle equilibration related
98 isotopic fractionation at either high (Polyakov, 2009) or low pressures (Elardo and Shaha,

99 2017) and (5) deep mantle recycling processes (Smith et al., 2021; Soderman et al., 2021).
100 Leshner et al. (2020) argued that the upper part of the Earth's core could be enriched in heavier
101 Fe isotopes by thermo-diffusion. If this isotopically heavier Fe is, as suggested in the study,
102 transported to the upper mantle by ascending plumes, it could explain the heavy Fe isotopic
103 signature of the BSE (bulk silicate Earth). However, core–mantle equilibration remains the
104 largest chemical mass transfer process that occurred on Earth, suggesting that it may have also
105 defined the observed isotopic signatures of its present-day core and mantle. It is therefore
106 paramount to understand the isotopic behaviour of Fe during core–mantle equilibration.

107 However, the degree and direction of Fe isotope fractionation between silicate and core-
108 forming alloy is influenced by a variety of variables. Early experimental work addressing this
109 question did not find any resolvable Fe isotopic fractionation between S-free metallic and
110 silicate phases over a range of pressures, from 1 to 60 GPa (Poitrasson et al., 2009; Hin et al.,
111 2012; Shahar et al., 2015; Liu et al., 2017), leading to the conclusion that, at the high
112 temperatures required for core formation on terrestrial bodies (≥ 2000 K, e.g., Righter and
113 Drake, 1996), equilibrium isotope fractionation between metal and silicate—which is
114 proportional to $1/T^2$ —should be negligible compared to the observed variations. Although some
115 of the metallic phases investigated contained a small fraction of Ni (~5–9 wt.%) as is relevant
116 to planetary cores, the effect of Ni on iron isotope fractionation was not explicitly investigated
117 prior to the study of Elardo and Shahar (2017). They reported piston cylinder experiments
118 conducted at 2123 K and 1 GPa in which the Ni content of the metal varied between 1 and 26
119 at.%, and observed a systematic increase of the isotopic fractionation factor with Ni content,
120 which defines the following relation: $\Delta^{57}\text{Fe}_{\text{met-sil}}=0.011(\text{Ni, at.}\%)+0.04$. Thus, adding Ni to the
121 metal phase enhances the Fe isotopic fractionation between metal and silicate, leading to an
122 enrichment of the silicate in the lighter Fe isotopes relative to the metal. Because the sense of
123 this isotopic fractionation is opposite to that observed in the mantles of differentiated bodies,

124 [Elardo and Shahar, \(2017\)](#) invoked significant isotopic fractionation during partial melting to
125 restore the light subchondritic mantle isotopic composition inferred from their experiments to
126 the superchondritic values observed in basaltic achondrites (*e.g.* [Sossi et al. 2016a](#)).
127 Importantly, such an isotopic effect implies that Fe–Ni alloys do not mix ideally, which is at
128 odds with the constancy of density, compressibility, and wave velocities of Fe–Ni alloys with
129 increasing Ni content (*e.g.* [Lin et al., 2003](#); [Kantor et al., 2007](#); [Martorell et al., 2013](#); [Badro et](#)
130 [al., 2014](#)). Moreover, this ideality has been assumed in numerous experimental studies on core
131 formation processes in which the effect of Ni was neglected. [Xia et al. \(2019\)](#) report Zn and Cu
132 metal–silicate isotope fractionation experiments with significant sensitivity to the Ni content of
133 the metal. Positive Ni-induced isotopic fractionations were measured for Fe ([Elardo and Shahar,](#)
134 [2017](#)), Zn and Cu ([Xia et al., 2019](#)), based on less than 10 experiments for each element. More
135 experimental results, involving a broader range of Ni contents, are needed to establish whether
136 there is a resolvable effect of the Ni content of an Fe–Ni alloy on various chemical and isotopic
137 parameters. Therefore, assessing the Fe isotope fractionation between metal and silicate has
138 profound implications for our understanding of core formation processes and for the physical
139 and chemical properties of core-forming alloys.

140 To address this question, twenty-two novel metal–silicate equilibrium experiments were
141 performed in order to characterise the effect of Ni on the Fe isotope fractionation. In particular,
142 a wider range of Ni content in the metal (from 0 to 70 *wt.*%) was covered compared to previous
143 studies (0 to 25 *wt.*%, [Elardo and Shahar, 2017](#)).

144 **Method**

145 **Experimental method**

146 Mixtures composed of 70 *wt.*% MORB with varying proportions of pure Fe and Ni were
147 prepared by weighing each component and grinding them in an agate mortar until complete

148 homogenisation. All experiments were performed in a 150-ton end-loaded piston cylinder
149 apparatus at the Institut de Physique du Globe de Paris (IPGP), Université de Paris, in ½” talc
150 pyrex assemblies using graphite furnaces. Pressure calibration of the apparatus was performed
151 using the alumina concentration in orthopyroxene in equilibrium with pyrope in a MgO–Al₂O₃–
152 SiO₂ system (Perkins and Newton, 1981). The friction coefficients reported by McDade et al.
153 (2002) were compared and found to be identical to the coefficients measured during the
154 calibration of the apparatus, allowing similar corrections to be applied for friction loss for
155 assembly materials. During the experiments, the temperature was measured using a type D
156 (W₉₇Re₃/W₇₅Re₂₅) thermocouple contained in a 4-hole alumina sleeve just above the capsule
157 lid. Uncertainties on pressure and temperature are estimated to be around 0.1 GPa and 50 K
158 (Siebert et al. 2011). All experiments were performed at 1 to 2 GPa and at 1873 K in order to
159 induce complete fusion and promote equilibrium between metal and silicate in the system. Four
160 capsule types—boron nitride, crushable MgO, single-crystal MgO and graphite—were tested
161 in order to assess their effect on the Fe isotopic fractionation factor.

162 **Sample collection and purification**

163 The metal and silicate were separated mechanically after each experiment. Clean pieces
164 from each phase were selected carefully under magnifying glass. Metal pieces were directly
165 dissolved in 6 N HCl. Silicate samples were sorted in order to select clean pieces devoid of
166 metal bead or capsule material. These pieces were roughly crushed and a magnet was used to
167 remove any stray pieces of metal (Kubik et al., 2021). The silicate was finely crushed in an
168 agate mortar and digested in a 1:3 solution of HF:HNO₃ in closed Teflon bombs on a hotplate
169 at 100°C. Silicate samples were then dried and further digested in aqua regia on a hot plate at
170 150°C to remove any residual fluoride complex. They were dried again and dissolved in 6 N
171 HCl for purification. The purification of Fe in the samples was performed following the method
172 described in Sossi et al. (2015), by anion exchange chromatography using AG1-X8 (200-400

173 mesh) and 0.4×7 cm Teflon columns. Columns were filled with 1 mL AG1-X8 resin and
174 cleaned with 5 mL 3 N HNO₃, 5 mL H₂O and conditioned with 5 mL 6 N HCl. The samples
175 were subsequently loaded in 0.5 mL of 6 N HCl. The matrix was eluted with 11 mL of 6 N HCl.
176 The Fe cuts were eluted with 3 mL of 0.5 N HCl, and dried to be redissolved in 0.5 N HNO₃.
177 They were diluted to 4 ppm Fe solutions and spiked with 8 ppm of Ni, following the method
178 described in [Sossi et al. \(2015\)](#).

179 **MC-ICPMS measurements**

180 Iron isotopic measurements were performed on a Neptune Plus MC-ICPMS at IPGP
181 (Université de Paris), used in medium resolution mode. The cups were configured as described
182 in [Sossi et al. \(2015\)](#) in order to collect the intensity on the masses 53, 54, 56, 57, 60 and 61.
183 The mass 53 was used to correct for any ⁵⁴Cr interference on ⁵⁴Fe, even though chromatographic
184 separation was shown to be very efficient, meaning the correction was insignificant. The
185 ⁶¹Ni/⁶⁰Ni ratios measured in all samples were used to correct for mass bias effects.
186 Measurements of IRMM-014 performed in between samples were used to calculate the delta
187 values reported in this study. International reference materials were measured along with the
188 experimental samples with Fe isotopic compositions reproducing the previously published
189 values (*e.g.* for BHVO-2: $\delta^{56}\text{Fe}=0.103\pm 0.04$, 2 *s.d.*).

190 **Evidence of metal–silicate equilibrium**

191 Two methods are typically used in order to assess metal–silicate isotopic equilibrium in
192 high-temperature experiments: time series and the “three-isotope method”. It has been known
193 for a few decades that elemental equilibrium can be reached very quickly at superliquidus
194 condition in metal–silicate experiments (5 seconds at 2300 K, [Thibault and Walter, 1995](#)). As
195 these diffusion rates cannot necessarily be extrapolated to the isotopic exchange rate, several
196 experimental studies report that isotopic exchange can actually be faster than chemical diffusion
197 while pointing to differences between systems ([Leshner et al., 1990](#); [Van der Laan, 1994](#)). In this

198 context, numerous studies report relatively short equilibration time experiments (e.g. [Hin et al.,](#)
199 [2013](#); [Kubik et al., 2021](#); [Poitrasson et al., 2009](#); [Shahar et al., 2011](#)). The attainment of isotopic
200 equilibrium after a few minutes can be explained by the superliquidus temperatures reached, at
201 which the entire sample is melted. The molten state promotes equilibration because (1)
202 diffusion rates are significantly higher in the liquid state than in presence of a solid phase, (2)
203 convection further stirs the melt inside the capsule, owing to the small thermal gradient endemic
204 to high pressure experiments, (3) homogenisation is additionally favoured by using a finely
205 crushed powder as a starting material. Time series experiments are an empirical way to establish
206 the time needed to achieve equilibrium. In this study specifically, (a) thorough SEM and EDX
207 characterisation of each phase allowed to provide proof that the entirety of the sample material
208 was fully molten and (b) resulted in chemically homogeneous phases (see supplementary
209 information). (c) The Fe isotopic fractionation factors follow a systematic trend that can be
210 statistically determined to good precision due to an extensive data set comprising 22
211 experiments. (d) Repeated time series experiments show no statistically resolvable evolution of
212 the Fe isotopic fractionation factor between runs of 3- and 30-minute duration (see
213 supplementary information), with experiments of 30 minutes and more exhibiting greater
214 variability, with both positive and negative isotopic fractionation factors observed. This is
215 attributed to progressive reaction of the silicate melt with the capsule material over time.
216 Moreover, the results reported in this study are in agreement with several other studies
217 performed in a range of laboratory facilities with different methodologies and apparatuses
218 ([Poitrasson et al., 2009](#); [Hin et al., 2012](#); [Liu et al., 2017](#); [Elardo and Shahar, 2017](#), Fig. 1a).
219 The results from our study are also in agreement with numerous pieces of evidence of Fe–Ni
220 alloy ideality ([Lin et al., 2003](#); [Kantor et al., 2007](#); [Martorell et al., 2013](#); [Badro et al., 2014](#);
221 [Huang and Badro, 2018](#)). With respect to demonstration of isotopic equilibrium, the three-
222 isotope method was not included in the protocol of this study. Although [Cao and Bao \(2017\)](#)

223 and Bourdon et al. (2018) reported artifacts that could induce non-linear trajectories, leading
224 the authors to delineate limitations of the method, other studies have argued for its robustness
225 (Shahar et al., 2008; Shahar and Young, 2020), and in particular its usefulness in verifying that
226 the system remained closed with respect to mass exchange throughout an experiment. In this
227 study, the use of single-crystal MgO capsules was employed to ensure minimal chemical and
228 isotopic interaction with the capsule (see supplementary information). Moreover, the
229 recalculation of the bulk isotope composition of the experiments based on measured $\delta^{56}\text{Fe}$ of
230 each phase by mass balance yields a good reproducibility (on average $\delta^{56}\text{Fe}_{\text{bulk}}=0.40\pm 0.08\%$,
231 1 s.d.). The three-isotope method is predicated on experiments that preserve a record of the
232 approach to equilibrium between two phases, and thus represent a form of time-series in which
233 equilibration times are necessarily slow. Because equilibrium is achieved within a few minutes
234 in our experiments, the three-isotope method is unfeasible from an experimental standpoint.
235 Namely, the timescale of equilibration of the piston cylinder assembly to ensure stable
236 conditions (e.g., Matjuschkin et al., 2015) is of the same order of that required for the three-
237 isotope method to produce dispersion in isotope composition. Each bulk starting material used
238 in this study was also measured for Fe isotopes and are found to reproduce the calculated bulk
239 value within error for 12 of them which further supports closed system and equilibrium
240 achievement.

241 **Iron isotopic behaviour in metal–silicate equilibrium experiments**

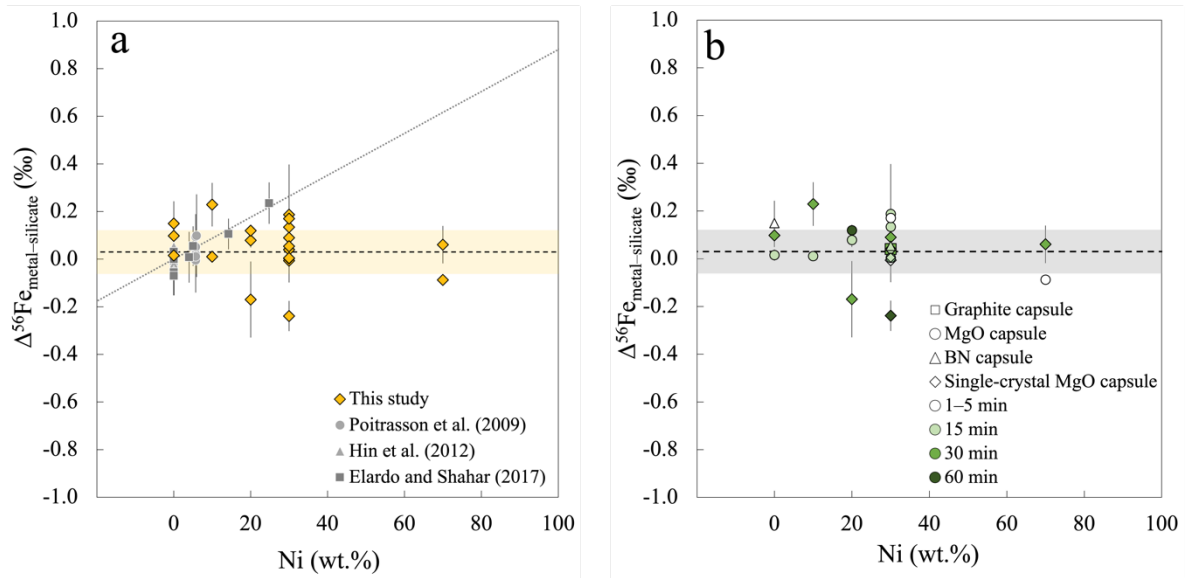
242 Twenty-two metal–silicate equilibrium experiments were performed at 1 and 2 GPa and
243 1973 K. Run durations were varied between 3 and 60 minutes in order to assess the timescales
244 required to approach isotopic equilibrium. Petrographic observations indicate that the starting
245 material was fully molten in all experiments (see supplementary materials). The metal
246 coalesced into a discrete sphere in most experiments, and subsequent to quenching, was

247 separated mechanically from the silicate phase. All experimental parameters and isotopic
248 measurements are available in Table 1.

249 Iron isotope fractionation results for all experiments from this study and literature are
250 presented in Fig. 1a. It should be noted that experiments from other studies were carried at
251 different temperature conditions and were therefore recalculated at 1873 K for comparison with
252 the dataset reported herein by using the relationship $\Delta^{56}Fe_{metal-silicate} = a \cdot \frac{1}{T^2}$ (e.g. Urey,
253 1947). Our results show no correlation between the Ni content of the metal and the Fe isotopic
254 fractionation factor between metal and silicate (Fig. 1b). There is also no resolvable difference
255 between the experiments using the different types of capsules, although from petrographic
256 observations single-crystal MgO capsules minimise the extent of reaction between capsule and
257 sample by containing the interactions within the first 30 μm of the capsule. Isotope
258 measurements on multiple parts of experiment E375 are presented in Fig. 2. This short-duration
259 experiment exhibits a glassy silicate in the center and partially crystallised silicate towards the
260 capsule boundary where skeletal olivine crystals grew as a result of MgO enrichment and the
261 relatively low quenching rates achievable in the piston cylinder (e.g. Green et al., 1975).
262 Measurements on these separated parts show no difference in Fe isotopic composition between
263 glass and crystallised silicates ($\delta^{56}\text{Fe}=0.30\pm 0.03\%$ and $0.29\pm 0.05\%$ respectively) which means
264 that MgO diffusion towards the center of the sample does not affect the Fe isotope composition
265 of the silicate. Therefore, in this particular case, MgO capsules are well-suited for isotope
266 fractionation experiments with respect to MgO diffusion. This experiment also presents an
267 isotopic composition of the metal identical to the silicate. The first 30 μm of the capsule in
268 contact with the melt contains less than 4 wt.% of Fe, however, exhibits a clear enrichment in
269 light Fe isotopes, even after a few minutes. At such superliquidus temperatures, chemical
270 reactions between the capsule and the sample progress with increasing run duration. Therefore,

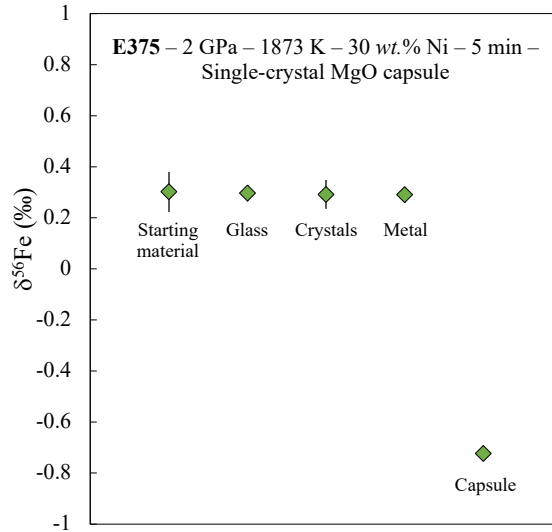
271 in the long term, measured isotopic fractionations can be driven by interactions between the
 272 capsule and the sample.

273 Iron isotopic fractionation factors from this study yield an average of $\Delta^{56}\text{Fe}_{\text{metal-silicate}}$
 274 $\text{sil}=0.05\pm 0.11\text{‰}$. This means that these results are not significantly different from 0.0‰, and no
 275 dependence on the Ni content of the metal is detected over a wide range of Ni concentrations.



276 **Figure 1: Results of Fe isotopic fractionation in metal-silicate equilibrium experiments.** Error bars correspond to 2
 277 standard deviations. **a.** $\Delta^{56}\text{Fe}_{\text{metal-silicate}}$ of all experiments of this study and from literature recalculated at 1873 K (Poitrasson et
 278 al., 2009; Hin et al., 2012; Elardo and Shahar, 2017) as a function of the Ni content of the metallic phase. The horizontal dashed
 279 line with orange error represents the average of all experiments presented on the graph, *i.e.* $0.03\pm 0.09\text{‰}$ (1 s.d.). The dotted
 280 line represents the trend of Ni content dependency on Fe isotopic fractionation factor determined by Elardo and Shahar (2017).
 281 **b.** $\Delta^{56}\text{Fe}_{\text{metal-silicate}}$ for all experiments of this study. Squares are experiments carried in graphite capsules, circles correspond to
 282 the ones in crushable MgO capsules, triangles for experiments using boron nitride capsules and diamonds for experiments
 283 carried in single-crystal MgO capsules. Experiments are color coded according to their time durations: white for 1-5 minutes,
 284 pale green for 15 minutes, light green for 30 minutes, and dark green for 60 minutes. The horizontal dashed line with grey error
 285 represents the average of all experiments presented on graph a., *i.e.* $0.03\pm 0.09\text{‰}$ (1 s.d.).

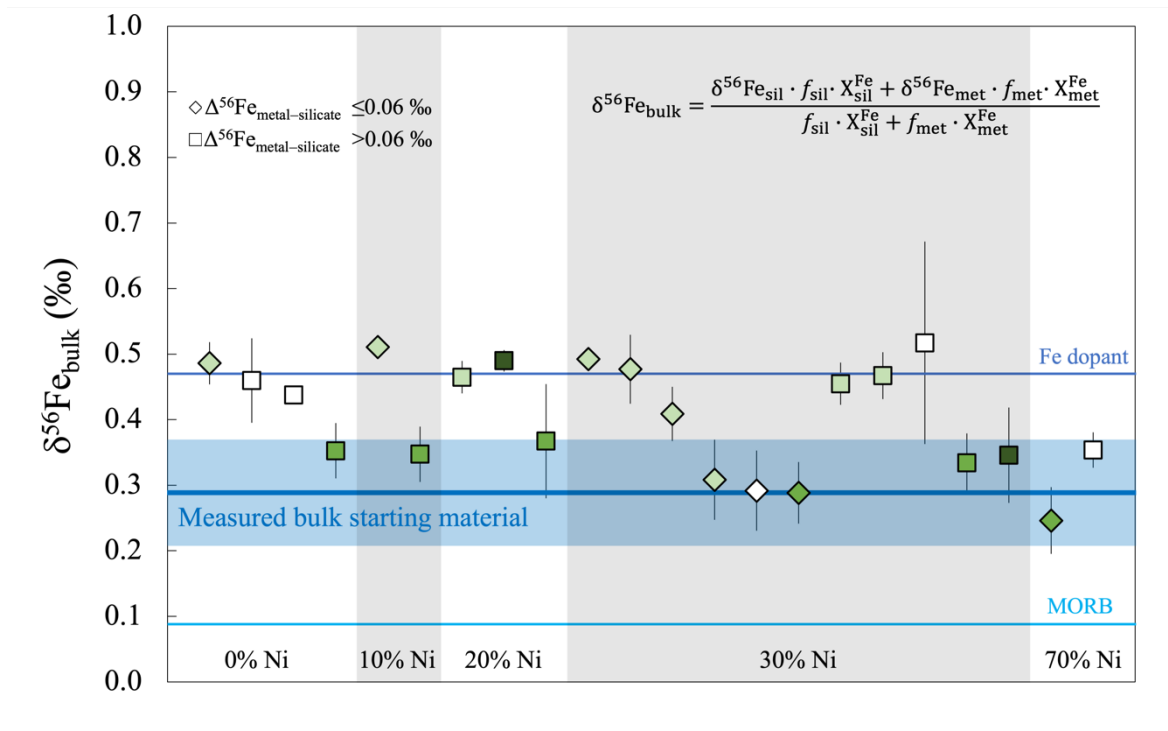
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287

288 **Figure 2: Results of Fe isotopic compositions on a single experiment.** E375 was performed at 2 GPa and 1873 K in a single-
 289 crystal MgO capsule with a time duration of 5 minutes. Its metal phase contains 5 wt.% of Ni. Iron isotopic measurements were
 290 performed on two silicate samples—a central glassy part and an outlying crystallised part—as well as the metal phase and the
 291 capsule. The two silicate parts and the metal present identical isotopic composition to the starting material whereas the inner
 292 part of the capsule (inner 30 μm) is enriched in light Fe isotopes. The diffusion of MgO from the capsule has no effect on the
 293 Fe isotopic composition of the silicate phase.

294 The Fe isotope compositions of the bulk starting materials were measured to assess
 295 potential Fe loss during the experiments (Table 1). These measured Fe isotope compositions of
 296 the starting material were compared to bulk values calculated by mass balance from the Fe
 297 isotopic composition of the metal and silicate from the run products (Fig. 3). Although there is
 298 no clear correlation between the fractionation factor and the agreement between the measured
 299 and calculated bulk values, both estimations of the bulk experimental Fe isotope composition
 300 coincide within error for 12 out of the 22 experiments of the reported data set. This indicates
 301 that experiments largely approached closed system behaviour, resulting in limited loss of Fe
 302 through the capsule. Thorough characterisation of the Fe content of experimental capsules after
 303 the experiments showing moderate Fe diffusion into the capsules also corroborates closed
 304 system behaviour, a necessary condition to properly investigate isotope fractionation processes
 305 experimentally. Iron loss quantified by the difference between the measured and calculated
 306 bulks shows that single-crystal MgO capsules present reduced Fe loss with respect to other
 307 capsule types (Supplementary Fig. 9).

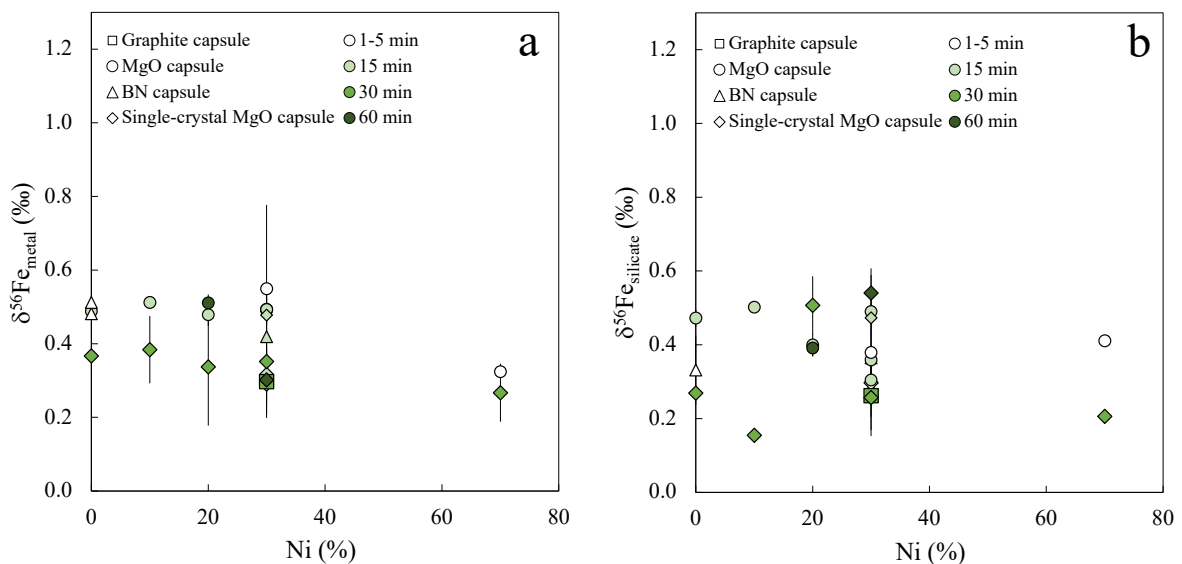


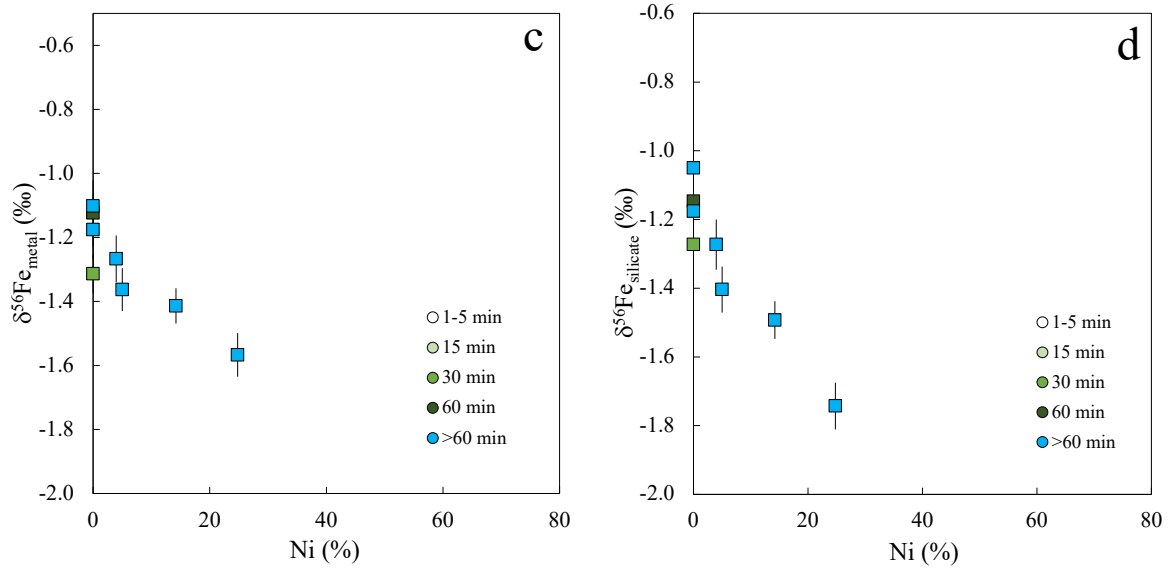
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310 **Figure 3: Comparison of measured and calculated Fe isotope compositions of bulk experiments.** The blue line represents
 311 the average Fe isotope composition measured from the powder mixtures used as starting materials in the experiments. The
 312 symbols correspond to calculated Fe isotope compositions of bulk experiments from mass balance using metal and silicate Fe
 313 isotopic measurements for each experiment (equation on the figure). Squares are used for experiments presenting a metal–
 314 silicate fractionation factor superior to 0.06‰ and unfractionated experiments correspond to diamonds. Computed bulk value
 315 symbols are color-coded according to the run duration: white for 1–5 min, pale green for 15 min, light green for 30 min and
 316 dark green for 60 min.

317 Fig. 4 displays the Fe isotope composition of single experimental phases from this study
 318 and [Elardo and Shahar \(2017\)](#) as a function of metal Ni content. The Ni-induced Fe isotope
 319 fractionation proposed by [Elardo and Shahar \(2017\)](#) implies that such a fractionation is driven
 320 by the composition of the metallic phase as Ni is predominantly hosted in the metallic phase.
 321 Therefore, a clear variation of the metal Fe isotope composition should be observed as a
 322 function of the metal Ni content. However, no systematic change in the metal Fe isotope
 323 composition is reported in the data set from this study (Fig. 4a). In fact, the composition of both
 324 experiments performed with 70 wt.% of Ni ($\delta^{56}\text{Fe}_{\text{metal}}=0.27\pm 0.01$ and 0.32 ± 0.01) are strictly
 325 identical to the measured bulk experimental starting material (0.27 ± 0.10 , 2σ). It should be noted
 326 that these two experiments also underwent negligible Fe loss (Fig. 3). This constitutes strong
 327 evidence for a very limited effect of Ni on the Fe isotope fractionation at the experimental

328 conditions of this study. The silicate Fe isotope compositions present a more scattered
 329 distribution (Fig. 4b), likely due to moderate interactions with the capsule, and equally show
 330 no correlation with the metal Ni content. Iron isotope compositions of single experimental
 331 phases from [Elardo and Shahar \(2017\)](#) show clear correlation with the Ni content (Fig. 4c and
 332 d). However, this is due to the fact that the silicate fraction of the starting mixtures was spiked
 333 with ^{54}Fe , resulting in starting materials with variable Fe isotope compositions with respect to
 334 their Ni content (Fig. 4c and d). The observed trends therefore reflect the evolution of the
 335 starting material rather than a metal–silicate isotope fractionation. We speculate that if this
 336 effect could be corrected by recalculating all the experiments for the same bulk starting material
 337 composition (by using the precise proportions of each component and/or Fe isotope
 338 compositions of starting materials as reported in our study), an effect of Ni content on the Fe
 339 isotope composition may not be detectable. Based on thorough study of comprehensive
 340 literature data and the novel experimental metal–silicate data set reported in this study, we
 341 conclude that there is no evidence for Ni-induced Fe isotope fractionation between metal and
 342 silicate.





343 **Figure 4: Iron isotope composition of separate phases** from experiments reported in this study and [Elardo and Shahar \(2017\)](#)
 344 as a function of the metal Ni content. **a.** Iron isotope composition of metal phases from this study. **b.** Iron isotope composition
 345 of silicate phases from this study. **c.** Iron isotope composition of metal phases from [Elardo and Shahar \(2017\)](#). **d.** Iron isotope
 346 composition of silicate phases from [Elardo and Shahar \(2017\)](#).

347 **Table 1: Iron isotopic compositions** of experimental run products and experimental parameters as well as compositions of all
 348 starting materials used this study. Replicated samples were split before column separation.

Run	P (GPa)	T (K)	Ni (wt.%)	Time (min)	Capsule	$\delta^{57}\text{Fe}_{\text{silicate}}$	2σ	$\delta^{57}\text{Fe}_{\text{metal}}$	2σ	$\Delta^{57}\text{Fe}_{\text{met-sil}}$	2σ	$\delta^{56}\text{Fe}_{\text{silicate}}$	2σ	$\delta^{56}\text{Fe}_{\text{metal}}$	2σ	$\Delta^{56}\text{Fe}_{\text{met-sil}}$	2σ	
E269	1	1873	20	15	MgO	0.61	0.03	0.73	0.02	0.12	0.03	0.40	0.02	0.48	0.01	0.08	0.02	
E270	1	1873	10	15	MgO	0.75	0.01	0.78	0.04	0.02	0.01	0.50	0.01	0.51	0.03	0.01	0.01	
E271	1	1873	20	60	MgO	0.60	0.02	0.77	0.03	0.17	0.02	0.39	0.01	0.51	0.01	0.12	0.01	
E276	1	1873	30	15	MgO	0.46	0.03	0.73	0.06	0.27	0.03	0.30	0.03	0.49	0.05	0.19	0.03	
E298	2	1873	30	15	MgO	0.78	0.02	0.75	0.02	-0.02	0.02	0.49	0.01	0.49	0.01	0.00	0.01	
E302	2	1873	0	15	MgO	0.72	0.02	0.75	0.05	0.04	0.02	0.47	0.03	0.49	0.04	0.02	0.03	
E318	2	1873	30	15	SC MgO	0.65	0.07	0.68	0.05	0.03	0.07	0.47	0.05	0.48	0.04	0.00	0.05	
E320	2	1873	0	3	BN	0.50	0.09	0.71	0.03	0.21	0.09	0.33	0.06	0.48	0.03	0.15	0.06	
E321	2	1873	30	15	BN	0.57	0.07	0.64	0.02	0.07	0.07	0.36	0.04	0.42	0.08	0.05	0.04	
E322	2	1873	30	15	MgO	0.52	0.04	0.70	0.08	0.17	0.04	0.36	0.03	0.49	0.05	0.13	0.03	
E323	2	1873	0	3	BN	0.54	0.07	0.77	0.01	0.23	0.07	0.00	0.00	0.51	0.00	0.00	0.00	
E324	2	1873	30	3	MgO	0.58	0.16	0.78	0.16	0.20	0.16	0.38	0.11	0.55	0.11	0.17	0.11	
E325	2	1873	70	3	MgO	0.59	0.01	0.47	0.02	-0.12	0.01	0.41	0.02	0.32	0.01	-0.09	0.02	
E373	2	1873	30	15	SC MgO	0.43	0.02	0.44	0.09	0.01	0.11	0.28	0.02	0.32	0.04	0.04	0.06	
E375	glass	2	1873	30	5	SC MgO	0.40	0.05	0.41	0.04	0.01	0.09	0.30	0.03	0.29	0.03	-0.01	0.06
E375	crystals						0.46	0.05				0.29	0.05					
E375	capsule						-1.07	0.07				-0.72	0.01					
E376	2	1873	30	30	SC MgO	0.43	0.03	0.48	0.00	0.05	0.03	0.26	0.03	0.35	0.02	0.09	0.04	
E377	2	1873	70	30	SC MgO	0.25	0.04	0.43	0.07	0.14	0.08	0.21	0.04	0.26	0.02	0.06	0.05	
E377	replicate							0.43	0.07					0.27	0.02			
E378	2	1873	0	30	SC MgO	0.40	0.07	0.50	0.01	0.15	0.05	0.28	0.05	0.37	0.02	0.10	0.04	

E378	replicate					0.34	0.05					0.23	0.03				
E379	2	1873	10	30	SC MgO	0.21	0.05	0.55	0.04	0.35	0.09	0.15	0.02	0.38	0.02	0.23	0.04
E380	2	1873	20	30	SC MgO	0.73	0.08	0.50	0.08	-0.23	0.16	0.51	0.04	0.34	0.04	-0.17	0.09
E381	2	1873	30	30	graphite	0.38	0.02	0.41	0.01	0.03	0.03	0.26	0.02	0.30	0.02	0.04	0.05
E382	2	1873	30	60	SC MgO	0.81	0.00	0.44	0.06	-0.37	0.06	0.54	0.03	0.30	0.05	-0.24	0.07
Material				n		$\delta^{57}\text{Fe}$	2σ	$\delta^{56}\text{Fe}$	2σ								
Fe dopant				5		0.69	0.06	0.47	0.08								
MORB				5		0.11	0.08	0.09	0.05								
Fe-Ni ₀				4		0.47	0.24	0.33	0.10								
Fe-Ni ₁₀				4		0.45	0.14	0.28	0.04								
Fe-Ni ₂₀				4		0.38	0.17	0.26	0.03								
Fe-Ni ₃₀				4		0.45	0.23	0.30	0.08								
Fe-Ni ₇₀				4		0.42	0.20	0.27	0.10								

349

350 Iron isotopic fractionation during core formation

351 Our experimental results include novel metal–silicate equilibrium Fe isotope
352 fractionation data with a wide range of Ni content. The large number of experiments in this
353 study provides enhanced statistical accuracy and shows that Ni proportion in the metal has a
354 limited effect on the Fe isotope fractionation between metal and silicate. While our conclusions
355 may differ, the results presented here are consistent (Fig. 1a) with those reported in the study
356 of [Elardo and Shahar \(2017\)](#) where the observed trend can be attributed to a relatively smaller
357 number of experiments. In fact, the data presented herein, combined with that of [Elardo and](#)
358 [Shahar \(2017\)](#) yields an average fractionation factor of $\Delta^{56}\text{Fe}_{\text{met-sil}}=0.04\pm 0.11\%$, indicating no
359 isotopic fractionation within uncertainty. Our results are also in agreement with previous
360 experimental studies on Fe isotopic fractionation ([Poitrasson et al., 2009](#); [Hin et al., 2012](#); [Liu](#)
361 [et al., 2017](#)) demonstrating the absence of Fe isotope fractionation at metal–silicate equilibrium.
362 Significant S contents in the alloy may induce a positive metal–silicate isotope fractionation
363 with light isotope enrichment in the silicate ([Shahar et al., 2014](#); [Liu et al., 2017](#); [Pinilla et al.,](#)
364 [2021](#)). A similar trend of isotopic fractionation has been observed for other elements such as Si
365 and C ([Elardo et al., 2019](#); [Shahar and Young, 2020](#)). Nevertheless, this vector of Fe isotopic

366 fractionation is opposite to that observed in Earth's mantle and in the mantles of other
367 differentiated bodies relative to chondrites. Moreover, iron meteorites present Fe isotopic
368 signatures heavier than chondrites by 0.1–0.2 ‰ ($\delta^{57}\text{Fe}$) (e.g. [Williams et al., 2006](#)), preventing
369 to explain heavy signatures in planetary mantles from differentiation of chondritic material.
370 Instead, the heavy signatures observed in iron meteorites have been explained by core
371 crystallisation with significant Fe isotopic fractionation measured experimentally between solid
372 and liquid iron alloys ([Ni et al., 2020](#); [Young 2021](#)). As such, to a first order there is no direct
373 evidence for core–mantle segregation to cause significant isotopic fractionation of Fe in
374 controlling the isotopic composition of planetary mantles. Indeed, equilibrium isotope
375 fractionation depends on $1/T^2$ so that enhanced fractionation is expected from low temperature
376 core formation. However, chondritic values are observed in small bodies that underwent lower
377 temperature core formation such as Mars and Vesta (~1900 K, [Righter and Drake, 1996](#))
378 compared to the non-chondritic Earth whose core equilibrated with the mantle at 2500–3500 K
379 ([Wood et al., 2006](#)). Therefore, core formation cannot explain alone the diversity of Fe isotope
380 compositions in the inner solar system, although it has been previously proposed from in situ
381 diamond anvil cell experiments coupled to nuclear resonant inelastic X-ray scattering
382 measurements ([Polyakov, 2009](#)).

383 **Planetary iron isotopic variability**

384 Core formation as the main process responsible for Fe isotopic variability among
385 planetary mantles is not well supported by the experimental results of this study. Other
386 processes including various accretion and deep mantle mechanisms need to be further
387 investigated as potential causes for the Fe isotopic variability between inner solar system
388 planetary bodies.

389 Investigating the differences in Fe isotope signatures between the Earth and the Moon,
390 an increasing amount of stable isotopic measurements on lunar rocks suggest that both bodies

391 share a common signature (Wang et al., 2015; Sossi and Moynier, 2017; Poitrasson et al., 2019),
392 while isotopic differences are only observed among volatile elements that were depleted from
393 the Moon. This result is in agreement with the widely held view that volatilisation during Moon
394 formation and evolution resulted in isotopic fractionation of multiple isotopic systems in the
395 lunar mantle on a much larger scale than in Earth's mantle (e.g. Gargano et al., 2020; Kato et
396 al., 2015; Pringle and Moynier, 2017; Sharp et al., 2010; Sossi et al., 2017, 2018; Wang and
397 Jacobsen, 2016). The observation of isotopically heavy Fe isotope signatures in ureilites and
398 angrites suggests that collisions between accreting bodies in the inner solar system may be
399 common and that the observed signatures in inner planetary bodies are the result of contrasted
400 accretional histories possibly involving multiple complex volatile-depleting events (Sossi et al.,
401 2016b). The corollary states that Mars and Vesta suffered very limited syn- and post-accretion
402 Fe loss as inferred from their chondritic signatures. The crystallisation of bridgmanite in large
403 planetary bodies such as the Earth may enrich the mantle in heavy Fe isotopes (Williams et al.,
404 2012) by disproportionation of Fe²⁺ into Fe³⁺ and metallic iron. Because metallic iron is
405 isotopically lighter than ferric iron-bearing bridgmanite, its sequestration into Earth's core
406 could produce a heavy Fe signature in the mantle without invoking volatilisation processes.
407 Note however that such effects have not been confirmed so far by *in situ* NRIXS measurements
408 and modelling of lower mantle crystallisation (Yang et al., 2019). Furthermore, this process
409 would not explain the heavy isotope compositions of achondritic meteorites whose parent
410 bodies were too small to have stabilised bridgmanite or Fe³⁺-rich silicate melt (Armstrong et
411 al., 2019) in equilibrium with iron metal. Therefore, taken together, the aforementioned
412 mechanisms provide possible means to explain the diverse Fe isotope signatures observed
413 amongst inner solar system bodies.

414 Leshner et al. (2020) argued that the core–mantle boundary could be enriched in the
415 heavier Fe isotopes and that pockets of this heavy core could be entrained in plumes towards

416 the upper mantle and crust. High temperature diffusion experiments over a thermal gradient of
417 250°C could provide a mechanism for the enrichment of the outer core and lowermost mantle
418 in heavy Fe isotopes. This process is predicted to be slower than the mantle convection and
419 recycling according to the study. Therefore, the proposed mechanism to transport heavier Fe
420 core diapirs in magmatic plumes towards the upper mantle could be tested by measurements on
421 OIBs spanning a wide age range. Although a subsequent study on OIBs does not support core
422 liquids entrainment as the source of observed heavy OIB signatures (Soderman et al., 2021),
423 the authors present a variety of potential processes explaining Fe isotopic variations in the
424 mantle (*e.g.* subduction processes, hydrothermal alteration, contribution from sediments,
425 peridotite and pyroxenite melting). Three main processes contributing to the establishment of
426 heavy Fe isotope signatures in magmatic rocks are identified: (1) processes enriching eclogite
427 in heavy Fe isotopes such as metamorphism, (2) lithospheric processing and (3) melting
428 processes in conditions preventing the dilution of heavy Fe isotope-enriched melts with lighter
429 isotope-enriched materials (Soderman et al., 2021). Diamond metallic inclusions presenting
430 heavy signatures (Smith et al., 2021) that could not be explained by iron disproportionation
431 were also proposed to originate from deep recycling processes. Despite the propensity for these
432 processes to generate isotopic variability locally, they are incapable of shifting the composition
433 of the entire mantle over geological time. This conclusion is founded on the observation of the
434 constancy in the Fe isotope compositions of komatiites through time (Hibbert et al. 2012;
435 Dauphas et al. 2010), and their concordance with those of peridotites that reflect the modern-
436 day mantle (*e.g.* Weyer and Ionov, 2007).

437 **On ideality in Fe–Ni alloys**

438 The amount of Ni in the core is estimated to be around 5 *wt.*% based on geochemical
439 and cosmochemical models (McDonough and Sun, 1995). Numerous studies show that physical
440 properties such as density, compressibility, and wave velocities in Fe–Ni alloys vary only

441 marginally as a function of their Ni content (e.g., [Lin et al. 2003](#); [Kantor et al. 2007](#); [Asker et](#)
442 [al., 2009](#); [Martorell et al. 2013](#); [Wakamatsu et al., 2018](#)). Importantly, the constant density of
443 such alloys does not uniquely constrain the amount of Ni in the core but implies that the entirety
444 of the observed density deficit must be due to the presence of ~10% of light elements in the
445 core ([Birch, 1952](#)). Although the insensitivity of the physical properties of Fe–Ni alloys to the
446 Ni content has been verified from multiple experimental studies ([Lin et al., 2003](#); [Kantor et al.,](#)
447 [2007](#)) and *ab initio* calculations ([Martorell et al., 2013](#)), this does not necessarily hold for their
448 chemical properties.

449 Presently, studies investigating experimentally the elemental and isotopic behaviour of
450 elements between metal and silicate which have considered the effect of the amount of Ni in
451 the metal are very scarce, largely because it has been widely assumed to be negligible for the
452 conditions relevant to core formation. Through the transpiration method and integration of the
453 Gibbs-Duhem relation, early studies illustrated that the dissolution of Ni had little effect on the
454 activity of Fe in binary alloys ([Oriani, 1953](#); [Zellars et al. 1959](#)). As such, it is frequently
455 assumed that the alloying of Fe with small quantities of Ni has a negligible effect on the
456 behaviour of the metal. More recent Knudsen effusion mass spectrometric investigations of the
457 activity-composition relations of liquid Fe–Ni alloys ([Fraser and Rammensee, 1982](#)) show that
458 the activity coefficient of Fe, γ_{Fe} , varies between 0.9 at $X_{\text{Ni}}=0.5$ to 1 at $X_{\text{Ni}}=0.05$ (X =mole
459 fraction), highlighting that for all likely core compositions, Fe dissolution in Fe–Ni alloys is
460 ideal at ambient pressures. At higher pressures (up to 94 GPa), [Huang and Badro \(2018\)](#)
461 demonstrated that Ni (between 3.5 to 48.7 wt.% Ni) has no effect on the metal–silicate
462 partitioning of Ni, Cr and V. Our study suggests that the Ni fraction in an Fe–Ni alloy has no
463 effect on Fe isotopic behaviour in a metal–silicate equilibrium, also pointing towards chemical
464 Fe–Ni ideality. [Xia et al. \(2019\)](#) report contrasting observations, in which the magnitude of Zn
465 and Cu isotope fractionation between metal and silicate was shown to be sensitive to the Ni

466 content of the alloy, which could be due to specific interactions between Ni and these elements.
467 The 22 experiments reported herein not only enhance statistical accuracy but were also designed
468 to explore a much broader range of Ni concentrations in the metal, from 0 to 70 *wt. %* (~25 *wt. %*
469 maximum in Xia et al., 2020 and Elardo and Shahar, 2017). The assumption of chemical Fe–
470 Ni ideality has extended implications regarding our understanding and knowledge of core
471 formation related processes.

472 **Conclusion**

473 We performed 22 metal–silicate equilibrium experiments with the objective of
474 establishing the effect of Ni content of Fe–Ni alloys on the Fe isotope fractionation factor
475 between metal and silicate. All experiments were carried out at 1–2 GPa and 1873 K, at which
476 a variety of capsule materials were tested. An experimental time series, as well as petrographic
477 characterisations of the samples were performed in order to assess the conditions at which
478 chemical equilibrium was achieved. No significant effect of Ni concentration on Fe isotope
479 fractionation was detected over a wide range of Ni contents (0–70 *wt. %* in the metal fraction),
480 supporting the common assumption of physical and chemical ideality of Fe–Ni alloys. Because
481 the observed fractionation factor between metal and silicate is indistinguishable from zero, our
482 data does not support core formation as the main mechanism causing the diversity in Fe isotope
483 signatures observed amongst inner solar system planetary bodies. A combination of multiple
484 accretion-related processes—including condensation from the solar nebula, volatile-depleting
485 events such as giant impacts, and disproportionation of ferrous iron by bridgmanite
486 crystallisation in larger bodies—as well as deep mantle and recycling processes, could together
487 contribute to the observation of heavier-than-chondritic signatures in the Earth and the Moon’s
488 mantles.

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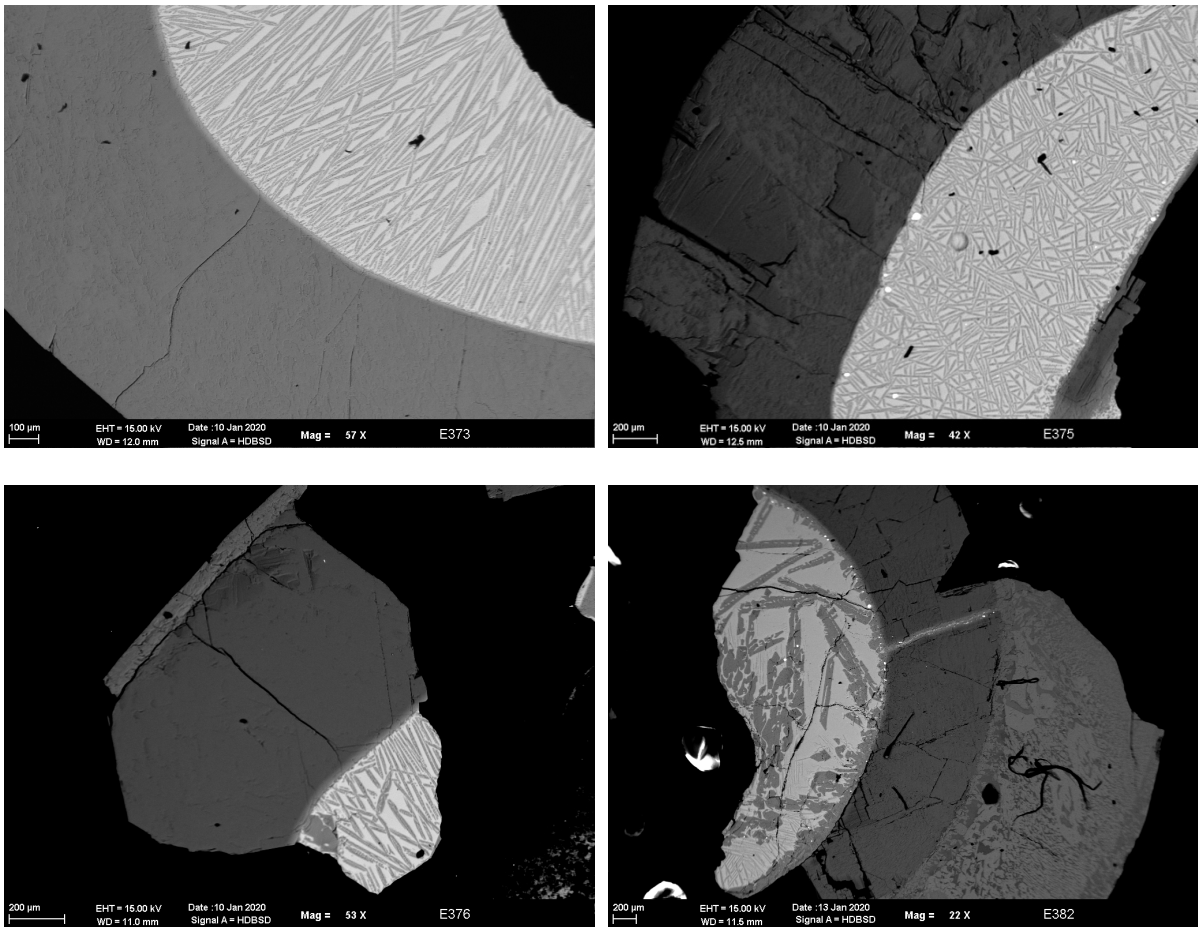
740 **Supplementary materials**

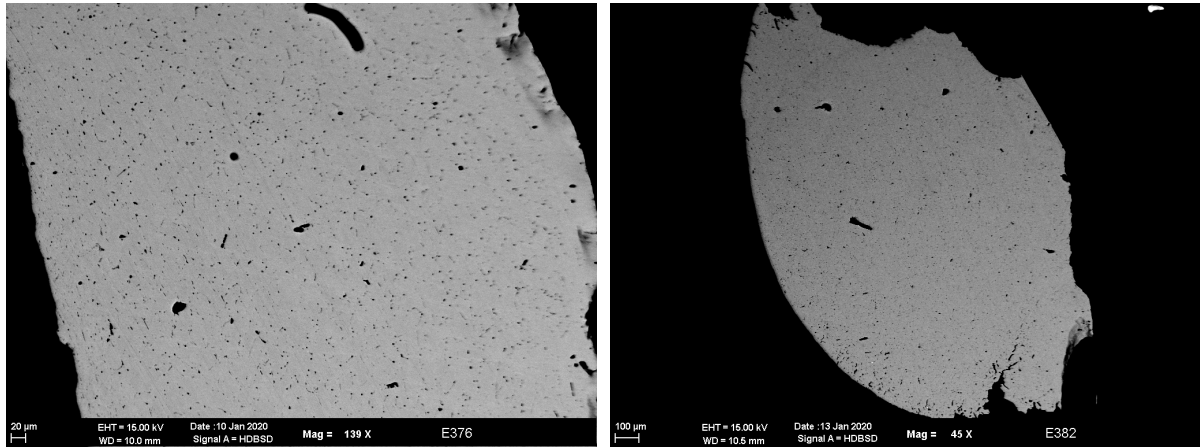
741 **Isotopic equilibrium**

742 In each experiment, metal coalescence into a single metal sphere of roughly 1 mm
743 diameter in the center of the capsule was observed as a result of achievement of superliquidus
744 temperatures during sufficient time duration to allow elemental and isotopic equilibrium. Fig.
745 5 represents backscatter electron images of typical run products. Silicate phases of the
746 experiments of the time series (Fig. 5a-d) show skeletal olivine (dark gray dendrites) due to
747 MgO enrichment and slow quenching rates, but their electron density is homogeneous. A thin,
748 dense ring of roughly 30 μm between the silicate and the capsule constitutes the transition zone
749 and no Fe was detected with EDX in the capsule beyond this zone. The capsule of run E382
750 (Fig. 5d) appears to have broken during the run and some silicate material can be observed in
751 the fracture. This may be the reason for the negative isotopic fractionation factor measured,
752 caused by light Fe loss from the capsule resulting in a heavier Fe measured in the silicate. The
753 metal phases (Fig. 5e-f) are also homogeneous in their elemental composition as determined by
754 electron microscopy. Fig. 6 and 7 present additional EDX measurements for a silicate and a
755 metal part. Major element compositions of the two phases are consistent across the samples,
756 demonstrating chemical homogeneity. Fig. 8 shows Fe isotopic fractionation results for
757 experiments of the time series carried at 2 GPa, 1873 K and with 30 wt. % Ni in the metal phase.
758 Up to 30 minutes, there is no resolvable change in the fractionation factor suggesting
759 achievement of equilibrium, which is consistent with strong evidence of full equilibration from
760 petrographic observations and EDX measurements previously described. As mentioned above,
761 the 60 min experiment may have interacted with the exterior of the capsule, causing a very

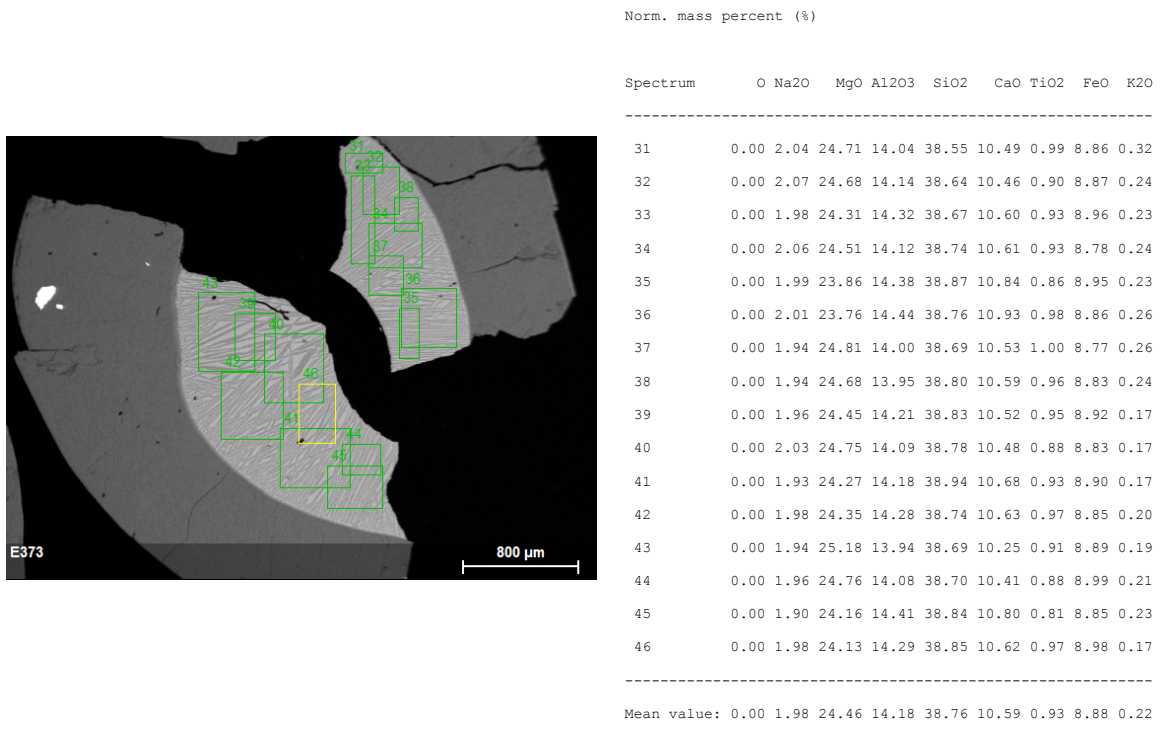
762 negative fractionation factor. Our results support isotopic equilibrium achievement within a few
763 minutes at the conditions of our experiments.

764 Therefore, primary petrological observations and EDX measurements—from 5 to 60
765 minutes run durations—showed the metal and silicate phases of the experiments of this study
766 to be fully molten with quench textures and, most importantly, chemically homogeneous which
767 is crucial for achievement of isotopic equilibrium.

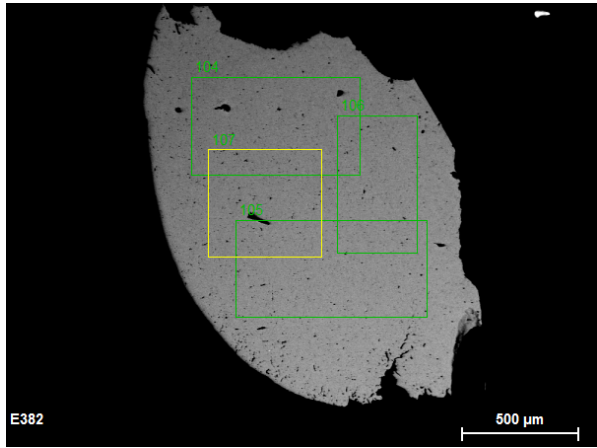




768 **Figure 5: Backscatter electron images of typical run products.** The first four images represent the silicate phase attached to
 769 its capsule—such that the silicate–capsule boundary is visible—for all experiments of the time series performed in single-
 770 crystal MgO capsules at 2 GPa and 1873 K and 30 wt.% Ni in the metal part. The last two images represent typical metal
 771 phases. **a.** Backscatter electron (BSE) image of the silicate of run E373. **b.** BSE image of the silicate part of run E375. **c.** BSE
 772 image of the silicate phase of run E376. **d.** BSE image of the silicate of run E382. **e.** BSE image of the metal of run E376. **f.**
 773 BSE image of the metal phase of run 382.



774 **Figure 6: Energy-dispersive X-ray spectroscopy (EDX) measurements on the silicate part of run E373** proving chemical
 775 homogeneity of the quenched melted silicate phase, even after 5 minutes run duration.

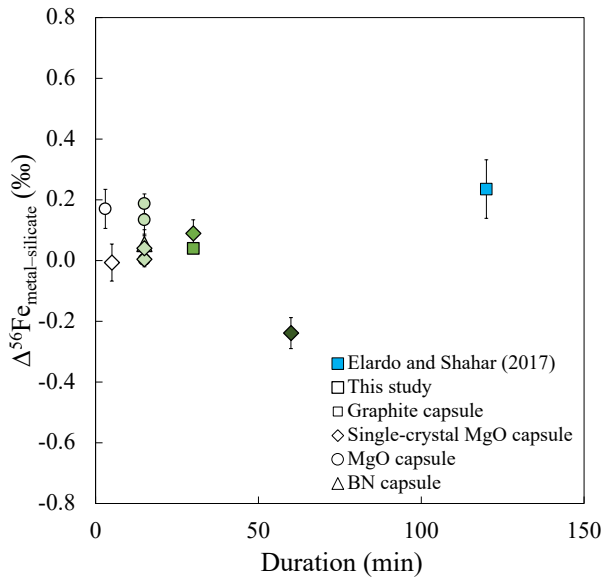


Norm. mass percent (%)

Spectrum	O	Si	P	S	Fe	Ni
104	-	0.10	0.13	0.36	68.58	30.84
105	-	-	-	0.31	68.69	30.99
106	-	0.14	-	0.35	68.59	30.92
107	1.70	0.14	-	0.31	67.64	30.20
Mean value:	1.70	0.12	0.13	0.33	68.38	30.74
Sigma:	0.00	0.02	0.00	0.03	0.49	0.36
Sigma mean:	0.00	0.01	0.00	0.01	0.25	0.18

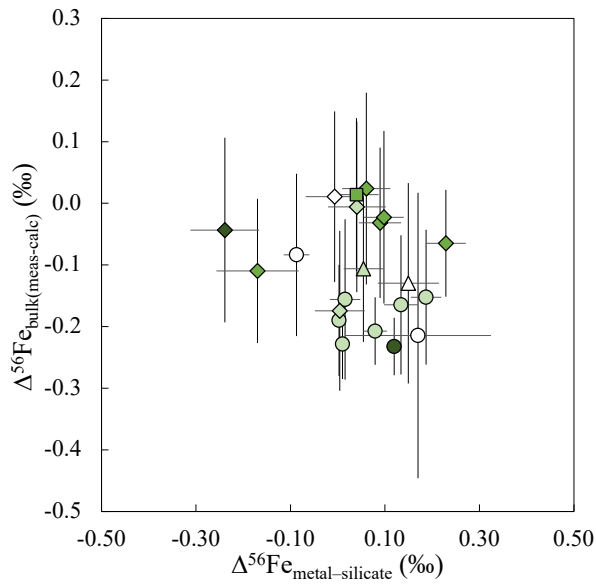
776 **Figure 7: Energy-dispersive X-ray spectroscopy (EDX) measurements on the metal part of run E382 presenting chemical**
 777 **homogeneity of the quenched melted metal.**

778



779

780 **Figure 8: $\Delta^{56}\text{Fe}_{\text{metal-silicate}}$ as a function of time duration for experiments containing 30 wt.% Ni in the metal fraction at 2 GPa**
 781 **and 1873 K. Experiments from this study are represented with a thick line symbol, experiment from Elardo and Shahar (2017)**
 782 **is represented with a blue thin line symbol. Graphite encapsulated experiments are represented by a square, experiments with**
 783 **single-crystal MgO capsules by a diamond, circles represent crushable MgO experiments, and BN encapsulated experiments**
 784 **are represented by a triangle. Experiments are color coded according to their equilibrium temperature (same color code as Fig.**
 785 **1b).**



786

787 **Figure 9:** $\Delta^{56}\text{Fe}_{\text{bulk}}$ corresponding to the difference between the measured Fe isotopic composition of the experimental
 788 starting material and the calculated bulk composition of the experiment by mass balance, as a function of $\Delta^{56}\text{Fe}_{\text{metal-silicate}}$.
 789 $\Delta^{56}\text{Fe}_{\text{bulk}}$ being an indicator of Fe loss during experiments, this figure demonstrates that there is no systematic effect of the
 790 moderate Fe loss occurring in our experiments on the Fe isotopic fractionation factor. This figure also shows that single-crystal
 791 MgO capsules systematically led to reduced Fe loss with respect to BN and crushable MgO capsules, as their $\Delta^{56}\text{Fe}_{\text{bulk}}$ is closer
 792 to zero.

793 **On the variability of isotopic fractionation data in metal–silicate**
 794 **experiments**

795 To further investigate the quality of our data, it was compared to those obtained from
 796 previous metal–silicate isotopic fractionation experiments. As scatter can be expected from
 797 experimental data resulting from random errors in the experimental preparation and run, such
 798 comparison allows to assess if the data from this study shows enhanced scatter or if it shares
 799 the same magnitude of scattering as in other studies. When compared to the scatter/amu of
 800 previous studies using the same method (Table 2), we find that the new data reported in this
 801 study is scattered to the same order of magnitude as other data sets, which is characteristic of
 802 the combined piston cylinder – MC-ICPMS approach. In this compilation, the scatter was
 803 determined using experiments sharing the same P, T and composition, and experiments with
 804 distinct parameters were only included if such a parameter was reported to have no effect on
 805 the fractionation factor.

806 **Table 2: Comparison of scatter/amu** for other metal–silicate isotopic fractionation studies. n corresponds to the number of
 807 experiments in each data set used for scatter determination.

	Element	Notation	n	Scatter ¹ (%)	Scatter/amu ¹ (%)	Scatter ² (%)	Scatter/amu ² (%)
This study	Fe	$\Delta^{56/54}\text{Fe}$	22	0.47	0.24	0.53	0.27
Elardo and Shahar (2017)	Fe	$\Delta^{57/54}\text{Fe}$	8	0.32	0.11	0.43	0.14
Hin et al. (2012)	Fe	$\Delta^{57/54}\text{Fe}$	10	0.33	0.11	0.84	0.28
Poitrasson et al. (2009)	Fe	$\Delta^{57/54}\text{Fe}$	4	0.09	0.03	0.41	0.14
Kubik et al. (2021)	Sn	$\Delta^{122/118}\text{Sn}$	2	0.28	0.07	0.34	0.08
Mahan et al. (2017)	Zn	$\Delta^{66/64}\text{Zn}$	9	0.54	0.27	0.63	0.31
Hin et al. (2014)	Si	$\Delta^{30/28}\text{Si}$	5	0.46	0.23	0.66	0.33

808
809

¹ Scatter corresponding to the maximum difference between data points of identical PT conditions excluding their error.

² Scatter corresponding to the maximum difference between data points of identical PT conditions including 2 S.D.