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# Silicon isotopic compositions of chondrule silicates in carbonaceous chondrites and the formation of primordial solids in the accretion disk

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## 33 **1. Introduction**

34

35         The evolution of the Solar protoplanetary disk led to the formation of solids through a  
36 wide range of processes such as evaporation/condensation (Komatsu et al., 2018; Krot, 2019),  
37 fusion/crystallization (Connolly and Jones, 2016; Jacquet and Marrocchi, 2017) and  
38 collisional impacts (Krot et al., 2005). The resulting dust provided the main building blocks of  
39 asteroids and planets (Johansen et al., 2015), either in the form of refractory inclusions (i.e.,  
40 CAIs = Calcium-Aluminum-rich Inclusions and AOAs = Amoeboid Olivine Aggregates),  
41 chondrules and fine-grained matrix. In theory, primordial dust should represent a powerful  
42 proxy for deciphering the conditions that prevailed in the protoplanetary disk. The translation  
43 into practice is however difficult as mineralogical, petrographic and isotopic features are  
44 commonly ambiguous, even notwithstanding secondary processes such as fluid circulation  
45 and thermal metamorphism that could have significantly blurred the messages carried by  
46 primitive meteorites (Brearley, 2006; Huss et al., 2006; Marrocchi et al., 2018a). These  
47 generally prevent straightforward interpretation and pose important uncertainties on the early  
48 times of the Solar System.

49         Chondrules are submillimeter-sized silicate spheroids and the favorite controversial  
50 subject of cosmochemists. This zeugma sums up the contrast between the relatively simple  
51 major mineralogy of chondrules (i.e., olivine, low-Ca pyroxene, glassy mesostasis  $\pm$  Fe-Ni  
52 metal beads) and the incalculable number of models attempting to describe their formation  
53 (see Connolly and Jones 2016 for a review). This (near)-cacophony stems from the fact that,  
54 under a relatively innocuous appearance, chondrules are complex objects whose mineralogy,  
55 textures, and chemical and isotopic compositions result from multi-step processes involving  
56 precursor recycling, melting event(s) and complex gas-melt interactions (Marrocchi et al.,  
57 2018b, 2019a; Libourel and Portail, 2018; Ebel et al., 2018). In addition, chondrule formation

58 likely took place for a long period of time (i.e., 4 Ma; Villeneuve et al., 2009; Bollard et al.,  
59 2017; Pape et al., 2019), in distinct reservoirs and under different conditions during the  
60 evolution of the protoplanetary disk (Jones et al., 2018). The most abundant chondrules are  
61 ferromagnesian porphyritic chondrules that can be classified to first order into type I and type  
62 II chondrules, depending of the valence state of iron (Scott and Taylor, 1983). While the limit  
63 is arbitrary defined for  $Mg\# \equiv 100 \times Mg/(Mg+Fe) = 90$ , there is a hiatus between the two,  
64 with few chondrules between  $Mg\#$  of 90 and 97 (e.g., Hertwig et al., 2018). Abundant Fe-Ni  
65 metal beads, FeO-poor silicates and volatile element depletion characterize type I chondrules  
66 whereas their type II counterparts shows FeO-rich silicates and more chondritic abundances  
67 of volatile elements. Another convenient classification is based on the modal abundance of  
68 silicates (olivine and pyroxene) in porphyritic chondrules, with PO being olivine-rich  
69 porphyritic chondrules, P pyroxene-rich and POP in between –this essentially subdivides a  
70 continuum, not to mention sectioning effects (Hezel et al., 2010).

71 The reduced type I chondrules have spawned drastically different formation models  
72 from planetary collisions (Faure et al., 2017) to crystallization of condensed melt (Varela and  
73 Zinner, 2018), through the incomplete melting of solid precursors (Hewins et al., 2005;  
74 Tenner et al., 2018). The recent characterization of the chemical and isotopic features of relict  
75 olivine grains suggest that type I chondrules derived from AOA-like precursors (Marrocchi et  
76 al., 2018b, 2019a), in agreement with trace element signatures (Ruzicka et al., 2007; Jacquet  
77 and Marrocchi 2017). Such models invoke gas-melt interactions with Mg- and SiO-rich gas to  
78 account for the isotopic differences observed between AOAs and the resulting chondrules  
79 (Ruzicka et al., 2007; Marrocchi et al., 2018b, 2019b). Furthermore, a protracted interaction  
80 with SiO-rich gas during chondrules formation has been invoked to explain some SiO<sub>2</sub>  
81 chemical zoning and the formation of low-Ca pyroxene shells in POP chondrules (Tissandier  
82 et al., 2002; Libourel et al., 2006; Chaussidon et al., 2008), as well as mineral chemical

83 zoning in palisadic olivine in PO chondrules (Libourel and Portail, 2018; Marrocchi et al.,  
84 2018b, 2019a). Considering type II chondrules, their oxidized nature compared to their  
85 reduced counterparts could either result from formation in regions with higher dust to gas  
86 ratios (Schrader et al., 2013) or lower carbon content (Connolly et al., 1994a,b). Recent  
87 experimental approach also proposed a genetic link between both types of chondrules; type II  
88 being derived from type I by oxidation (Villeneuve et al., 2015), although an independent  
89 origin is also possible (Jacquet et al., 2015a).

90 Silicon isotopes may provide insights into the formation conditions of both type I and  
91 type II chondrules and their potential relationship. A recent study reports that AOAs  
92 –as mentioned above, a notorious suspect as chondrule precursors (or precursor cousins)–  
93 show large, mass-dependent, light Si isotope enrichments (Marrocchi et al., 2019b). Measured  
94 bulk type I chondrules are also isotopically variable, and generally light for Si (Clayton et al.,  
95 1983; Molini-Vesko et al., 1986; Clayton & Mayeda, 1985, 1999; Georg et al., 2007; Hezel et  
96 al., 2010) potentially pointing at even larger isotopic variations at the mineral scale, perhaps  
97 comparable to those observed in AOAs. If crystallization of low-Ca pyroxene in type I POP  
98 and PP chondrules stems from protracted SiO-rich gas-melt interactions during chondrule  
99 formation, this could result in different silicon isotopic compositions between olivine and  
100 low-Ca pyroxene. Buffering by the gas for type II chondrules could result in relatively  
101 constant silicon isotopic compositions such as those recently observed in pyroxene-rich type I  
102 chondrules in enstatite chondrites (Kadlag et al., 2019), but variations might still be expected  
103 from their common relict magnesian olivine grains possibly inherited from type I chondrules  
104 (Wasson and Rubin, 2003; Schrader et al., 2008) or the same precursors as the latter's. We  
105 thus report a comprehensive survey of the silicon isotopic compositions of type I and type II  
106 chondrules in Allende (CV3<sub>oxA</sub>), Kaba (CV3<sub>oxB</sub>) and NWA 5859 (C2-ung, CM-related). We  
107 also included isolated olivine grains (IOs) that are likely chondrule-derived (e.g., McSween

108 1977; Desnoyers et al., 1980; Jones 1992). We use our data to quantify the conditions of  
109 formation of these two types of II chondrules and discuss the implications on the reprocessing  
110 of primordial dust in the Solar protoplanetary disk.

111

## 112 **2. Material and methods**

113

114 We surveyed all chondrules in two sections of Kaba (thin sections N4075 and O229  
115 from the Natural History Museum, Vienna, Austria), three sections of Allende (thin section  
116 Allende-4 from the Muséum national d'Histoire naturelle, Paris, France, thin sections YM1  
117 and YM2 from CRPG), in one section of Northwest Africa (NWA) 5958 (thick section NWA  
118 5958-1 from the Muséum national d'Histoire naturelle, Paris, France) and a thin section of  
119 Miller Range (MIL) 07342 (thick section 07342,9 from the NASA Antarctic Search for  
120 Meteorites program). Kaba is an oxidized Bali-like CV chondrite whereas Allende is the  
121 eponymous chondrite of the oxidized Allende-like CV sub-group. NWA 5958 correspond to  
122 a C2-ung CM-like chondrite, whose type II chondrule olivine Cr content as well as opaque  
123 petrography indicate minimal thermal metamorphism ( $< 300^{\circ}\text{C}$ ), yet chondrule mesostases  
124 have undergone extensive aqueous alteration, which did not affect olivine (Jacquet et al.,  
125 2016; Jacquet and Marrocchi 2017). MIL 07342 is a CO chondrite deemed of type 3.0-3.2 by  
126 the Antarctic Meteorite Petrographic Description database. Despite evidence of alteration on  
127 opaque assemblages and incipient metasomatism on chondrule mesostasis, olivine textures  
128 and compositions in chondrules show no indication of diffusional exchange. Within these  
129 three chondrites, we selected 29 porphyritic chondrules and 5 isolated olivines for  
130 determining the Si isotopes compositions of their olivine and low-Ca pyroxene crystals. This  
131 corresponds to (i) 6 type I chondrules (1 PO, 5 POP) in Kaba, (ii) 12 type I chondrules (8 PO  
132 and 4 POP), 5 type II chondrules (PO) and 2 IOs in Allende, (iii) 3 type I chondrules (2 PO, 1

133 POP), 1 type II chondrules (PO) and 1 IO in NWA 5958 and (iv) 2 type II chondrules (PO)  
134 and 2 IOs in MIL 07342.

135 Scanning electron microscope observations of chondrules were performed at CRPG-  
136 CNRS (Nancy, France) using a JEOL JSM-6510 with 3 nA primary beam at 15 kV.  
137 Quantitative compositional analyses of chondrule olivine and low-Ca pyroxene crystals were  
138 performed using a CAMECA SX-100 electron microprobe (at CAMPARIS, Sorbonne  
139 Université, Paris, France). A 150 nA focused beam accelerated to 15 kV potential difference  
140 was used for spot analyses of olivine with 20 s analysis times. The PAP software was used for  
141 matrix corrections.

142 We determined the silicon isotopic compositions of silicates by secondary ion mass  
143 spectrometry (SIMS) using the multi-collector CAMECA IMS 1270 E7 at CRPG. Olivines  
144 were sputtered with a ~5 nA primary Cs<sup>+</sup> beam set in Gaussian mode and accelerated at 10 kV  
145 (Villeneuve et al., 2019). Secondary negative <sup>28,29,30</sup>Si<sup>-</sup> ions were accelerated at 10 kV and  
146 analyzed in multi-collection mode on three off-axis Faraday cups (L'2, C, and H1,  
147 respectively). Charge accumulation on the sample surface was neutralized with an electron  
148 gun. The mass resolving power was set at M/ΔM = 5000 (slit 2) to completely resolve  
149 interferences on masses 28, 29, and 30. The yields and backgrounds of the Faraday cups were  
150 calibrated at the beginning of each analytical session. Automatic centering of the transfer  
151 deflectors and mass was implemented in the analysis routine. A 10×10 μm<sup>2</sup> raster was applied  
152 to the primary beam to ensure flat-bottomed pits. We used a set of terrestrial and synthetic  
153 standard olivine yielding Mg# ranging from 36 to 100 and a set of terrestrial standard low-Ca  
154 pyroxene with Mg# from 70 to 98 to calibrate matrix effects for Si isotopes (Villeneuve et al.,  
155 2019). Measurements typically consisted of a 90 s pre-sputtering during which backgrounds  
156 of FCs are measured, automatic mass and beam centering, and 50 cycles of 4 s integrations  
157 separated by 1 s waiting times. Thus, each measurement took ~7 min. Under these conditions,

158 internal precision on  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  was  $\pm 0.05$ – $0.20\text{‰}$  and  $\pm 0.10$ – $0.40\text{‰}$  ( $2\sigma$  standard error)  
159 respectively, depending on the sample and the external reproducibility on  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  for  
160 olivine and low-Ca pyroxene standards was  $\pm 0.12\text{‰}$  and  $\pm 0.21\text{‰}$  respectively ( $2\sigma$  standard  
161 error).

162

### 163 **3. Results**

164

165 Olivine and low-Ca pyroxene in chondrules and isolated olivines investigated herein  
166 show Mg# in the range 44.6 - 99.9 and 90 - 99.2 respectively (Supplementary table S1). A  
167 total of 644 individual Si isotopes analyses were performed among the 29 chondrules and 5  
168 isolated olivines. Since the data (reported in table S1 and plotted in Fig. 1) fall on a mass-  
169 dependent fractionation line ( $\delta^{29}\text{Si} = 0.511 \times \delta^{30}\text{Si}$ ), we will only discuss  $\delta^{30}\text{Si}$  values in the  
170 following. Overall, the silicon isotopic composition in chondrule olivine and low-Ca  
171 pyroxene show large variations, up to  $\sim 5\text{‰}$  per amu, with  $\delta^{30}\text{Si}$  values ranging from -4.5 to  
172 1.9 ‰ in Allende, from -7.0 to 1.2 ‰ in Kaba, from -6.9 to 2.6 ‰ in NWA 5958 and -1.9 to  
173 0.8 ‰ in MIL 07342 (Fig. 1, table S1). Isotopic compositions in 4 type I POP chondrules  
174 from Allende reveal systematically lighter compositions of low-Ca pyroxene compared to  
175 olivine from the same chondrule, with an average shift of  $\delta^{30}\text{Si}$  values comprised between 0.3  
176 and 1.2 ‰ (Fig. 2, Table 1). Furthermore,  $\delta^{30}\text{Si}$  values of low-Ca pyroxene show a narrow  
177 range of variation compared to olivine from the same chondrule (Fig. 2, Table 1,  
178 Supplementary table 1). Among the olivine grains, we identified relicts, whether as Mg-rich  
179 olivine in type II chondrules or Ti-Al-poor olivine with oxygen isotope compositions  
180 deviating from host olivine in type I chondrules (as measured by Marrocchi et al., 2018b,  
181 2019a). Relicts in 1 Allende chondrule, 3 Kaba chondrules and 5 NWA 5958 chondrules do  
182 not show any systematic  $\delta^{30}\text{Si}$  shift (nor any correlation) relative to host olivines (Table 1)



183 with possibly more (intra-chondrule) variability. *Notwithstanding relicts, the most extreme*  
184  *$\delta^{30}\text{Si}$  values tend to lie in the outer olivine grains in type I chondrules (Fig. 3).* However, the  
185 behavior of Si isotopic composition varies strongly with the Mg# of olivine. It indeed yields  
186  $\sim 10$  ‰ variations of  $\delta^{30}\text{Si}$  values (up to  $\sim 6$  ‰ within a single chondrule) in Mg-rich olivine,  
187 i.e. in type I chondrules, but variations smaller than 2 ‰ in Fe-rich olivine, i.e. in type II  
188 chondrules (Fig. 4, Table S1). Even though  $\delta^{30}\text{Si}$  values in MgO-rich olivine are scattered  
189 toward extreme values, the chondrule averages span ranges similar (if extended to  $\sim 1$  ‰  
190 lighter compositions) to their FeO-rich counterparts (Fig. X) and the grand average is only  
191 marginally lighter ( $-0.89 \pm 1.41$  ‰ (1SD) vs.  $-0.31 \pm 0.57$  ‰ (1SD) respectively). This is  
192 within range of variations previously observed for bulk chondrules (Fig. 5, Clayton et al.,  
193 1983; Molini-Vesko et al., 1986; Clayton & Mayeda, 1999; Georg et al., 2007; Hezel et al.,  
194 2010).

195

## 196 **4. Discussion**

197

### 198 **4.1 Origin of type I chondrules**

199

200 More than two centuries after their first description by Jacques Louis de Bournon in  
201 1802, the origin of chondrules is still the subject of an intense debate. Over time, nebular and  
202 planetary theories have experienced ups and downs that led to the development of drastically  
203 different models attempting to explain their peculiar characteristics (Connolly and Jones,  
204 2016). Our results reveal that Mg-rich olivine grains registered large mass-dependent silicon  
205 isotope variations that can reach up to  $\sim 6$  ‰ in  $\delta^{30}\text{Si}$  within a single type I chondrule (Figs. 1,  
206 4; Table S1). These results are at odds with the very limited Si-isotopic fractionation (a few  
207 tenths of permil at most, e.g. Savage et al., 2014) expected in models where chondrule

208 olivines would result from the crystallization of (i) closed-system magma droplets in regions  
209 with extreme dust/gas ratios (Alexander et al., 2018) or (ii) magma ocean-like environments  
210 in fully or partially molten differentiated planetesimals (Faure et al., 2017). Furthermore, the  
211 latter scenario is not supported by the large *mass-independent* oxygen isotope variations  
212 commonly reported in type I chondrules (e.g. Ushikubo et al., 2012; Marrocchi et al., 2018b,  
213 2019a; Tenner et al., 2018) as magmatic processes would only produce sub-permil *mass-*  
214 *dependent* O-isotope variations (Richet et al., 1977; Eiler et al., 2001). Our results thus raise  
215 the question of the origin of the isotopic variability observed in chondrules for major rock-  
216 forming elements such as Si and O. Based on trace element and oxygen isotope features of  
217 olivine grains, it has been recently proposed that relict olivine grains in type I chondrules  
218 were inherited from AOA-like precursors (Marrocchi et al., 2018b, 2019a). In addition,  
219 similarly to chondrules Mg-rich olivines, AOA olivines show large, mass-dependent, light Si  
220 isotope enrichments (Marrocchi et al., 2019b), with  $\delta^{30}\text{Si}$  ranging from  $-9\text{‰}$  to  $-1\text{‰}$ . These  
221 are also seen in the relicts analyzed herein (Fig. 6–7). Taken together, this suggests that  
222 isotopic features of Mg-rich olivine in type I chondrules reflect (i) the legacy of the precursor  
223 isotopic variabilities and (ii) the important role of gas-melt interaction during chondrule  
224 formation.

225 Relict and host olivines previously characterized for O-isotopes display very similar  
226 Si-isotope distributions (Fig. 7; Marrocchi et al., 2018b, 2019a). No specific correlation was  
227 observed between trace elements abundances and  $\delta^{30}\text{Si}$ , and thus between  $\Delta^{17}\text{O}$  and  $\delta^{30}\text{Si}$  in  
228 relict and host olivine grains (Fig. 8). Considering AOAs as plausible chondrule precursors,  
229 this lack of correlation, for the relicts, likely results from the large intrinsic Si-isotope  
230 heterogeneities observed in AOAs (Marrocchi et al., 2019b) despite their relative O-isotope  
231 homogeneity (Krot, 2019). Such decoupling between Si and O-isotope behaviors in AOAs is  
232 not surprising since they resulted from different processes one mass-dependent, and the other

233 mass-independent: condensation for the former and variable exchange with later  $^{16}\text{O}$ -poor gas  
234 for the latter.

235

## 236 **4.2 Gas-melt interaction during type I chondrule formation**

237

238 The question of gas-melt interactions is of the utmost importance as growing evidence  
239 suggests that chondrule formation took place under non-canonical conditions with enhanced  
240 partial pressure of condensable species such as alkali oxides (Tissandier et al., 2002; Krot et  
241 al., 2006; Libourel et al., 2006; Fedkin & Grossman, 2013; Marrocchi & Libourel 2013; Piani  
242 et al., 2016). Chondrule formation in such environment must result in strong Si and O isotopic  
243 exchanges with the gas since Si and O isotopic compositions of chondrules.

244 The clustering of host olivine grains around the same  $\Delta^{17}\text{O}$  suggests that the  
245 chondrules readily exchanged oxygen isotopes with the gas after melting, and were buffered  
246 at the oxygen isotopic composition of their formation region (e.g., Marrocchi et al., 2018b,  
247 2019a). Approach to isotopic equilibrium is supported by limited Si isotopic variations (close  
248 to bulk carbonaceous chondrite compositions) in host olivine grains from chondrule interiors.

249 The more variable Si isotopic compositions seen in the exterior of "palisades"  
250 (Libourel and Portail, 2018) however suggest some kinetic effects. Recent studies based on  
251 cathodoluminescence and high-current X-rays maps have invoked that those grains grew  
252 asymmetrically toward the exterior as a result of SiO and Mg dissolution onto the melt  
253 (Libourel and Portail, 2018; Marrocchi et al., 2018b, 2019a). The condensation of SiO may  
254 have taken place under some level of supersaturation, hence a light isotope enrichment first,  
255 but as the residual gas became (by mass balance) isotopically heavier, later increments of  
256 olivine would have been heavier, hence the two extremes seen in these olivines.

257 Open-system behavior does not stop with olivine. Laboratory experiments have shown  
258 that low-Ca pyroxene shells can form in chondrule melts by incorporation of SiO from the  
259 nebular gas, during the partial dissolution of olivine precursors (Tissandier et al., 2002). Since  
260 host olivine and low-Ca pyroxene would have formed from a melt buffered by the ambient  
261 gas (itself largely due to evaporation of chondrule precursors), both should carry the same  
262  $\Delta^{17}\text{O}$  as generally observed (Ushikubo et al., 2012, Tenner et al., 2013, 2015, 2018) despite  
263 contrary earlier results by Chaussidon et al (2008). Still, olivine tends to have  $\delta^{18}\text{O}$  higher by  
264  $\sim 1$  ‰ than co-existing phases in CO and CR chondrites (Tenner et al. 2013, 2015, 2018),  
265 which these authors ascribed to kinetic (mass-dependent) effects during  
266 evaporation/recondensation. Our data show the same phenomenon for silicon isotopes with  
267 the measured average difference (0.3-1.2 ‰; Fig. 2) well in excess of the  $< 0.1$  ‰ equilibrium  
268 fractionation predicted at equilibrium at 1700 K (Méheut et al., 2009). Such  $^{28}\text{Si}$  enrichments  
269 of low-Ca pyroxene shells have been previously observed in CR and CV chondrules and  
270 ascribed to near-equilibrium condensation of Si from a  $\text{SiO}_{(\text{g})}$  with partial pressure slightly  
271 higher than the equilibrium partial pressure of SiO (Harju and Young, 2013; Harju et al.,  
272 2015). This, however, represents a break from the heavy signatures seen in some palisadic  
273 olivine analyses, as the residual SiO gas would have been isotopically heavier than it was  
274 when these grains were growing. This could be overcome by invoking a higher  
275 supersaturation at that stage, as a result of an increased cooling rate. Rapid cooling of order of  
276 100-1000 K/h are suggested by the large proportion of monoclinic enstatite (e.g., Soulié,  
277 2014), at variance with the days suggested by Ca diffusion in interior olivines (e.g.,  
278 Marrocchi et al., 2018b). Non-linear chondrule cooling histories invoking quenching after a  
279 subisothermal phase having been already proposed (Jacquet et al., 2013, Villeneuve et al., 2015;  
280 Libourel and Portail, 2018). The palisadic olivine discussed above may then correspond to an  
281 intermediate stage in this cooling acceleration. Late supersaturation of  $\text{SiO}_{(\text{g})}$  would explain

282 the marginally lighter Si isotopic composition of type I chondrules compared to the whole-  
283 rock carbonaceous chondrite (e.g., Dauphas et al., 2015).

284

### 285 **4.3 The link between type I and type II chondrules**

286

287 While they are more abundant in ordinary chondrites, type II chondrules are also  
288 commonly observed in carbonaceous chondrites (Fig. 6; Scott & Krot, 2014). Although they  
289 have spawned fewer competing models than their type I counterparts, they remain  
290 controversial as well. In the early nineties, on the basis of petrographic, mineralogical and  
291 chemical observations and also experiments, type II chondrules were interpreted as closed-  
292 system fractionally crystallized droplets heated at near-liquidus temperatures and cooled at  
293 ~1-500 K/h (e.g. Jones, 1990; Radomsky and Hewins, 1990; Jones and Lofren, 1993; see also  
294 review by Jones et al., 2018). Although open- vs. closed-system chondrule formation has been  
295 strongly debated, most observations point toward important gas-melt interactions and  
296 therefore non-canonical nebular environments of formation (see for instance review by Ebel  
297 et al., 2018). The important concentrations of volatiles and moderately volatile elements (i.e.,  
298 Na, K, Mn, Cr, Sr and Fe) and the larger average size type II chondrules compared to type I  
299 chondrules were used as arguments for type II chondrule formation (i) as the precursors of  
300 type I chondrules, which would formed *via* high-temperature reduction and evaporation  
301 processes (Hewins et al., 2005; Ruzicka et al., 2008, 2012) or (ii) in a different nebular  
302 (sub)reservoir than that at the origin of type I chondrules (e.g. Jones, 2012; Hewins & Zanda,  
303 2012; Jacquet et al., 2015a). On the other hand, recent chemical and isotopic observations  
304 have suggested that type II chondrules were derived from type I chondrules via high-  
305 temperature oxidation and protracted gas-melt interactions (Connelly et al., 2008, Ruzicka et  
306 al., 2008, Schrader et al., 2008). A comprehensive experimental approach proved that such

307 process is feasible and succeeded in reproducing many type II chondrules features, such as  
308 chemical zonings in olivine and the preservation of Mg-rich olivine relics (Fig. 6; Villeneuve  
309 et al., 2015).

310 Our results show that FeO-rich olivine in type II chondrules are characterized by more  
311 homogeneous Si isotope compositions compared to type I chondrules (Figs. 4, 5). This could  
312 be taken as a supporting closed-system crystallization. However, the silicon isotopic  
313 heterogeneity observed within type II chondrules containing Mg-rich olivine relics (Fig. 6,  
314 Table S1) necessarily implies a formation of their precursors under open-system conditions.  
315 As their variability mimics that of type I chondrules (Fig. 6, Table S1), these could have been  
316 derived from reduced type I chondrules. This would indicate a genetic link between type I and  
317 type II chondrules as already proposed based on the observational and experimental evidence  
318 (Connelly et al., 2008, Ruzicka et al., 2008, Schrader et al., 2008, Villeneuve et al., 2015). If  
319 correct, this would imply that type II chondrules experienced important gas-melt interactions;  
320 at least for volatile elements that would have been substantially enriched.

321

## 322 **5. Concluding remarks**

323

324 We have determined the silicon isotope compositions of silicates (olivine and low-Ca  
325 pyroxene) in type I and type II chondrules in the carbonaceous chondrites Allende (CV3<sub>oxA</sub>),  
326 Kaba (CV3<sub>oxB</sub>), NWA 5958 (C2-ung) and Miller Range (MIL) 07342 (CO). Our main results  
327 are:

328 1- Type I chondrule silicates are characterized by large, mass-dependent, silicon  
329 isotope variations with  $\delta^{30}\text{Si}$  ranging from -7 to + 2.6 ‰. Low-Ca pyroxene crystals define a  
330 narrow range of isotopic values and show systematically lighter Si isotope compositions  
331 compared to olivine grains.

332           2- Type II chondrule FeO-rich silicates show Si isotope variations smaller than 2 ‰.  
333 When present within type II chondrules, Mg-rich relict olivine grains exhibit larger Si isotope  
334 variations than their FeO-rich counterparts.

335           From this, we drew the following inferences:

336           1- As magmatic processes would only generate Si-isotope fractionation at a level of  
337 few tenths of permil, this implies that type I chondrules could result neither from the  
338 crystallization of closed-system magma droplets under extreme dust/gas ratios nor from the  
339 crystallization of molten differentiated planetesimals.

340           2- Si-isotope composition of type I chondrules represent the legacy of the precursor  
341 isotope variabilities and kinetic effects during gas-melt interactions, possibly as a result of  
342 accelerated cooling near the end of olivine crystallization and during pyroxene formation.  
343 This supports models where type I chondrules results from the recycling of AOA-like  
344 precursors.

345           3- The Si isotope heterogeneity observed within type II chondrules containing Mg-rich  
346 olivine relics implies a formation of their precursors under open-system conditions. This also  
347 supports models where type II are derived from type I chondrules *via* drastic changes in the  
348 oxidation conditions.

349

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356

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358

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382 **Figure captions**

383

384 Fig.1: Three silicon-isotope diagram plot of all individual analyses performed by SIMS in  
385 olivine and low-Ca pyroxene from the 21 type I (in red, n=467), 8 type II (in blue, n=133)  
386 chondrules and 5 IOs (in green, n=44) studied. The data show a large range of mass-  
387 dependent fractionation from  $\sim -7\text{‰}$  to  $\sim 2.5\text{‰}$ . Error bars are 2 SE

388

389 Fig.2: Average  $\delta^{30}\text{Si}$  compositions of MgO-rich olivine and low-Ca pyroxene in four POP  
390 chondrules from Allende showing a systematic shift of low-Ca pyroxene toward lighter  
391 compositions by  $\sim 0.3 - 1.2 \text{‰}$ . As shown by the error bars (1 SD) low-Ca pyroxene  
392 compositions are less scattered than MgO-rich olivine compositions.

393

394 Fig.3: Representative chondrules and the Si isotopic composition of their olivines, (A) Kaba  
395 N4075 - Ch11 and (B) NWA 5958 - Ch1. SIMS measurements are indicated by ellipses  
396 whose colors vary with the Si isotopic composition.

397

398 Fig. 4: Silicon isotopic composition of olivine and low-Ca pyroxene crystals of type I and  
399 type II chondrules from NWA 5958 (C2-ung), MIL 07342 (CO), Kaba (CV3<sub>oxB</sub>) and Allende  
400 (CV3<sub>oxA</sub>) plotted against their respective Mg contents. Type I chondrule silicates show larger  
401 isotopic variabilities than type II chondrule silicates characterized by near-constant  $\delta^{30}\text{Si}$ . The  
402 light brown area indicates bulk silicon isotopic compositions from literature (Clayton et al.,  
403 1983; Molini-Vesko et al., 1986; Clayton & Mayeda, 1999; Georg et al., 2007; Hezel et al.,  
404 2010).

405 Fig. 5: Curves show probability density function of  $\delta^{30}\text{Si}$  of type I and type II chondrule  
406 silicates (olivine and low-Ca pyroxene) from NWA 5958 (C2-ung), MIL 07342 (CO), Kaba  
407 (CV3<sub>oxB</sub>) and Allende (CV3<sub>oxA</sub>).

408

409 Fig. 6: Curves show probability density function of  $\delta^{30}\text{Si}$  of relict and host olivine grains  
410 inferred from previous oxygen isotope compositions (Marrocchi et al., 2018b, 2019a). No  
411 specific Si isotope difference is observed between relict and host olivine grains.

412

413 Fig. 7: Diagram showing  $\Delta^{17}\text{O}$  versus  $\delta^{30}\text{Si}$  of relict and host olivine grains (distinguished  
414 from previous oxygen isotope compositions; Marrocchi et al., 2018b, 2019a) in Kaba and  
415 NWA 5958. The absence of correlation suggests that different cosmochemical processes  
416 control oxygen and silicon isotope compositions.

417

418 Fig. 8: (A) Back-scattered electron image of a FeO-rich type II chondrule from Allende-YM1  
419 showing relict Mg-rich olivine grains. (B) Silicon isotopic composition of FeO- and Mg-rich  
420 olivine grains. Mg-rich olivine grains show larger isotopic variability than FeO-rich olivine  
421 crystals. The light blue area indicates bulk silicon isotopic compositions from literature  
422 (Clayton et al., 1983; Molini-Vesko et al., 1986; Clayton & Mayeda, 1999; Georg et al., 2007;  
423 Hezel et al., 2010).

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430 Table 1: Average  $\delta^{30}\text{Si}$  and Mg# of chondrules and isolated olivines (IOs) from Allende,  
431 Kaba, NWA 5958 and MIL 07342 studied. Mg Ol. = Mg-rich olivine, low-Ca Px. = low-Ca  
432 pyroxene, Fe Ol. = FeO-rich olivine. Relict are either Mg-rich olivines enclosed in FeO-rich  
433 olivines in type II chondrules or Mg-rich olivines with O isotopic compositions different from  
434 host olivines (see Marrocchi et al., 2018, 2019). N is the number of individual analyses.  
435 Errors are one standard deviation.

name	type	Mineral	$\delta^{30}\text{Si}$ av	1 SD	Mg# av	1 SD	N
All YM2-Ch13-1	I POP	Mg Ol.	0.60	0.56	98.13	2.97	12
		low-Ca Px.	0.10	0.44	94.75	1.11	7
All YM2-Ch13-2	I POP	Mg Ol.	0.51	0.74	91.98	2.82	10
		low-Ca Px.	-0.47	0.67	94.96	0.35	3
All YM2-Chc2	I PO	Mg Ol.	-0.59	0.76	92.12	3.91	16
All YM2-Ch20	I POP	Mg Ol.	-0.66	0.62	93.23	1.92	11
		low-Ca Px.	-0.94	0.40	94.26	1.74	8
All YM2-Ch6	I PO	Mg Ol.	-1.23	0.95	98.16	2.43	19
All YM2-Ch27	I PO	Mg Ol.	-0.41	0.52	99.12	1.54	31
All YM2-Ch24	I PO	Mg Ol.	0.44	0.79	97.87	1.40	16
All 4-Ch36	I PO	Mg Ol.	0.12	1.00	95.56	1.76	18
All 4-Ch32	I PO	Mg Ol.	0.53	0.84	96.30	2.00	20
All 4-Ch40	I PO	Mg Ol.	0.10	0.87	96.99	2.67	21
All 4-Ch31	I PO	Mg Ol.	-2.02	0.49	99.22	0.64	10
All 4-Ch39-2	IO	Mg Ol.	-2.45	1.35	93.10	11.77	6
All YM1-Ch18	I POP	Mg Ol.	-1.34	1.04	95.59	0.40	3
		low-Ca Px.	-2.51	0.44	98.76	0.34	5
All YM2-Ch15	II PO	Fe Ol.	-0.03	0.48	65.80	4.52	25
All YM2-Ch23	II PO	Fe Ol.	0.00	0.27	52.17	3.55	7
All YM2-Ch9	II PO	Fe Ol.	-0.40	0.20	75.79	5.51	14
All YM2-Ch14	IO	Fe Ol.	-0.76	0.39	68.53	4.20	11
All YM1-Ch5	II PO	relict Mg Ol.	-1.42	1.53	89.28	3.08	25
		Fe Ol.	-0.65	0.53	69.69	6.24	7
All YM2-Ch5	II PO	Fe Ol.	-0.27	0.40	89.58	1.44	23
Kaba N4075-Ch11	I PO	relict Mg Ol.	-1.54	1.48	98.59	0.25	3
		host Mg Ol.	-1.55	0.97	98.63	0.08	17
Kaba N4075-Ch18	I POP	relict Mg Ol.	-5.57	-	96.28	-	1
		host Mg Ol.	-1.85	1.90	96.06	0.44	6
Kaba N4075-Ch25	I POP	host Mg Ol.	-0.88	1.12	99.29	0.42	26
Kaba N4075-Ch1	I POP	host Mg Ol.	-1.66	1.53	98.69	0.48	43

Kaba N4075-Ch12	I POP	host Mg Ol	-0.60	1.12	98.71	0.23	37
Kaba 0229-Ch1	I POP	host Mg Ol	0.21	0.64	98.50	0.37	4
		relict Mg Ol.	-1.82	1.45	98.58	0.06	6
NWA 5958-Ch1	I PO	relict Mg Ol.	-1.12	0.99	99.39	0.03	13
		host Mg Ol	-1.56	1.42	99.36	0.12	33
NWA 5958-Ch7	I PO	relict Mg Ol.	-1.29	2.34	99.26	0.03	4
		host Mg Ol	-1.56	1.49	99.28	0.07	41
NWA 5958-Ch2	I POP	relict Mg Ol.	-2.27	2.28	95.11	0.32	3
		host Mg Ol	-0.53	1.98	95.09	0.36	20
NWA 5958-Ch20	II PO	relict Mg Ol.	-1.89	0.55	96.22	0.46	4
		Fe Ol.	0.55	0.36	62.77	6.89	2
NWA 5958-IO-A	IO	Fe Ol.	-1.39	0.27	70.10	2.75	10
MIL 07342-ChB	II PO	Fe Ol.	0.11	0.48	81.87	4.76	11
MIL 07342-ChA	II PO	Fe Ol.	0.20	0.31	54.57	5.32	15
MIL 07342-ChC	IO	Fe Ol.	-0.29	0.29	81.64	4.29	12
MIL 07342-ChD	IO	Mg Ol.	-0.94	0.61	99.31	0.24	5

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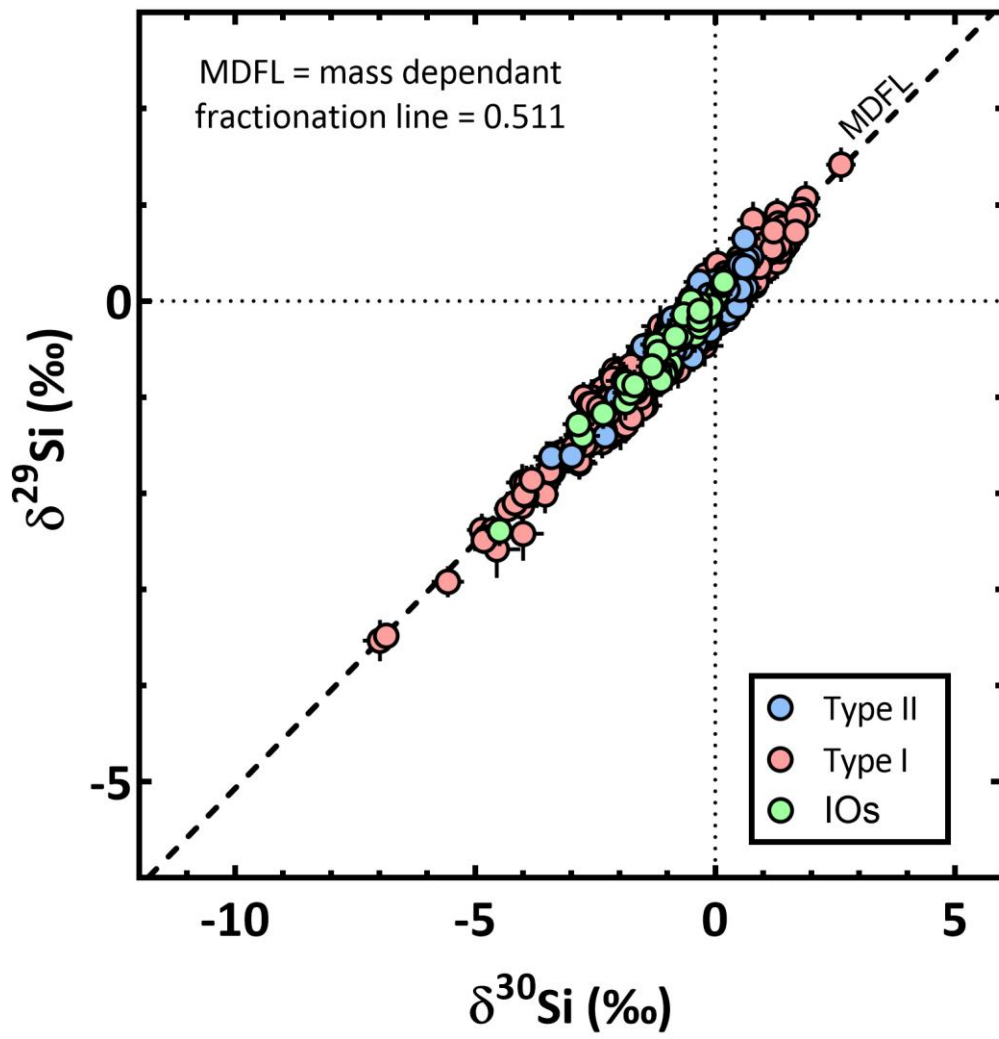
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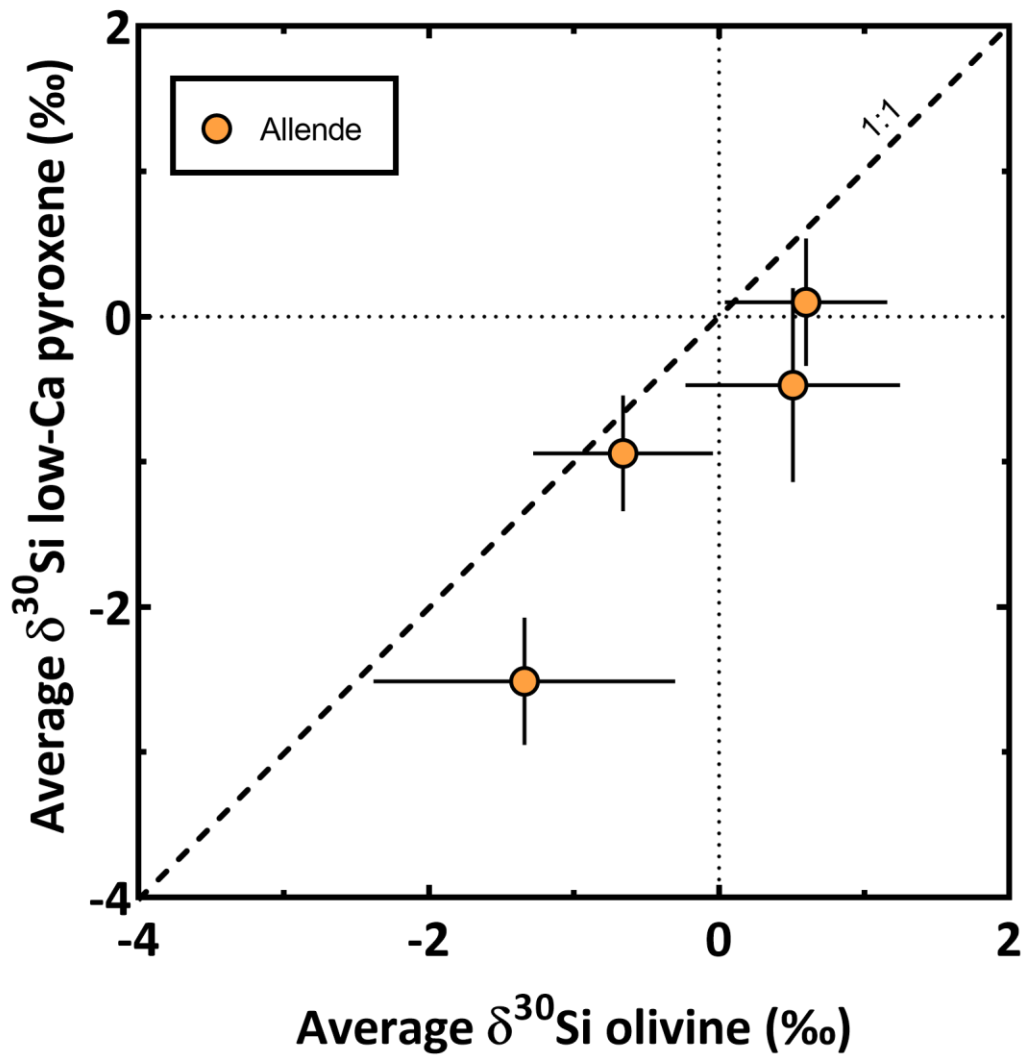
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446 Fig. 1



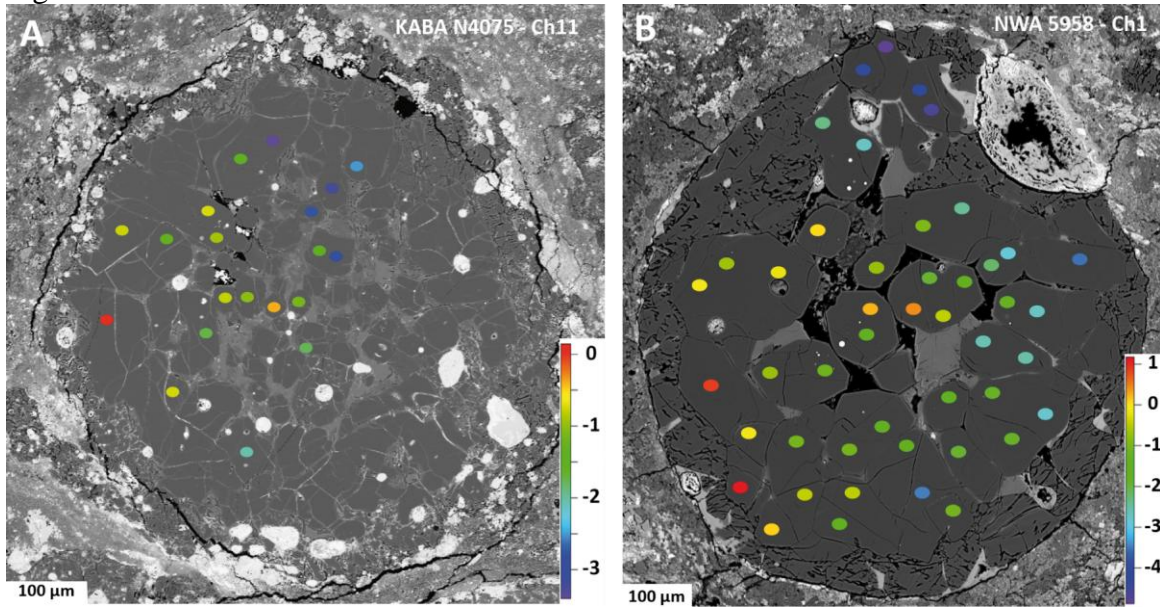
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450 Fig.2



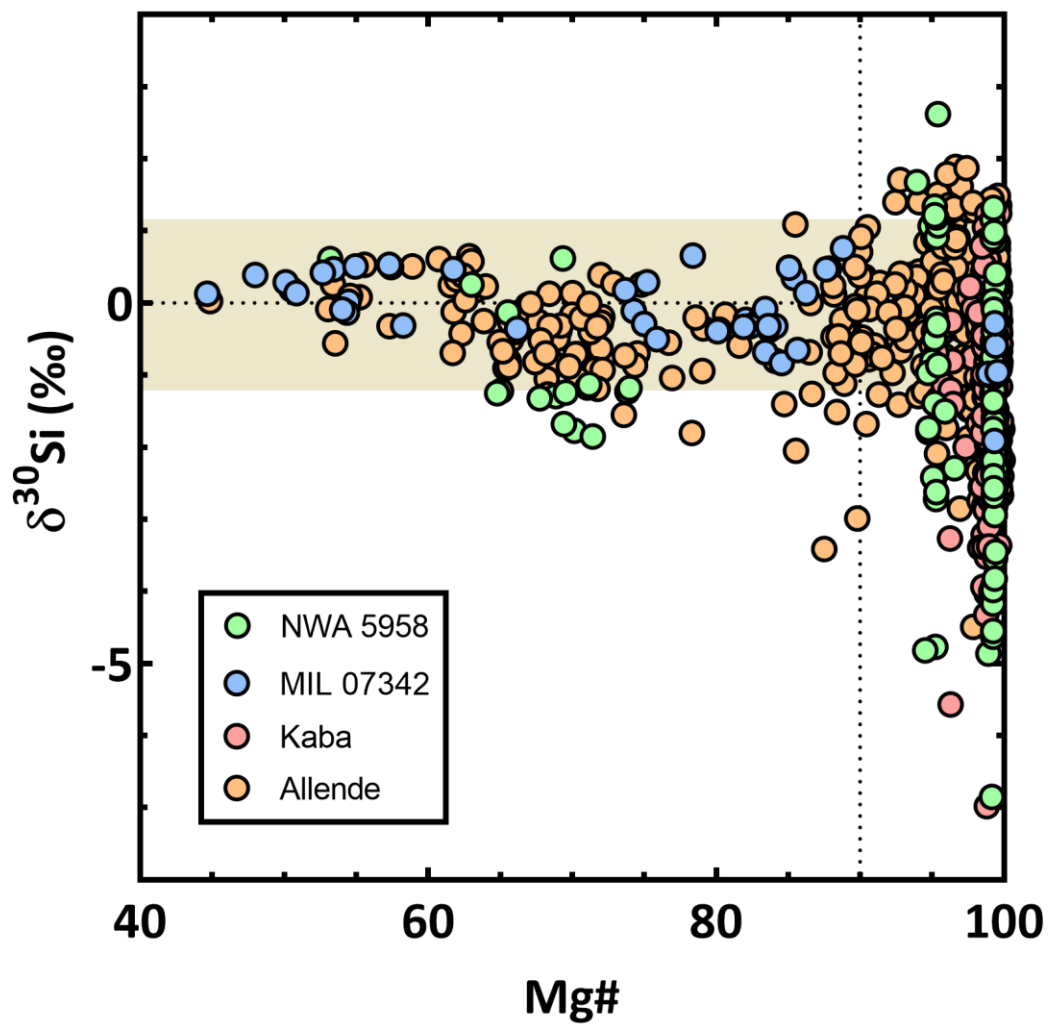
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455 Fig. 3



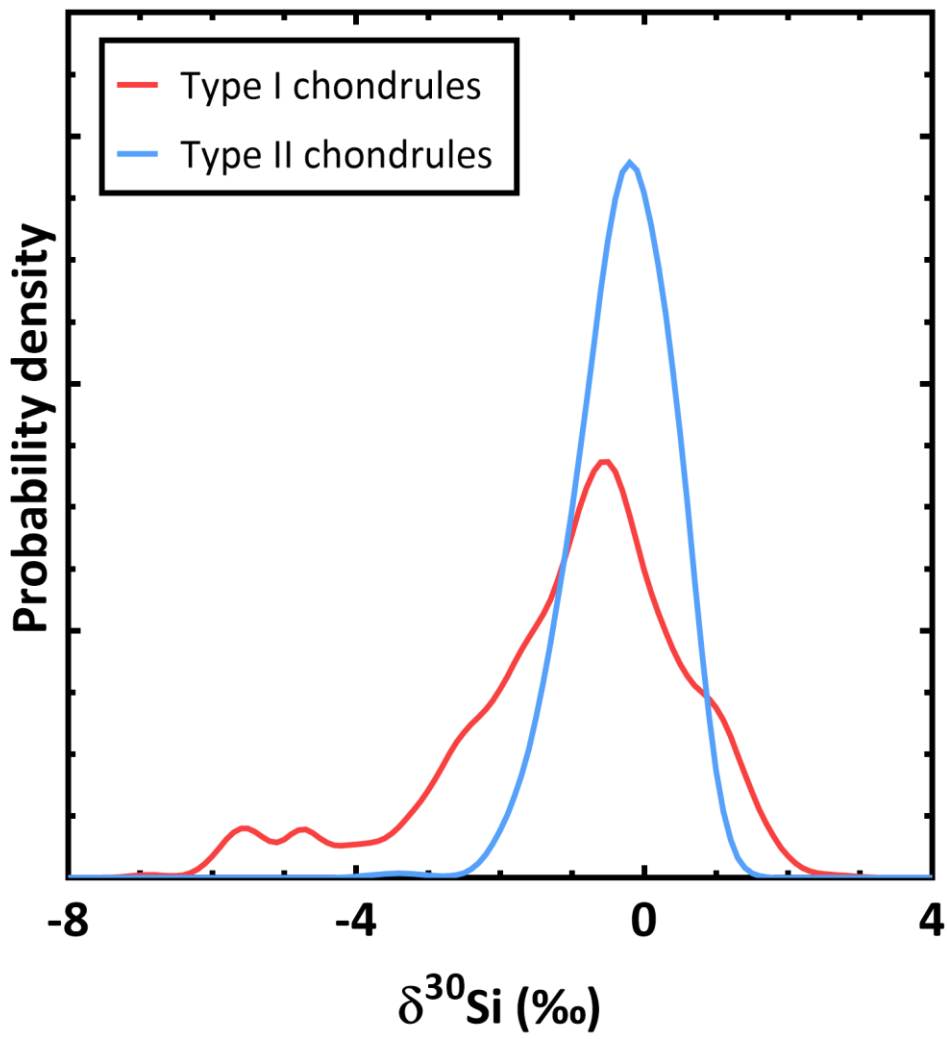
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460 Fig. 4

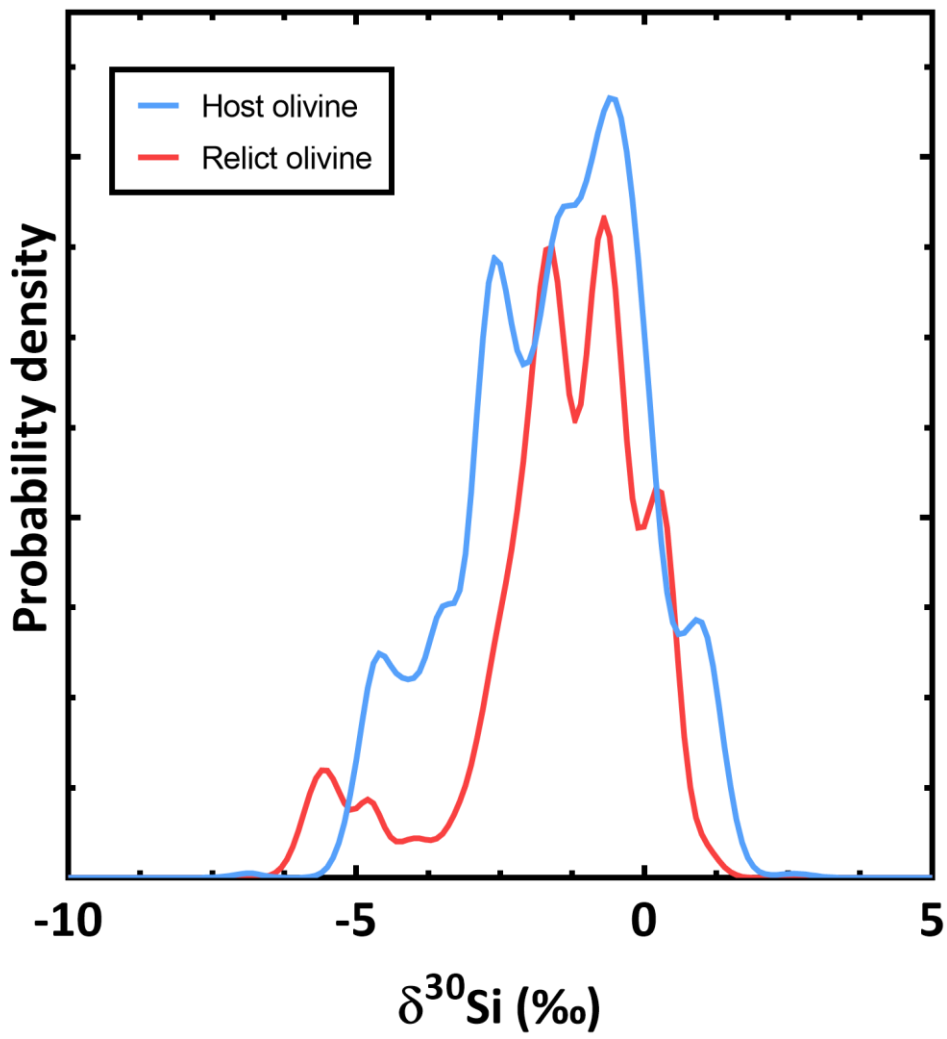


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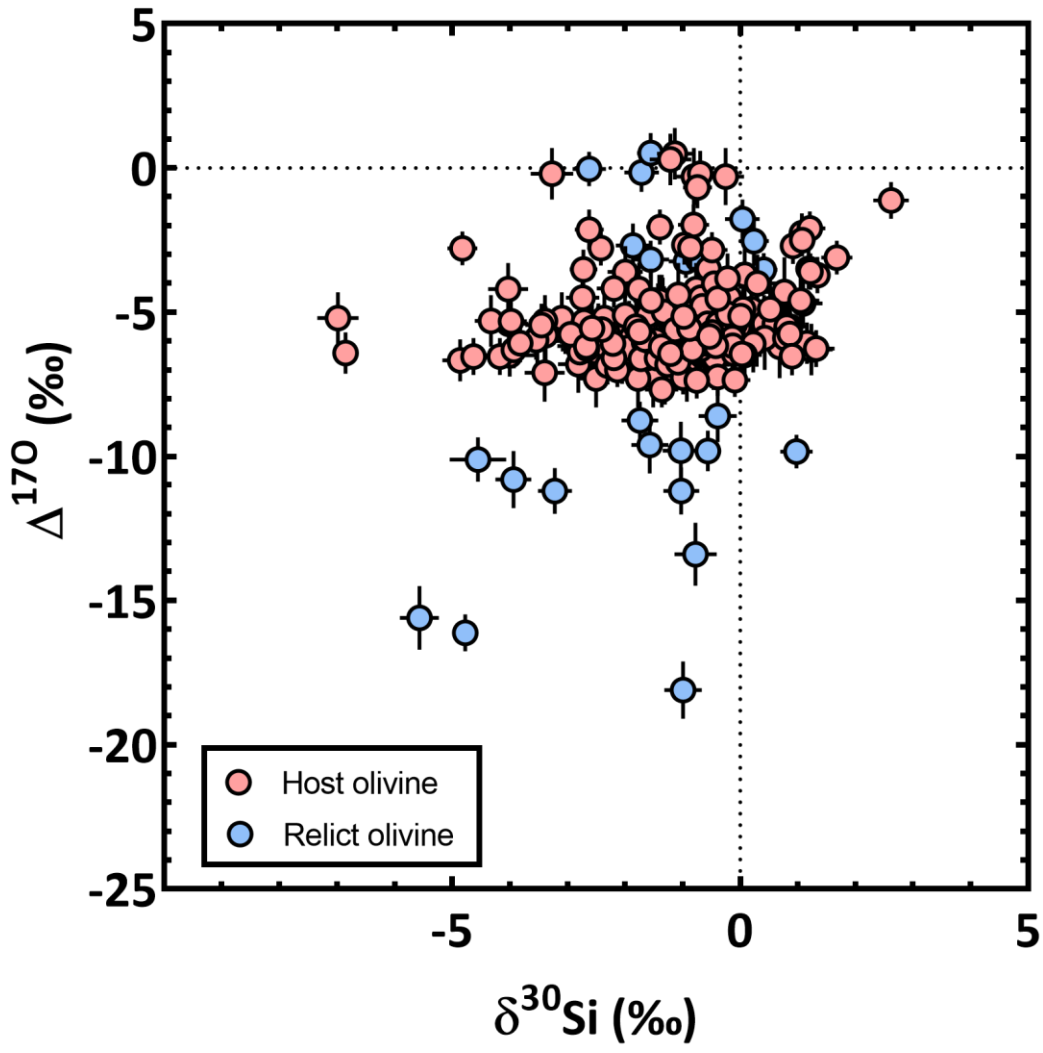


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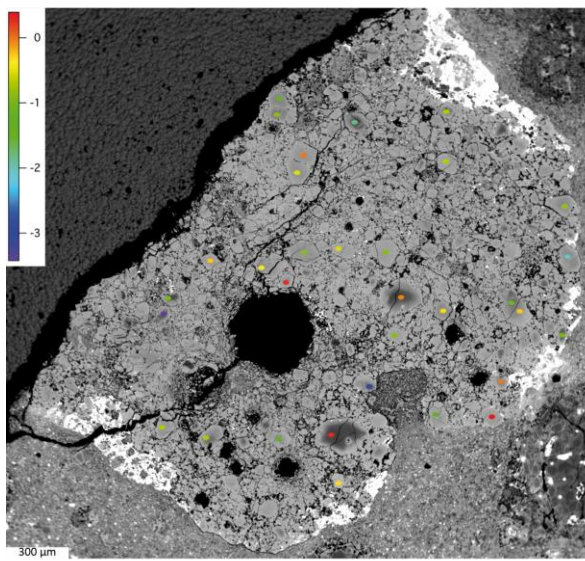
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472 Fig. 7



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476 Fig. 8



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