



HAL
open science

Oxygen isotopic diversity of chondrule precursors and the nebular origin of chondrules

Yves Marrocchi, Johan Villeneuve, Valentina Batanova, Laurette Piani,
Emmanuel Jacquet

► **To cite this version:**

Yves Marrocchi, Johan Villeneuve, Valentina Batanova, Laurette Piani, Emmanuel Jacquet. Oxygen isotopic diversity of chondrule precursors and the nebular origin of chondrules. *Earth and Planetary Science Letters*, 2018, 496, pp.132-141. 10.1016/j.epsl.2018.05.042 . hal-02357534

HAL Id: hal-02357534

<https://hal.univ-lorraine.fr/hal-02357534>

Submitted on 10 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Oxygen isotopic diversity of chondrule precursors and the**
2 **nebular origin of chondrules**

3
4

5 Yves Marrocchi^{1,*}, Johan Villeneuve¹, Valentina Batanova², Laurette Piani¹ and Emmanuel
6 Jacquet³

7
8

9 ¹CRPG, CNRS, Université de Lorraine, UMR 7358, Vandoeuvre-lès-Nancy, 54501, France.

10 ²Université Grenoble Alpes, ISTerre, CNRS, UMR 5275, Grenoble, F-38000, France.

11 ³IMPMC, CNRS & Muséum national d'Histoire naturelle, UMR 7590, CP52, 57 rue Cuvier,
12 75005 Paris, France

13

14

15

16 Correspondence: *yvesm@crpg.cnrs-nancy.fr

17

18

19

20 **Abstract**

21

22

23

24 FeO-poor (type I) porphyritic chondrules formed by incomplete melting of solid dust
25 precursors *via* a yet-elusive mechanism. Two settings are generally considered for their
26 formation: (i) a nebular setting where primordial solids were melted, e.g. by shock waves
27 propagating through the gas and (ii) a collisional planetary setting. Here we report a method
28 combining high-current electron microprobe X-ray mapping and quantitative measurements
29 to determine the chemical characteristics of relict olivine grains inherited from chondrule
30 precursors. We find that these olivine crystals are Ca-Al-Ti-poor relative to host olivine
31 crystals. Their variable $\Delta^{17}\text{O}$, even in individual chondrule, is inconsistent with derivation
from planetary interiors as previously argued from 120° triple junctions also exhibited by the

32 chondrules studied herein. This indicates that chondrule precursors correspond to solid
33 nebular condensates formed under changing physical conditions.

34 We propose that porphyritic chondrules formed during gas-assisted melting of nebular
35 condensates comprising relict olivine grains with varying $\Delta^{17}\text{O}$ values and Ca-Al-Ti-rich
36 minerals such as those observed within amoeboid olivine aggregates. Incomplete melting of
37 chondrule precursors produced Ca-Al-Ti-rich melts (CAT-melts), allowing subsequent
38 crystallization of Ca-Al-Ti-rich host olivine crystals *via* epitaxial growth on relict olivine
39 grains. Incoming MgO and SiO from the gas phase induced (i) the dilution of CAT-melts, as
40 attested by the positive Al-Ti correlation observed in chondrule olivine crystals, and
41 (ii) buffering of the O-isotope compositions of chondrules, as recorded by the constant $\Delta^{17}\text{O}$
42 values of host olivine grains. The O-isotopic compositions of host olivine grains are
43 chondrule-specific, suggesting that chondrules formed in an array of environments of the
44 protoplanetary disk with different $\Delta^{17}\text{O}$ values, possibly due to variable solid/gas mixing
45 ratios.

46

47 .

48

49

50

51

52

53

54

55

56 **Keywords:** chondrule, oxygen isotopes, relict olivine, epitaxial growth, gas-melt interactions

57 **1- Introduction**

58

59 Chondrules (millimeter-sized igneous spheroids containing silicates, metal, sulfides,
60 and glass) are the major high-temperature components of primitive meteorites (chondrites),
61 suggesting that most inner solar system materials were affected by their formation. However,
62 the underlying mechanism(s) of their formation remains a mystery and diverse scenarios are
63 debated in contemporaneous literature. A key clue to their origin would be the identification
64 of the precursor material that was melted to form chondrules. In this effort, cosmochemists
65 may find help in the incomplete melting of most chondrules, as evidenced by their widespread
66 porphyritic texture (Hewins et al., 2005). Indeed, *relict* grains inherited from chondrule
67 precursors are identifiable. Forsteritic grains in high-FeO (type II) porphyritic chondrules
68 were presumably inherited from precursors formed in more reducing conditions than their
69 current host (Nagahara, 1981; Scott and Jones, 1990). Conversely, “dusty” grains, i.e.,
70 crystals speckled with Fe-rich metal beads, in low-FeO (type I) chondrules are commonly
71 attributed to oxidized precursors that underwent reduction during formation of their host
72 chondrules (Lemelle et al., 2001; Leroux et al., 2003; Nagahara, 1981; Rambaldi, 1981).
73 These examples represent only a fraction of the existing relicts. In type I chondrules—the
74 dominant type in carbonaceous chondrites and hence the main asteroid belt—relict grains
75 from *reduced* precursors are not so easily recognizable.

76 Oxygen isotopic systematics may help to identify such relicts (Kimura et al., 2011;
77 Kunihiro et al., 2004, 2005; Rudraswami et al., 2011; Schrader et al., 2013; 2015; Tenner et
78 al., 2013, 2015; Ushikubo et al., 2012). Indeed significant isotopic diversity is observed
79 among solar system materials, from ^{16}O -rich refractory inclusions (calcium-aluminum-rich
80 inclusions (CAIs), amoeboid olivine aggregates (AOA)) to ^{16}O -poorer chondrules (Clayton,
81 2003). Type I chondrules exhibit significant variability and define a broad line in the oxygen

82 three-isotope diagram that is not specific to chondrules of a given chondrite or to particular
83 chondrite type and known as the primitive chondrule minerals (PCM) line (Ushikubo et al.,
84 2012). The underlying ^{16}O variability could result from (i) physical mixing of grains of
85 different origins within the solid chondrule precursors (Hezel & Palme, 2007; Tenner et al.,
86 2015) and/or (ii) high-temperature exchanges between the chondrule melt and the surrounding
87 gas (Marrocchi and Chaussidon, 2015). Secondary ion mass spectrometer (SIMS) analyses of
88 olivines within a single chondrule typically reveal homogeneous oxygen isotopic
89 compositions (Chaussidon et al., 2008; Tenner et al., 2015). Yet, in some chondrules, some
90 olivines are ^{16}O -enriched compared to their neighbors (Kunihiro et al., 2005; Rudraswami et
91 al., 2011): these are generally considered to be relict grains, even if they are not
92 petrographically manifest (Ushikubo et al., 2012).

93 Despite these additions to the known inventory of relict grains, their origin remains
94 unclear. Relict olivine grains could correspond to (i) early condensates from the gas of the
95 solar protoplanetary disk (Cohen et al., 2004; Jacquet and Marrocchi, 2017; Russell et al.,
96 2005; Yurimoto and Wasson, 2002), (ii) collisional debris from early-generation
97 planetesimals (Libourel and Chaussidon, 2011; Libourel and Krot, 2007) and/or (iii) earlier
98 generations of chondrules (e.g., Ruzicka et al., 2007). Progress on the identification of the
99 origin of relict olivine grains is frustrated by our poor understanding of their abundance,
100 distribution and specific chemical compositions (Pack et al., 2005; 2004; Ruzicka et al.,
101 2007). Among isotopic studies, only a few *in situ* measurements of olivine are generally
102 performed within a single chondrule (usually 2–10; Rudraswami et al., 2011), leading to an
103 misestimate of the abundance of relict olivine grains (and relict-bearing chondrules) and a
104 lack of knowledge of their isotopic characteristics. Furthermore, there are no clear major-
105 element signatures and/or textural features that facilitate the recognition of relict olivine
106 grains (Jones et al., 2004; Ushikubo et al., 2012). Consequently, the message carried by relict

107 olivine grains remains difficult to decipher, however fundamental it would be to understand
108 the origin of chondrules.

109 Here we report a new method combining high-resolution X-ray maps, electron
110 microprobe analyses, and SIMS oxygen isotope measurements to quantitatively assess for the
111 first time the nature of relict olivine grains in type I chondrules. This method was successfully
112 applied to type I porphyritic chondrules in the CM-related ungrouped chondrite Northwest
113 Africa (NWA) 5958 (Jacquet et al., 2016) and provides new information on the formation
114 conditions of the first solids of the solar system.

115

116 **2- Material and methods**

117

118 NWA 5958 is a carbonaceous chondrite found in the Moroccan desert in 2009 that
119 shares numerous similarities with the CM chondrite group. This meteorite shows limited
120 terrestrial weathering and a low degree of aqueous alteration (Jacquet et al., 2016). Its bulk
121 oxygen isotopic composition ($\Delta^{17}\text{O} = -4.3\text{‰}$) is more ^{16}O -rich than all CM chondrites, further
122 supporting a limited alteration episode (Marrocchi et al., 2018; Verdier-Paoletti et al., 2017).
123 As previous O isotope studies have revealed CO chondrules to be richest in relicts (Tenner et
124 al., in press), this meteorite, as a member of the CM-CO clan, was a sample of choice to
125 increase their chances of discovery.

126 We surveyed all type I chondrules in thick section NWA 5958-1 (from the Muséum
127 national d'Histoire naturelle collection, Paris, France) of NWA 5958. The X-ray map of
128 NWA5981-1 was reported elsewhere (Fig. 1 of Jacquet et al., 2016). Chondrules were
129 examined microscopically in reflected light. Scanning electron microscope observations were
130 performed at CRPG using a JEOL JSM-6510 with 3 nA primary beam at 15 kV. Among 32
131 Mg-rich porphyritic Type I chondrules examined, we selected 3 olivine-rich chondrules (Fig.

132 1, 2, S1–S3). High-resolution X-ray element distribution maps were performed at the Institut
133 des Sciences de la Terre (ISTerre, Grenoble, France), using a JEOL JXA-8230 electron
134 microprobe analyzer (EMPA) equipped with five wavelength-dispersive spectrometers (WDS)
135 and one silicon drift detector energy-dispersive spectrometer (EDS; Batanova et al., 2015).
136 Analysis were performed with an acceleration voltage of 20 kV, beam current of 500 nA, 1.5-
137 μm step size, and dwell time of 500 ms. Al, Ca, Cr, Mn and Ti were measured by WDS while
138 Fe, Si and Mg were measured by EDS. Each map last 24 hours followed by 8 hours of
139 quantitative analyses. Detection limits were below 40 ppm for Al, Ca, Ti, Cr and Mn as
140 estimated from minimum differences between the average concentrations of the visually
141 distinct homogeneous zones and standard deviations of concentration of homogeneous zones.
142 These X-ray maps are semi-quantitative, as the background was not quantified by performing
143 similar off-peak maps. However, quantitative analyses of all olivine grains large enough to be
144 isotopically characterized by SIMS were then performed with the following conditions:
145 accelerating voltage 20 kV, probe current 900 nA, beam diameter 1 μm , and 320 s total
146 peak/background counting time. Such a high current and long counting time allow very low
147 detection limits estimated to be 10 ppm for Al, Ca, Ti, Cr and Mn. The ZAF software was
148 used for matrix corrections (see Batanova et al. 2015 for further details).

149 We measured the oxygen isotopic compositions of chemically characterized olivine
150 crystals with a CAMECA ims 1270 E7 at CRPG-CNRS (Nancy, France). $^{16}\text{O}^-$, $^{17}\text{O}^-$, and $^{18}\text{O}^-$
151 ions produced by a Cs^+ primary ion beam ($\sim 15 \mu\text{m}$, $\sim 4 \text{ nA}$) were measured in multi-collection
152 mode with two off-axis Faraday cups (FC) for $^{16,18}\text{O}^-$ and the axial FC for $^{17}\text{O}^-$. To remove
153 $^{16}\text{OH}^-$ interference on the $^{17}\text{O}^-$ peak and to maximize flatness atop the $^{16}\text{O}^-$ and $^{18}\text{O}^-$ peaks, the
154 entrance and exit slits of the central FC were adjusted to obtain mass resolution power of
155 ~ 7000 for $^{17}\text{O}^-$. The multicollection FCs were set on exit slit 1 (MRP = 2500). Total
156 measurement times were 240 s (180s measurement + 60s pre-sputtering). We used three

157 terrestrial standard materials (San Carlos olivine, magnetite and diopside) to define the
158 instrumental mass fractionation line for the three oxygen isotopes and correct for instrumental
159 mass fractionation for olivine. To obtain good precision on analytical measurements, we
160 analyzed, in order, 4 standards, 8 chondrule olivine crystals and 4 standards. Typical count
161 rates obtained on the San Carlos olivine standards were 2.5×10^9 cps for ^{16}O , 1.0×10^6 cps
162 for ^{17}O , and 5.4×10^6 cps for ^{18}O . The number of Mg-rich olivines analyzed per chondrule
163 were 45, 45 and 28, with typical uncertainties of 0.2, 0.4 and 0.7‰ for $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ (measured
164 relative to standard mean ocean water, SMOW, as $\delta^{17,18}\text{O} =$
165 $[(^{17,18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{17,18}\text{O}/^{16}\text{O})_{\text{SMOW}} - 1] \times 1000$ ‰), and $\Delta^{17}\text{O}$ ($= \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$),
166 respectively (Table S1).

167

168 **3- Results**

169

170 All porphyritic chondrule textural types are present in NWA 5958, i.e., porphyritic
171 olivine-rich (PO), porphyritic olivine-pyroxene (POP), and porphyritic pyroxene-rich (PP);
172 Figs. 1–3). Among the chondrules examined, two PO chondrules (Ch-1 and Ch-7) were
173 chosen for detailed examination. They are characterized by many variably-sized (≈ 30 – 300
174 μm) subhedral to euhedral olivine grains meeting in 120° triple junctions (Figs. 1, 2, S1–S2)
175 first described by (Libourel and Krot, 2007), altered mesostases, and Fe-Ni metal beads (Figs.
176 1, 2A, and S1–S2). Large, euhedral low-Ca pyroxenes surround both chondrules, with
177 resorbed or poikilitically enclosed olivines (Figs. 1, 2, S1–S2, Friend et al., 2016). The third
178 chondrule selected, Ch-2, was a POP chondrule showing radial zoning with an olivine- and
179 (altered) mesostasis-rich interior and an outer zone dominated by low-Ca pyroxenes parallel
180 to the surface (Fig. S3).

181 Chondrule olivine crystals appear homogeneous in back-scattered electron images
182 (Fig. 2A, S2–S3) but high-resolution titanium X-ray maps reveal important chemical
183 variations in the three chondrules (Fig. 2B, S1–S3). In some cases, these compositional
184 variations occur within single crystals, with Ti-rich olivine engulfing Ti-poor olivine,
185 implying overgrowth on a relict crystal (Fig. 2B). Ti-poor olivine grains are mainly located in
186 the center of chondrule (Fig. 2B) but also occur as the center of olivine crystals dispersed
187 throughout the chondrules (Fig. S2–S3). The overall zoning is comparable to the “inverse
188 zonings” in some cathodoluminescence maps of porphyritic chondrules by (Pack et al., 2004;
189 e.g. their Fig. 2D and 10B) and Kita et al. (2010). Outer-chondrule olivine crystals show
190 oscillatory Ti zoning over thickness ranging from 10 to 30 μm (Fig. 2B, S2–S3), with a
191 tendency to return to lower Ti contents (also seen at the edge of inner-chondrule crystals).
192 This is the first time oscillatory zoning is reported in chondrule olivine (notwithstanding the
193 single-oscillation high-FeO grain of Jacquet and Marrocchi, 2017) for elements other than the
194 slow diffuser phosphorus (McCanta et al., 2016) although such zoning has long been
195 described in pyroxene (e.g. Baecker et al., 2017; Jones, 1996). The overgrowths sometimes
196 exhibit variable thicknesses, with thicker overgrowths toward the exterior of the chondrule
197 (Fig. 2B). High-resolution quantitative analyses of olivine reveal trace element variations
198 within each chondrule, with aluminum and titanium contents varying from 0.02 to 0.2 wt%
199 and 0.01 to 0.08 wt%, respectively (Table S1). Importantly, both elements are positively
200 correlated in PO chondrules (Fig. 3E and 4E, Tables S1 and S2) whereas the POP chondrule
201 shows no specific correlation (Fig. S4E, Tables S1 and S2). Other well-defined correlations
202 were observed in PO chondrules (Table S1 and S2): (i) Cr is positively correlated to Fe and
203 Mn and negatively to the Mg# (= molar $\text{MgO}/(\text{MgO}+\text{FeO})$), (ii) Fe is positive correlated with
204 Mn.

205 A total of 118 SIMS spot analyses were performed in one session and used to assess
206 oxygen isotope systematics of the three mapped and chemically characterized chondrules.
207 Olivine O-isotope compositions plot along the PCM line with $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ ranging from
208 -30.3 to $+2.75\text{‰}$ and from -27.3 to $+5.1 \text{‰}$, respectively (Fig. 3A, 4A and S4A, Table S1).
209 All chondrules show internal mass-independent O-isotope heterogeneity beyond analytical
210 uncertainties, with $\Delta^{17}\text{O}$ varying by $>5 \text{‰}$ (Fig. 3A, 4A and S4A, Table S1). Most of this
211 variability is carried by Ti, Ca, Al-poor olivine grains whereas (varyingly) Ti, Ca, Al-rich
212 grains cluster around the same $\Delta^{17}\text{O}$ value, producing “orthogonal” relationships (i.e.
213 conjunction of an horizontal and a vertical trends) in $\Delta^{17}\text{O}$ vs. minor element plots (Fig. 3A,
214 4A, and S4). In each chondrule, the horizontal trend which regroups the majority of the grains
215 can be taken as representing the host. That of the two PO chondrules ($\Delta^{17}\text{O} = -6.0$ and -6.3
216 ‰) belongs to the ^{16}O -rich group of (Ushikubo et al., 2012) whereas the POP chondrule’s
217 ($\Delta^{17}\text{O} = -3.0 \text{‰}$) fits in the ^{16}O -poor one.

218

219 **4- Discussion**

220

221 **4-1 Chemical characterization of relict olivines**

222

223 Our high-resolution titanium X-ray maps of porphyritic chondrules reveal different
224 populations of olivine grains characterized by variable titanium contents (Fig. 2B, S2–S3).
225 Most Ti-poor olivine grains have oxygen isotopic compositions markedly distinct from their
226 hosts (olivine grains with higher Ti concentrations; Fig. 3B, 4B and S4B, Tables S1 and S2).
227 Following (Ushikubo et al., 2012), we consider olivines with $\Delta^{17}\text{O}$ deviating by $>3\sigma$ from
228 their host $\Delta^{17}\text{O}$ as relicts (host being the olivine grains showing homogeneous values with
229 $\Delta^{17}\text{O}$ $2\text{SD} \leq 1\text{‰}$; Ushikubo et al., 2012). So most of these Ti-poor olivines are relict grains.

230 They may be ^{16}O -richer (Ch-2 and Ch-7) or ^{16}O -poorer (Ch-1) than their host olivine. Our
231 results thus demonstrate that olivine Ti concentrations can constitute a *chemical* marker of
232 relicts, in addition to isotopic data. Relict olivine grains are also systematically Al-poor (Fig.
233 3C, 4C and S4C, table S1) and, in one chondrule (Ch2), Ca-poor (Fig. 4D) relative to host
234 olivines. However, relict olivine grains are not systemically depleted in Ca relative to the host
235 (Table S1).

236 Ambiguity remains though regarding those Ti-poor olivine crystals with $\Delta^{17}\text{O}$ similar
237 to the range defined by the host grains (Fig. 3, 4, S4, Table S1). Such grains could correspond
238 to (i) relict grains with O-isotopic compositions coincidentally similar to host crystals or
239 (ii) host olivine with lower Ti content relative to other host grains. Obvious relict olivine
240 grains (i.e. with $\Delta^{17}\text{O}$ outside 3σ of the host), are mainly located in the center of chondrules
241 (Fig. 5), whereas the aforementioned ambiguous grains occur at the outer edge of chondrules
242 (Fig. 2, 5, S2–S3), suggesting an host origin (see also next subsection).

243 Our finding that relict chondrule olivine are Ca, Al, Ti-poor contrasts with the
244 previous notion that refractory-*enriched* olivines were the relict grains (Pack et al., 2004;
245 Pack and Palme, 2003) but even those workers had reported “inverse zonings” similar to
246 those of this study when dealing with *bona fide* porphyritic chondrules (Pack et al., 2004).
247 Since refractory forsterite crystals do occur independently in chondrites (Jacquet and
248 Marrocchi, 2017; Pack et al., 2004), the possibility remains that some contributed to
249 chondrule precursors although they were not found in this study.

250 At any rate, this study demonstrates that high-current EMPA mapping (at 500 nA) and
251 quantitative analyses (at 900 nA) constitute a powerful method for characterizing relict
252 olivine crystals as it allows very low detection limits for trace elements in olivine (≈ 10 ppm
253 for Al, Ca, Mn & Ti; Sobolev et al., 2016) to be reached with limited interaction and emission
254 volumes of X-rays in olivine grains (i.e., $\leq 6 \mu\text{m}^3$; Batanova et al., 2015).

255 **4-2 Origin of relict grains and nature of chondrule precursors**

256

257 Coarse-grained olivine aggregates showing 120° triple junctions, such as in our PO
258 chondrules analyzed, were interpreted by (Libourel and Krot, 2007) as potential fragments of
259 differentiated planetesimals that experienced disruption early in the Solar System history. In
260 such a scenario, all Mg-rich olivine grains would represent relict minerals that survived the
261 chondrule-forming event(s). However, experimental samples with olivine triple junctions
262 were produced during thermal annealing under nebular conditions, challenging the planetary
263 origin of granoblastic olivine aggregates (GOA; Whattam and Hewins, 2009; Whattam et al.,
264 2008). Our results show that large mass-independent O-isotope variations occur within
265 chondrules showing triple junctions (Fig. 1). This does not support a planetary origin of GOA
266 as crystallization from a magma ocean would result in very limited *and* mass-dependent O-
267 isotopic fractionation (Richet et al., 1977). For instance, oxygen isotope compositions of
268 primitive basaltic rocks vary within narrow ranges with mass-dependent fractionation limited
269 to less than 1‰ (Eiler, 2001). Consequently, it appears that 120° triple junctions of olivines
270 are not the result of lithostatic pressure (Whattam et al., 2008; Whattam and Hewins, 2009)—
271 ours even seem to be shaped by overgrowths rather than the relicts themselves—arguing
272 against a planetary origin of chondrules (Jacquet et al., 2012; Jacquet and Marrocchi, 2017).
273 While derivation of neighboring relicts from *independent* planetary bodies remains unlikely
274 but conceivable, known (macroscopic) achondrites sample a much more restricted range of O
275 isotopic compositions (Greenwood et al., 2016).

276 The relict olivine grains in NWA 5958 are too poor in refractory elements to
277 correspond to phenocrysts in refractory condensed melts as envisioned by (Pack et al., 2004).
278 Their chemical features (Ca-Al-Ti-poor; Fig. 3, 4 & S4, Table S1) are however similar to
279 olivine in amoeboid olivine aggregates (AOAs; Ruzicka et al., 2012; Sugiura et al., 2009;

280 Weisberg et al., 2004), which result from condensation from the nebular gas (Krot et al.,
281 2004): for example AOA olivines in the same meteorite analyzed by Jacquet and Marrocchi
282 (2017) have concentrations ranging 0.01-0.03 wt% TiO₂, 0.03-0.08 wt% Al₂O₃, comparable
283 with our relicts (see section 4.1). Furthermore, olivines within individual AOAs commonly
284 show variable $\Delta^{17}\text{O}$ values that could result from condensation under changing physical
285 conditions (Krot et al., 2004). This support a kinship between AOAs and chondrule precursors,
286 similar to that inferred for part of the precursors of agglomeratic chondrules in CR chondrites
287 (Schrader et al., 2018). The presence of refractory inclusions among chondrule precursors is
288 supported in the literature by the observation of (rare) relict CAIs and AOAs in chondrules
289 (Aléon & Bourot-Denise, 2008; Krot et al. 2009; Yurimoto and Wasson 2002), aluminum-
290 rich chondrules (Russell et al. 2000; Krot and Keil 2002) and volatility-fractionated rare earth
291 element patterns in bulk chondrules (Misawa and Nakamura 1988; Jacquet and Marrocchi
292 2017 and references therein). However, chondrule precursors are unlikely to be solely AOAs
293 as the latter are ¹⁶O-rich ($\Delta^{17}\text{O} = -15$ to -22 ‰; Krot et al., 2004) whereas relict olivine grains
294 in NWA 5958 chondrules are isotopically diverse with $\Delta^{17}\text{O}$ ranging from -16.1 to $+0.5$ ‰
295 (Fig. 6, Table S1). Additionally, relict olivines in Ch-1 are enriched in ^{17,18}O relative to the
296 host grains (Fig. 3, Table S1) and literature data indeed show relict olivine grains either
297 enriched or depleted in ¹⁶O relative to the host (Jones et al., 2004; Kita et al., 2010;
298 Rudraswami et al., 2011; Tenner et al., 2015; 2013; Ushikubo et al., 2012). Since the oxygen
299 isotopic characteristics of precursors should be better preserved than minor elements because
300 of slower diffusion of oxygen: e.g., Ryerson et al., 1989), these cannot have been solely
301 AOAs but were plausibly nebular condensates mineralogically analogous to them but
302 characterized by a significant oxygen isotopic diversity. It is interesting to note that the
303 analyzed relict olivines (Table 1) define a $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ correlation (Fig. 6), described by $\delta^{17}\text{O} =$
304 $(1.04 \pm 0.06) \times \delta^{18}\text{O} - (2.78 \pm 0.60)$ that is indistinguishable within errors from the PCM line

305 defined by SIMS measurements in chondrules (i.e., amalgamated host and relict data) from
306 different carbonaceous chondrites (Ushikubo et al., 2012). The PCM line may thus have been
307 already established in the chondrule precursors rather than being a result of chondrule
308 formation, although some of the relicts (presumably among those in the range of host
309 compositions) may be recycled chondrule debris.

310 We note that relict olivine grains are systematically studded with Fe-Ni metal beads
311 (Fig. 2B). Such mineralogical associations could either result from (i) co-condensation of
312 olivine and Fe-Ni metal beads, as observed in some AOAs (Krot et al., 2004) or (ii) sub-
313 solidus reduction of FeO in olivine grains (Lemelle et al., 2001; Leroux et al., 2003). The
314 latter produces peculiar textures with micron-sized Ni-poor (i.e., < 2 wt%) metal beads
315 surrounded by silica-rich glass layers (Leroux et al., 2003) and defining lines in olivine
316 crystals (Rambaldi, 1981), which are not observed in NWA 5958 chondrules (Fig. 2 and S2).
317 If, on the contrary, the mineralogical association is pristine, the relicts must have condensed at
318 a total pressure >10 Pa (i.e., 0.1 mbar) to produce Fe-Ni metal beads before condensation of
319 Mg-rich olivine (Ebel, 2006; Ebel and Grossman, 2000; Petaev et al., 2005).

320

321 **4-3 Chondrule melting and epitaxial growth of host olivine**

322

323 The systematic Al-Ti-enrichments (and in some case in Ca, Fig. 4D) of host olivine
324 grains compared to relicts suggest their formation from Ca-Al-Ti-melts (hereafter CAT-
325 melts). Because the surviving relicts are (Ca)-Al-Ti-poor olivine, the melts generated upon
326 heating should have been enriched in those elements compared to the bulk (more or less
327 chondritic) precursor. Specifically, such melts could result from melting of CAI-like nodules
328 and ribbons like those observed within AOAs, which are mainly composed of spinel, Ti-Ca-
329 rich pyroxene and anorthite (Krot et al., 2004; Ruzicka et al., 2012; Weisberg et al., 2004).

330 Except spinel, all those phases have lower melting temperatures than Mg-rich olivine and
331 their fusion during the high-temperature chondrule-forming event(s) would generate CAT-
332 melts while preserving ^{16}O -rich spinel relicts as occasionally observed in type I chondrules
333 (Rudraswami et al., 2011; Tenner et al., 2015; 2013; Ushikubo et al., 2012). According to
334 equilibrium Ca-partitioning between forsterite and melt (Libourel, 1999) and the large range
335 of CaO concentrations observed in PO chondrule mesostasis (i.e., 5-22 wt%, Jones and Scott,
336 1989; Libourel et al., 2006; Marrocchi and Libourel, 2013), the host olivine grains could
337 present (i) similar Ca concentration than relict grains (e.g., Ch-1 and Ch-2, Table S1) or
338 (ii) Ca-enrichment comparing to relicts (e.g., Ch-7; Fig. 4D, Table S1). In addition, sodium-
339 enrichments in the CAT-melts would increase the degree of polymerization of the melt and
340 the activity of CaO, thereby promoting the crystallization of Ca-rich host olivine (Libourel et
341 al., 1999, Piani et al., 2016).

342 The presence of CAT-melt would then allow the crystallization of olivine overgrowths
343 around the olivine relicts, by-passing the thermodynamic barrier of nucleation (Fokin et al.,
344 2006). Such a process is attested by the textures of olivine grains inferred from Ti X-ray maps
345 that reveal host-olivine crystallization on relict olivine grains *via* epitaxial growth (Fig. 2B).
346 Such olivine subtraction from the melt would have further enriched the melt in incompatible
347 elements, contributing to the Ca-Al-Ti-rich character of the overgrowths. Interestingly, Ca-
348 Al-Ti-rich melt inclusions could be observed along the boundary between relict and host
349 olivine grains (Fig. S1). Similar textures have been observed in terrestrial olivine phenocrysts
350 that present olivine overgrowths on relict olivine cores (Sakyi et al., 2012), thus supporting
351 the crystallization of chondrule host olivine grains *via* epitaxial growth on relict olivine grains
352 inherited from chondrule precursors.

353 Because relicts are still visible in the X-ray maps, diffusion was not efficient enough
354 to homogenize the olivine grains in Al and Ti. This runs counter to the batch crystallization

355 inferred by (Jacquet et al., 2015) and (Jacquet and Marrocchi, 2017) for type I chondrules, at
356 least for this type of texture, in contradistinction to the largely homogeneous isolated
357 refractory forsterites. For diffusion coefficients of order 10^{-14} m²/s in the temperature interval
358 of olivine crystallization, the duration of this high-temperature episode must have been
359 limited to no more than a few hours, though possibly not much shorter than this as e.g. Ca
360 zonings appear significantly smoother and thus diffusion-affected.

361

362 **4-4 Open system behavior**

363

364 The enhanced thickness of host-olivine overgrowths near the periphery of the
365 chondrules (Fig. 2B) indicates that olivine “nutrients” were sourced from outside, i.e. open
366 system behavior. Indeed, the low Mg content of PO chondrule mesostases (<5 wt% MgO;
367 Libourel et al., 2006; Marrocchi and Libourel, 2013) suggest that olivine may have become
368 unstable in the CAT-melt and partially dissolved (Soulié et al., 2016)— it is also possible that
369 the rounded to subhedral shapes of the relict olivines observed in NWA 5958 (Fig. 2B) reflect
370 early such partial dissolutions (rather than only diffusive exchange with overgrowths). Under
371 those conditions, further olivine crystallization may have required an influx of SiO and MgO
372 from the gas phase. Such an influx has been invoked to account for the pyroxene-rich
373 peripheries of porphyritic chondrules (Libourel et al., 2006; Piani et al., 2016; Marrocchi et al.,
374 2016; Tissandier et al., 2002, Hezel et al., 2003, 2006; Krot et al. 2004; Friend et al. 2016)
375 and thus may have similarly occurred during an earlier stage of chondrule crystallization. This
376 is supported by the decreasing Ca, Al, and Ti contents of host olivine grains from the center
377 toward the edge of chondrules (Fig. 2B) that likely results from the dilution of CAT-melts by
378 gas-melt interactions (see Jacquet and Marrocchi, 2017). Our emerging scenario thus bears
379 some similarity with the “Open System Fractional Crystallization” model of (Pack et al.,

380 2004), despite their different assumed (refractory) starting conditions. In such a scheme, the
381 positive relationships between Al and Ti contents in olivine grains (Figs. 3E and 4E) simply
382 reflect their common incompatibility in olivine, and their varied abundances (by at least a
383 factor of 10; Table S1) would result from (i) the dilution of CAT-melts by incoming SiO and
384 MgO from the gas phase and (ii) progressive crystallization of olivine, *concentrating* Al and
385 Ti in the melt. The competition between these two processes may have produced the
386 oscillatory character of some of the zoning.

387 While the Ca-Al-Ti contents of host olivine grains varied during chondrule formation,
388 their O-isotope composition (i.e. $\Delta^{17}\text{O}$; Fig. 3B, 4B and S3B) remained constant. As the host-
389 olivine O isotope composition nowhere approaches the mean of the observed relicts among
390 the chondrules studied, rather than corresponding to the bulk precursor, must result from
391 exchange with the gas. The O-isotopic composition of the gas must have been different for
392 each chondrule, as host olivine grains in NWA 5958 show different average values ($\Delta^{17}\text{O} \approx -$
393 6 and -3% ; Figs. 3B, 4B, and S3B; Jacquet and Marrocchi, 2017). These estimates are in
394 agreement with those reported for different types of carbonaceous chondrites (Libourel and
395 Chaussidon, 2011; Rudraswami et al., 2011; Tenner et al., 2015; 2013; Ushikubo et al., 2012),
396 implying that within a single chondrite, chondrules formed in different environments of the
397 protoplanetary disk with varying $\Delta^{17}\text{O}$ values (Tenner et al., 2015; 2013; Ushikubo et al.,
398 2012). As chondrules in individual chondrites largely formed within a clan-specific reservoir
399 (Jones, 2012), such variations occurred on limited spatial and/or temporal scales, e.g., owing
400 to variable solid/gas mixing ratios.

401

402

403

404

405 **5-Concluding remarks**

406

407 We developed a method combining high-current electron microprobe X-ray mapping
408 (at 500 nA) and quantitative measurements (at 900 nA) to determine the chemical
409 characteristics of relict olivine grains in chondrules. They are Ca-Al-Ti-poor compared to
410 their host olivine crystals and are mainly located in the center of chondrules. Ti-poor relict
411 olivines show variable $\Delta^{17}\text{O}$ values in each chondrule, suggesting that chondrule precursors
412 correspond to nebular condensates that formed under changing physical conditions but at
413 pressures above 0.1 mbar. This holds in particular for GOAs with 120° triple junctions whose
414 mass-independent O-isotope variations preclude a planetary origin.

415 The important chemical and O-isotope variations observed within each chondrule
416 suggest that chondrules formed *via* melting of nebular precursors comprising olivine grains
417 with varying $\Delta^{17}\text{O}$ values and CAI-like nodules and ribbons as those observed within AOA's.
418 The resulting CAT-melts allowed subsequent epitaxial growth of Ca-Al-Ti-rich host-olivines
419 on relict olivine grains. Incoming MgO and SiO from the gas phase induced (i) dilution of the
420 CAT-melts, as attested by the positive Al-Ti correlation observed in chondrule olivine
421 crystals, and (ii) buffering of the O-isotope compositions of chondrules, as attested by the
422 constant $\Delta^{17}\text{O}$ values of host olivines. The O-isotopic variations between host olivine grains
423 of different chondrules within a single chondrite demonstrate that the chondrules formed in
424 different environments of the protoplanetary disk with different $\Delta^{17}\text{O}$ values, possibly due to
425 variable solid/gas mixing ratios.

426

427

428

429

430 **Acknowledgments**

431

432 All the data used in the present article are available by contacting Yves Marrocchi. Laurent
433 Tissandier, Andrey Gurenko and Mathieu Roskosz are thanked for helpful scientific
434 discussions. Nordine Bouden is thanked for his assistance with isotopic measurements. We
435 thanked Dominik Hezel and Ryoji Tanaka for constructive comments and Associate Editor
436 Frederic Moynier for careful editing. This is CRPG-CNRS contribution #2564.

437

438

439

440

441

442

443

444

445

446

447

448

449

450

451

452

453

454 **Figure captions**

455

456 **Fig. 1:** Reflected-light optical images of chondrules (A) Ch-1 and (B) Ch-7 from CM-related
457 chondrite NWA 5958. Schematic representations of olivine grains in chondrules (C) Ch-1 and
458 (D) Ch-7 show the numerous 120° triple junctions (some indicated by red arrows) between
459 Mg-rich olivine crystals.

460

461 **Fig. 2:** (A) Back-scattered electron image of PO chondrule Ch-1 in NWA 5958. Ol = olivine,
462 lpx = low-Ca pyroxene, Fe-Ni = Fe-Ni metal beads and m = altered mesostasis. (B) X-ray
463 map of the Ti distribution in Ch-1, revealing internal structures. Most olivine grains are
464 composed of a Ti-poor core and an epitaxially grown Ti-rich olivine margin. Most Ti-poor
465 olivine is located near the center of the chondrule, whereas outer olivine grains are enriched in
466 Ti. Oscillatory Ti zoning and a decrease in Ti content are observed in peripheral olivine grains
467 (see text).

468

469 **Fig. 3:** (A) Oxygen isotopic composition of olivine crystals in PO chondrule Ch-1 from
470 chondrite NWA 5958, highlighting important mass-independent variations. The terrestrial
471 fractionation line (TFL) and primary chondrule mineral line (PCM) are also drawn.
472 Incompatible element concentrations plotted against $\Delta^{17}\text{O}$ reveal that relict olivine grains are
473 systematically depleted in (B) TiO_2 and (C) Al_2O_3 relative to their host olivine crystals, which
474 are characterized by variable concentrations of these elements. (D) Mg# vs. $\Delta^{17}\text{O}$, showing
475 that relict olivine grains have lower iron contents than their host olivines. (E) The positive
476 relationship between Al_2O_3 and TiO_2 in olivine grains (both oxide concentrations vary by at
477 least a factor of 5) suggests a dilution effect due to incoming MgO and SiO from the gas
478 phase (see section 4-2). (F) CaO vs. FeO concentrations in olivine grains.

479

480 **Fig. 4:** (A) Oxygen isotopic composition of olivine crystals in PO chondrule Ch-7 from
481 chondrite NWA 5958. The terrestrial fractionation line (TFL) and primary chondrule minerals
482 line (PCM) are drawn. $\Delta^{17}\text{O}$ vs. (B) TiO_2 , (C) Al_2O_3 , and (D) CaO in olivine are displayed.
483 (E) Al_2O_3 vs. TiO_2 in olivine grains. (F) CaO vs. FeO in olivine crystals.

484

485 **Fig. 5:** (A) X-ray map of the Ti distribution showing the locations of ion probe measurements
486 (colored circles). The color code indicates the deviation from the average $\Delta^{17}\text{O}$ value of the
487 host olivine grains of this chondrule: $<3\sigma$ = blue, $3-6\sigma$ = green, $6-9\sigma$ = yellow, and $>9\sigma$ =
488 red.

489

490 **Fig. 6:** Oxygen three-isotope plot showing the isotopic compositions of relict olivines from
491 NWA 5958. The data define a linear trend that is indistinguishable, within errors, from the
492 PCM line ($\delta^{17}\text{O} = [0.997 \pm 0.013] \times \delta^{18}\text{O} - [2.70 \pm 0.11]$; (Ushikubo et al., 2012)).

493

494

495

496

497

498

499

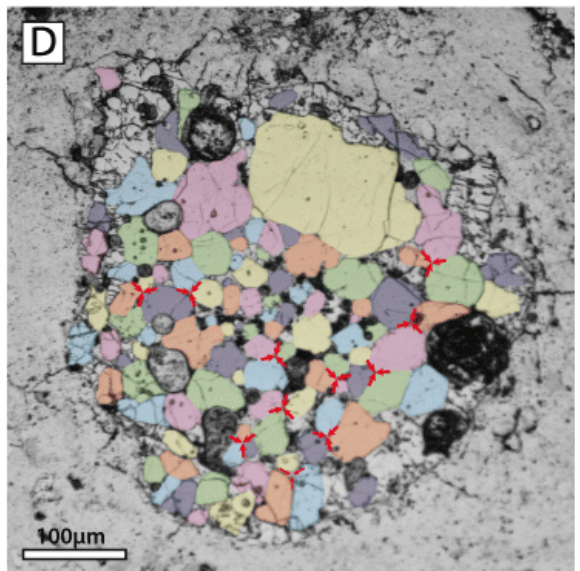
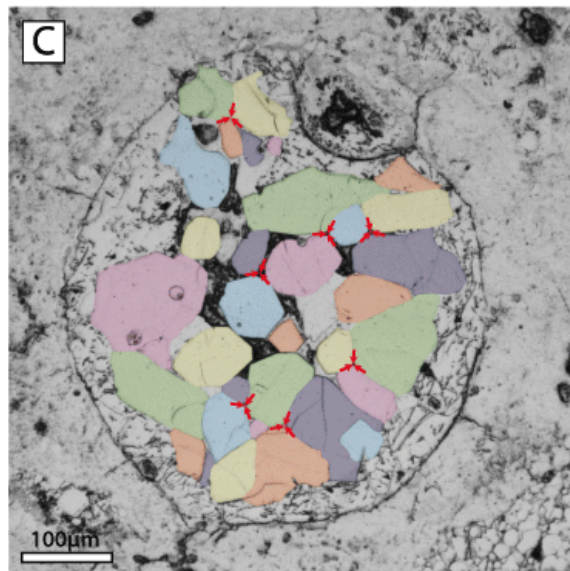
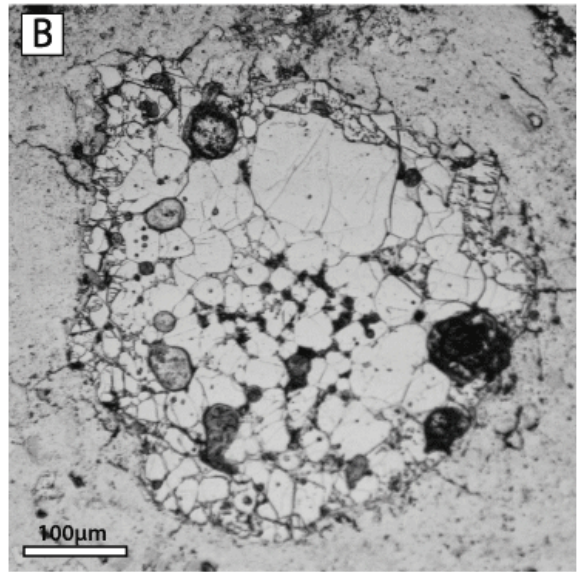
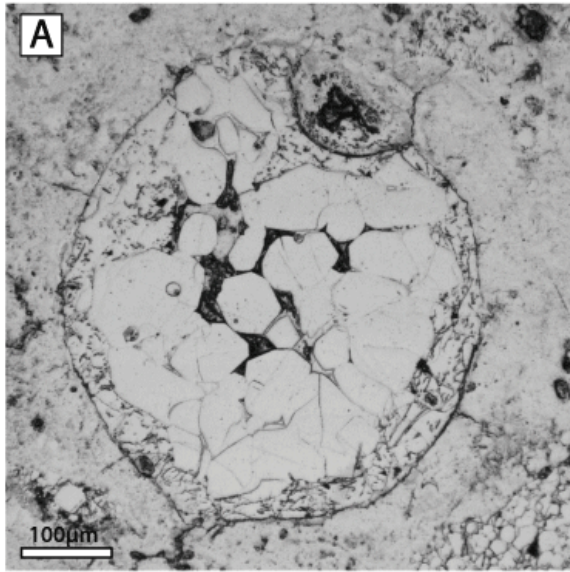
500

501

502

503

504



505

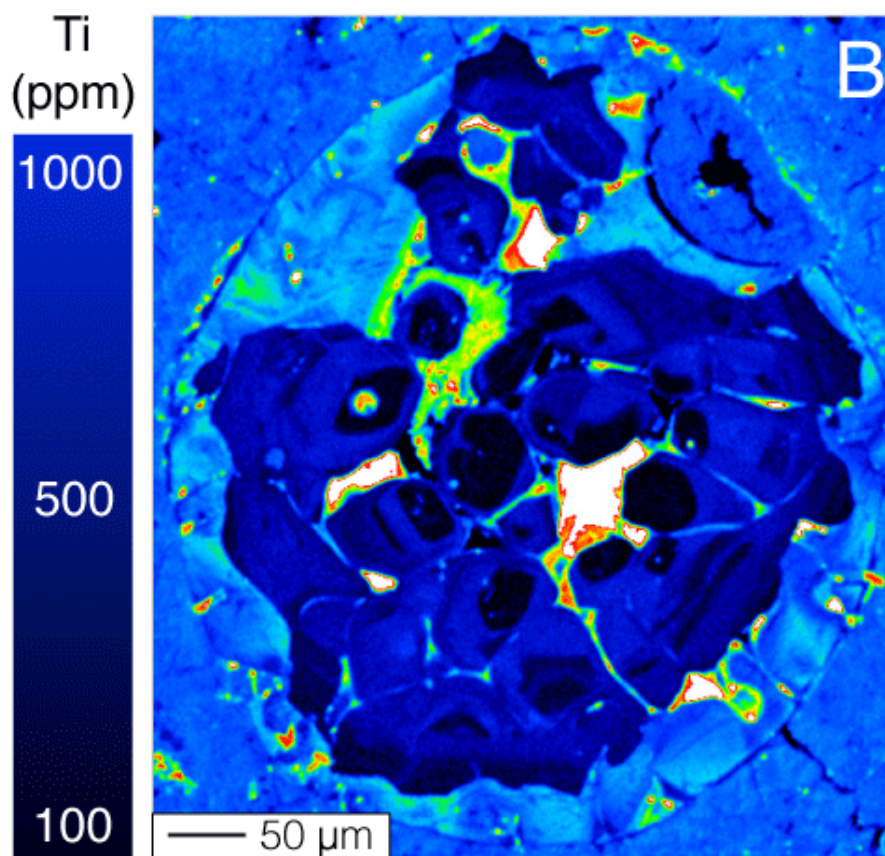
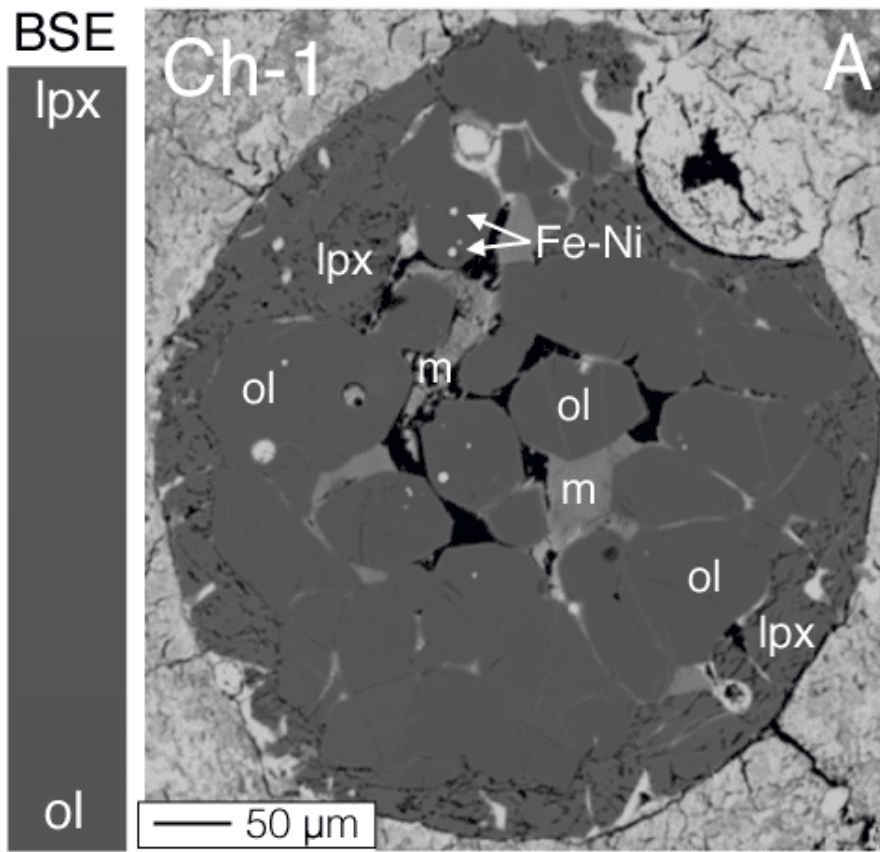
506

507

508

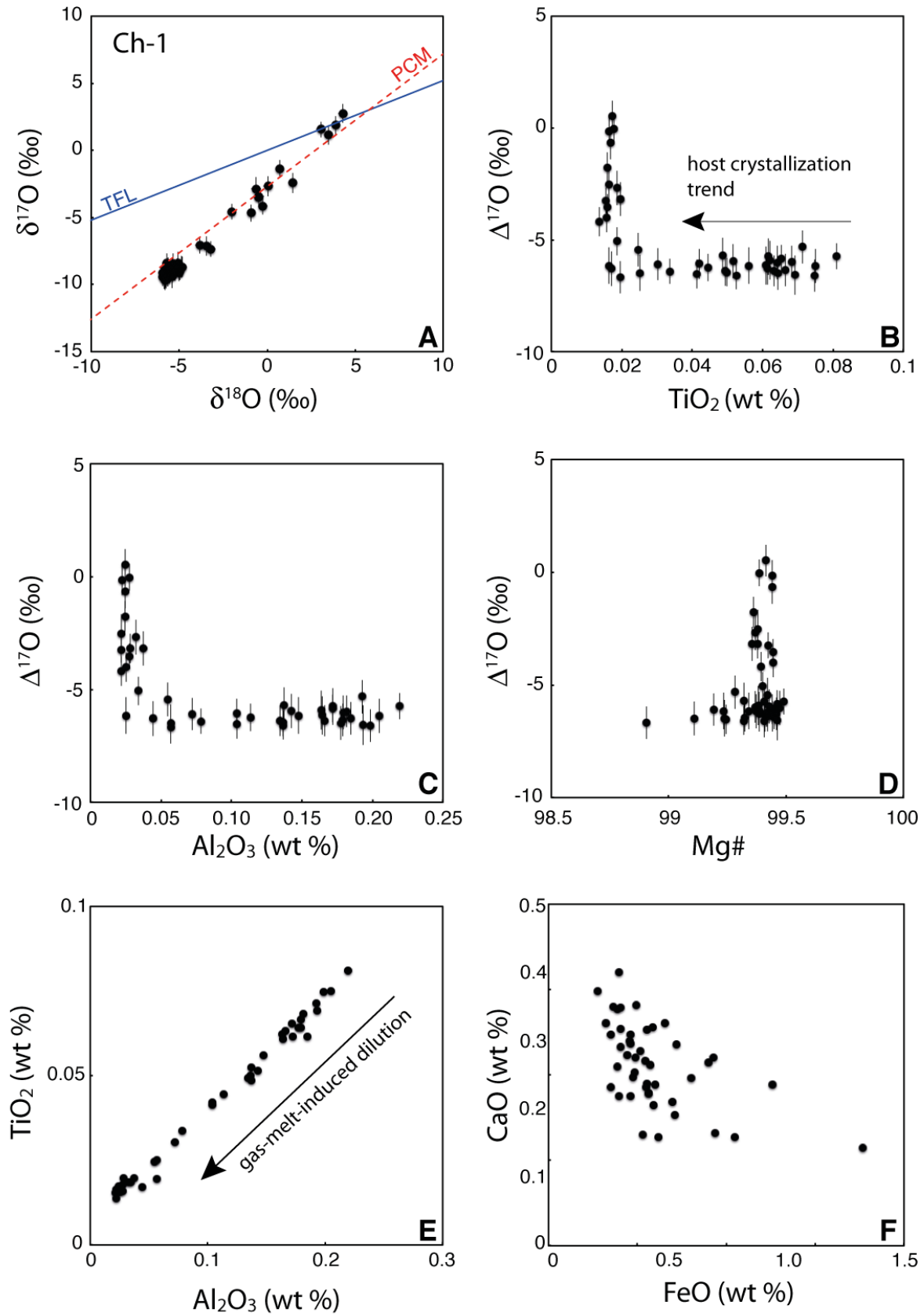
509

Fig. 1



510
511

Fig. 2



512
513

Fig. 3

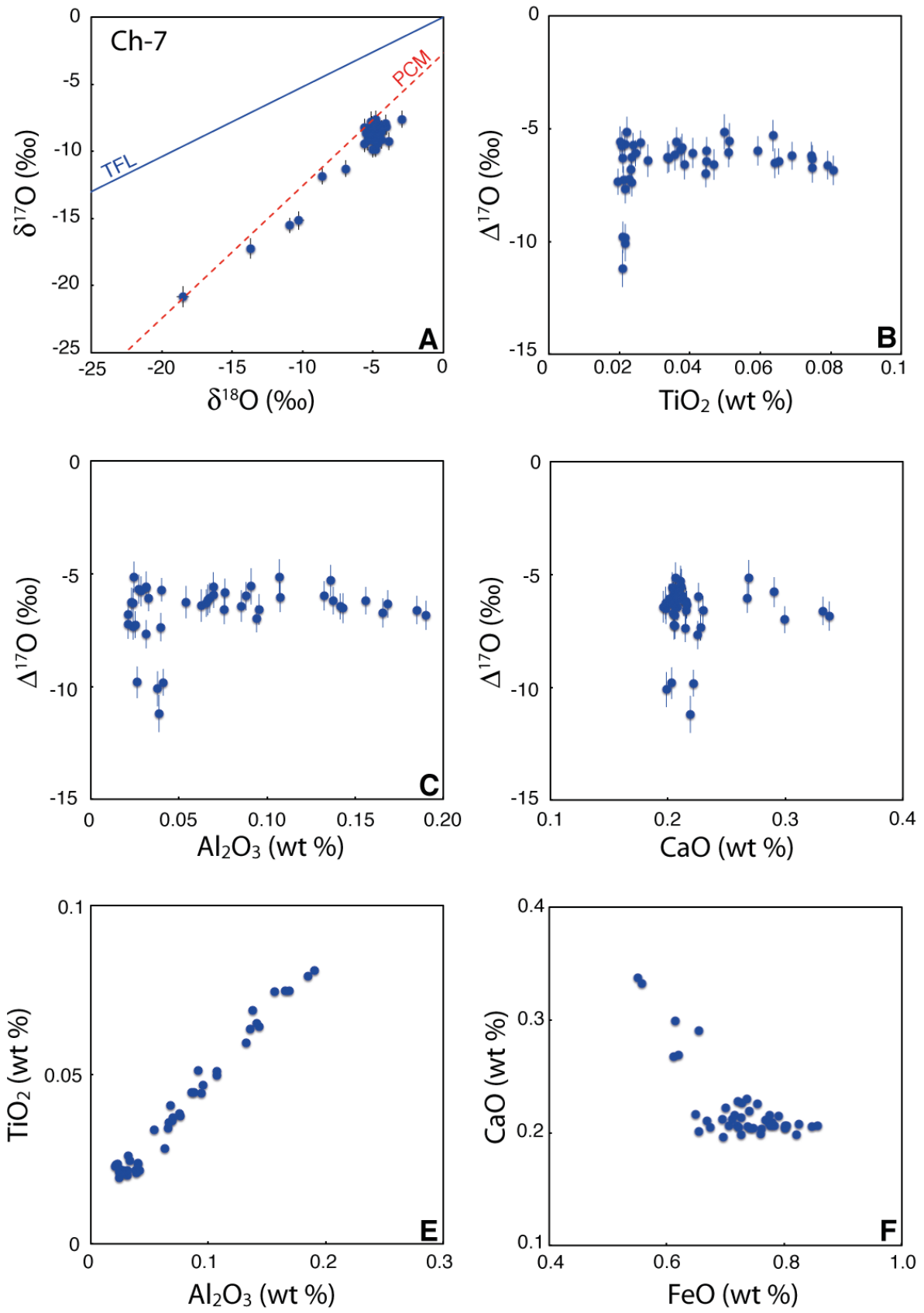


Fig. 4

514
515
516
517
518

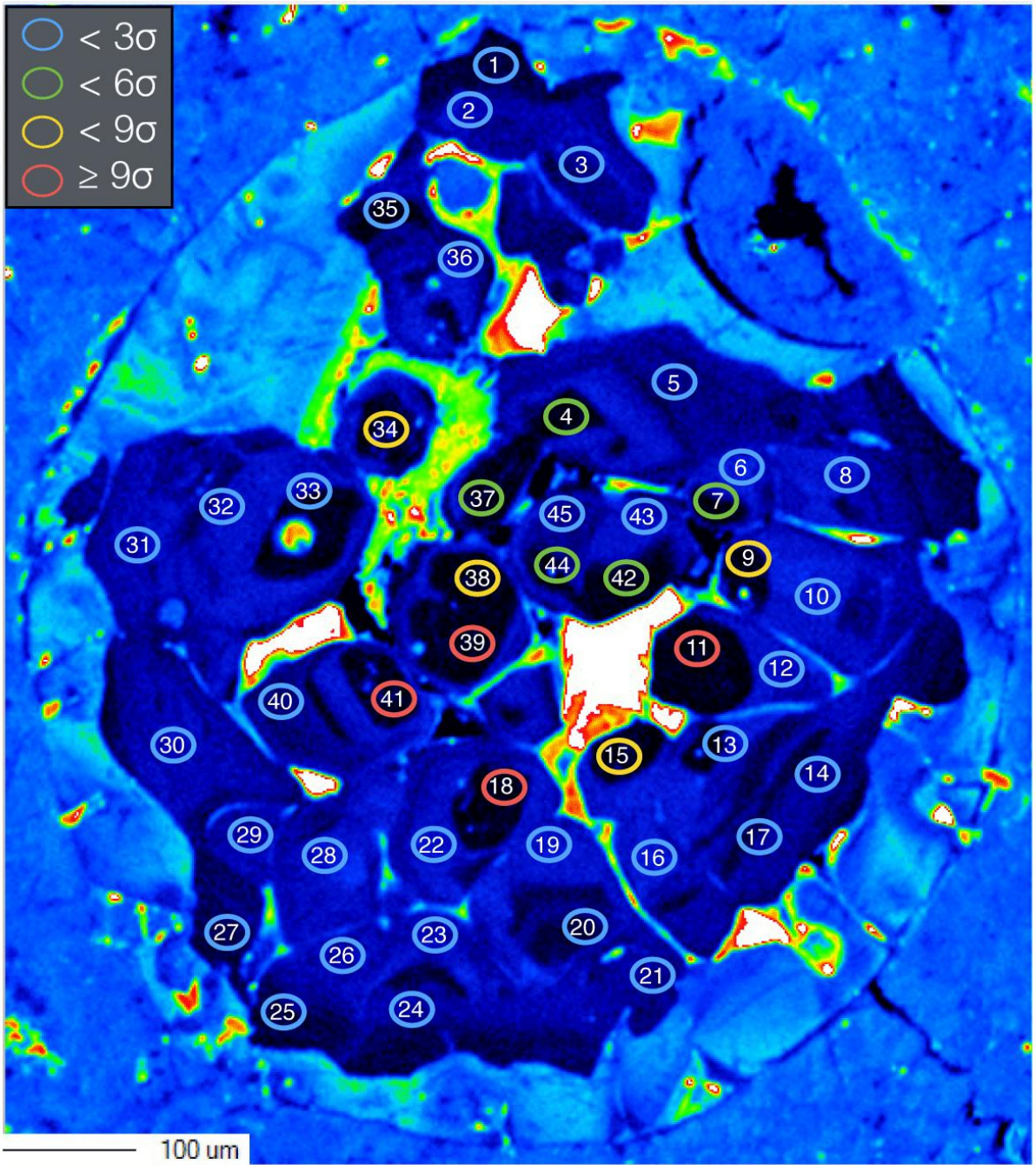
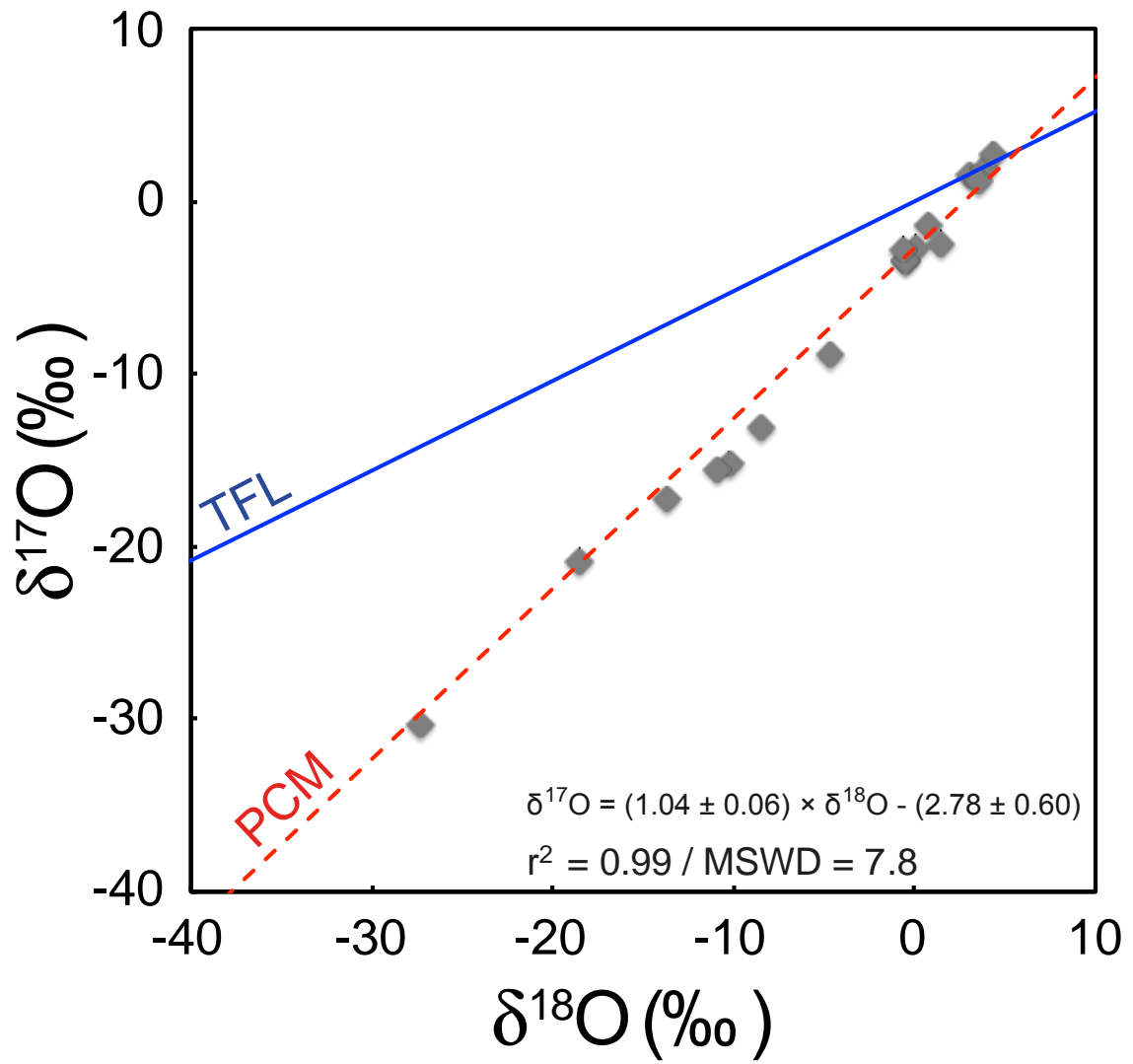


Fig. 5

519
520
521



522
 523
 524
 525
 526
 527
 528
 529

Fig. 6

chondrite	chondrule#	olivine#	n	$\delta^{18}\text{O}\text{‰}$	2σ	$\delta^{17}\text{O}\text{‰}$	2σ	$\Delta^{17}\text{O}\text{‰}$	2σ
NWA5958	Ch-1(P)	host	35	-4.99	0.25	-8.61	0.71	-6.02	0.72
		relict		-0.48	0.22	-3.49	0.56	-3.24	0.57
		relict		0.05	0.25	-2.67	0.75	-2.69	0.76
		relict		3.06	0.26	1.56	0.59	-0.03	0.60
		relict		-0.46	0.28	-3.42	0.63	-3.18	0.65
		relict		3.90	0.26	1.87	0.66	-0.15	0.68
		relict		0.74	0.22	-1.39	0.68	-1.77	0.69
		relict		1.46	0.25	-2.42	0.75	-3.18	0.76
		relict		-0.63	0.28	-2.86	0.88	-2.54	0.89
		relict		4.30	0.25	2.75	0.68	0.52	0.70
		relict		3.49	0.25	1.15	0.72	-0.67	0.73
NWA5958	Ch-7(P)	host	41	-4.90	0.23	-8.82	0.63	-6.27	0.64
		relict		-10.26	0.37	-15.15	0.68	-9.81	0.71
		relict		-10.91	0.26	-15.51	0.57	-9.83	0.59
		relict		-13.70	0.24	-17.23	0.76	-10.11	0.77
		relict		-18.49	0.42	-20.82	0.79	-11.20	0.82
NWA5958	Ch-2(P)	host	25	1.97	0.26	-1.97	0.66	-3.00	0.67
		relict		-27.35	0.23	-30.34	0.63	-16.12	0.64
		relict		-4.63	0.27	-8.85	0.68	-6.44	0.69
		relict		-8.50	0.23	-13.16	0.65	-8.75	0.66

Table 1: Oxygen isotopic compositions of host and relict olivine grains in chondrules of chondrite NWA 5958. Relict grains correspond to those with low Ti contents and $\Delta^{17}\text{O}$ values outside 3σ of the average homogenous chondrule phase $\Delta^{17}\text{O}$ value (Ushikubo et al., 2012).

References

- Aléon J. & Bourrot-Denise M., 2008, Mineralogy and petrography of a spectacular refractory inclusion that underwent chondrule formation (abstract #1638). 39th Lunar and Planetary Science Conference. CD-ROM.
- Baecker, B., Rubin, A.E., Wasson, J.T., 2017. Secondary melting events in Semarkona chondrules revealed by compositional zoning in low-Ca pyroxene. *Geochim. Cosmochim. Acta* 211, 256–279. doi:10.1016/j.gca.2017.05.013
- Batanova, V.G., Sobolev, A.V., Kuzmin, D.V., 2015. Trace element analysis of olivine: High precision analytical method for JEOL JXA-8230 electron probe microanalyser. *Chemical Geology* 419, 149–157. doi:10.1016/j.chemgeo.2015.10.042
- Chaussidon, M., Libourel, G., Krot, A.N., 2008. Oxygen isotopic constraints on the origin of magnesian chondrules and on the gaseous reservoirs in the early Solar System. *72*, 1924–1938. doi:10.1016/j.gca.2008.01.015
- Clayton, R.N., 2003. Oxygen Isotopes in Meteorites, In *Treatise on Geochemistry*, Volume 1. Editor: Andrew M. Davis. Executive Editors: Heinrich D. Holland and Karl K. Turekian. 129-142. doi:10.1016/b0-08-043751-6/01063-x
- Cohen, B.A., Hewins, R.H., Alexander, C.M.O., 2004. The formation of chondrules by open-system melting of nebular condensates. *Geochim. Cosmochim. Acta* 68, 1661–1675. doi:10.1016/j.gca.2003.09.009
- Ebel, D.S., 2006. Condensation of rocky material in astrophysical environments. In *Meteorites and the Early Solar System II*, D. S. Lauretta and H. Y. McSween Jr. (eds.), University of Arizona Press, Tucson, 943 pp., p.253-277.
- Ebel, D.S., Grossman, L., 2000. Condensation in dust-enriched systems. *Geochim. Cosmochim. Acta* 64, 339–366. doi:10.1016/s0016-7037(99)00284-7
- Eiler, J.M., 2001. Oxygen Isotope Variations of Basaltic Lavas and Upper Mantle Rocks. *Reviews in Mineralogy and Geochemistry* 43, 319–364. doi:10.2138/gsrmg.43.1.319
- Friend P., Hezel D.C., Mucershi D., 2016, The conditions of chondrule formation, Part II: Open System, *Geochim. Cosmochim. Acta* 173, 198-209.
- Fokin, V.M., Zanotto, E.D., Yuritsyn, N.S., Schmelzer, J.W.P., 2006. Homogeneous crystal nucleation in silicate glasses: A 40 years perspective. *Journal of Non-Crystalline Solids* 352, 2681–2714. doi:10.1016/j.jnoncrysol.2006.02.074
- Greenwood, R.C., Burbine, T.H., Miller, M.F., Franchi, I.A., 2016. Melting and differentiation of early-formed asteroids: The perspective from high precision oxygen isotope studies. *Chemie der Erde - Geochemistry* 1–43. doi:10.1016/j.chemer.2016.09.005
- Hewins, R. H., Connolly, H. C., Logfren, G. E. J., and Libourel, G., 2005, Experimental Constraints on Chondrules Formation, Chondrites and the Protoplanetary Disk, ASP Conference Series, Vol. 341, San Francisco: Astronomical Society of the Pacific, Hawai'i, p. 286.
- Hezel D. C., Palme H., Brenker F. E., and Nasdala L. 2003. Evidence for fractional condensation and reprocessing at high temperatures in CH chondrites. *Meteoritics & Planetary Science* 38:1199–1215.
- Hezel, D. C., Palme, H., Nasdala, L., and Brenker, F. E., 2006. Origin of SiO₂-rich components in ordinary chondrites. *Geochemica and Cosmochemica Acta* 70, 1548-1564.
- Hezel D.C., Palme H., 2007. The conditions of chondrule formation, Part 1: Closed system. *Geochim. Cosmochim. Acta* 71, 4092-4107. doi: 10.1016/j.gca.2007.06.035
- Jacquet, E., Alard, O., Gounelle, M., 2015. Trace element geochemistry of ordinary chondrite chondrules: The type I/type II chondrule dichotomy. *Geochim. Cosmochim. Acta* 155, 47–67. doi:10.1016/j.gca.2015.02.005
- Jacquet, E., Alard, O., Gounelle, M., 2012. Chondrule trace element geochemistry at the mineral scale. *Meteoritics & Planetary Science* 47, 1695-1714. doi:10.1111/maps.12005
- Jacquet, E., Barrat, J.-A., Beck, P., Caste, F., Gattacceca, J., Sonzogni, C., Gounelle, M., 2016. Northwest Africa 5958: A weakly altered CM-related ungrouped chondrite, not a CI3. *Meteorit Planet Sci* 51, 851–869. doi:10.1111/maps.12628

- Jacquet, E., Marrocchi, Y., 2017. Chondrule heritage and thermal histories from trace element and oxygen isotope analyses of chondrules and amoeboid olivine aggregates. *Meteorit Planet Sci* 58, 3451–23. doi:10.1111/maps.12985
- Jones, R.H., 2012. Petrographic constraints on the diversity of chondrule reservoirs in the protoplanetary disk. *Meteoritics & Planetary Science* 47, 1176–1190. doi:10.1111/j.1945-5100.2011.01327.x
- Jones, R.H., 1996. FeO-rich, porphyritic pyroxene chondrules in unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta* 60, 3115–3138. doi:10.1016/0016-7037(96)00152-4
- Jones, R.H., Leshin, L.A., Guan, Y., Sharp, Z.D., 2004. Oxygen isotope heterogeneity in chondrules from the Mokoia CV3 carbonaceous chondrite. *Geochim. Cosmochim. Acta* 68, 3423–3438. doi:10.1016/j.gca.2004.01.013
- Jones, R. H. and Scott, E. R. D., 1989, Petrology and thermal history of type IA chondrules in the Semarkona (LL3.0) chondrite, Lunar and Planetary Science Conference 19th, Lunar Planet. Inst., Houston, 523-536
- Kimura, M., Grossman, J.N., Weisberg, M.K., 2011. Fe-Ni metal and sulfide minerals in CM chondrites: An indicator for thermal history. *Meteoritics & Planetary Science* 46, 431–442. doi:10.1111/j.1945-5100.2010.01164.x
- Kita, N.T., Nagahara, H., Tachibana, S., Tomomura, S., Spicuzza, M.J., Fournelle, J.H., Valley, J.W., 2010. High precision SIMS oxygen three isotope study of chondrules in LL3 chondrites: Role of ambient gas during chondrule formation. *Geochim. Cosmochim. Acta* 74, 6610–6635. doi:10.1016/j.gca.2010.08.011
- Krot A. N. and Keil K. 2002. Anorthite-rich chondrules in CR and CH carbonaceous chondrites: Genetic link between Ca, Al-rich inclusions and ferromagnesian chondrules. *Meteoritics & Planetary Science* 37:91–111.
- Krot, A.N., Petaev, M.I., Russel, S.S., Itoh, S., Fagan, T.J., Yurimoto, H., Chizmadia, L., Weisberg, M.K., Komatsu, M., Ulyanov, A.A., Keil, K., 2004. Amoeboid olivine aggregates and related objects in carbonaceous chondrites: records of nebular and asteroid processes. *Chemie der Erde - Geochemistry* 64, 185–239. doi:10.1016/j.chemer.2004.05.001
- Krot A. N., Amelin Y., Bland P., Ciesla F. J., Connelly J., Davis A. M., Huss G. R., Hutcheon I. D., Makide K., Nagashima K., Nyquist L. E., Russell S. S., Scott E. R. D., Thrane K., Yurimoto H., and Yin Q.-Z. 2009. Origin and chronology of chondritic components: A review. *Geochimica et Cosmochimica Acta* 73:4963–4997.
- Kunihiro, Tak, Rubin, A.E., Wasson, J.T., 2005. Oxygen-isotopic compositions of low-FeO relicts in high-FeO host chondrules in Acfer 094, a type 3.0 carbonaceous chondrite closely related to CM. *Geochim. Cosmochim. Acta* 69, 3831–3840. doi:10.1016/j.gca.2005.01.031
- Kunihiro, Takuya, Rubin, A.E., McKeegan, K.D., Wasson, J.T., 2004. Oxygen-isotopic compositions of relict and host grains in chondrules in the Yamato 81020 CO3.0 chondrite. *Geochim. Cosmochim. Acta* 68, 3599–3606. doi:10.1016/j.gca.2004.02.011
- Lemelle, L., Guyot, F., Leroux, H., Libourel, G., 2001. An experimental study of the external reduction of olivine single crystals. *American Mineralogist* 86, 47–54. doi:10.2138/am-2001-0106
- Leroux, H., Libourel, G., Lemelle, L., Guyot, F., 2003. Experimental study and TEM characterization of dusty olivines in chondrites: Evidence for formation by in situ reduction. *Meteoritics & Planetary Science* 38, 81–94. doi:10.1111/j.1945-5100.2003.tb01047.x
- Libourel, G., 1999. Systematics of calcium partitioning between olivine and silicate melt: implications for melt structure and calcium content of magmatic olivines. *Contrib Mineral Petrol* 136, 63–80. doi:10.1007/s004100050524
- Libourel, G., Chaussidon, M., 2011. Oxygen isotopic constraints on the origin of Mg-rich olivines from chondritic meteorites. *Earth Planet. Sci. Lett.* 301, 9–21. doi:10.1016/j.epsl.2010.11.009
- Libourel, G., Krot, A., Tissandier, L., 2006. Role of gas-melt interaction during chondrule formation. *Earth and Planetary Science Letters* 251, 232–240. doi:10.1016/j.epsl.2006.09.011
- Libourel, G., Krot, A.N., 2007. Evidence for the presence of planetesimal material among the precursors of magnesian chondrules of nebular origin. *Earth and Planetary Science Letters* 254, 1–8. doi:10.1016/j.epsl.2006.11.013

- McCanta M.C., Beckett J.R. & Stolper E.M. (2016) Correlations and zoning patterns of phosphorous and chromium in olivine from H chondrites and the LL chondrite Sermakona. *Meteoritics & Planetary Science* 51, 520-546.
- Marrocchi Y., Chaussidon M., Piani L. and Libourel G. (2016) Early scattering of the solar protoplanetary disk recorded in meteoritic chondrules. *Sci. Adv.* 2, e1601001.
- Marrocchi, Y., Bekaert, D.V., Piani, L., 2018. Origin and abundance of water in carbonaceous asteroids. *Earth and Planetary Science Letters* 482, 23–32. doi:10.1016/j.epsl.2017.10.060
- Marrocchi, Y., Chaussidon, M., 2015. A systematic for oxygen isotopic variation in meteoritic chondrules. *Earth Planet. Sci. Lett.* 430, 308–315. doi:10.1016/j.epsl.2015.08.032
- Marrocchi, Y., Libourel, G., 2013. Sulfur and sulfides in chondrules. *Geochim. Cosmochim. Acta* 119, 117–136. doi:10.1016/j.gca.2013.05.020
- Misawa K. and Nakamura N. 1988. Demonstration of REE fractionation among individual chondrules from the Allende (CV3) chondrite. *Geochimica et Cosmochimica Acta* 52:1699–1710.
- Nagahara, H., 1981. Evidence for secondary origin of chondrules. *Nature* 292, 135–136. doi:10.1038/292135a0
- Pack, A., Palme, H., 2003. Partitioning of Ca and Al between forsterite and silicate melt in dynamic systems with implications for the origin of Ca, Al-rich forsterites in primitive meteorites. *Meteoritics & Planetary Science* 38, 1263-1281. doi:10.1111/j.1945-5100.2003.tb00312.x
- Pack, A., Palme, H., Shelley, J.M.G., 2005. Origin of chondritic forsterite grains. *Geochim. Cosmochim. Acta* 69, 3159–3182. doi:10.1016/j.gca.2005.01.013
- Pack, A., Yurimoto, H., Palme, H., 2004. Petrographic and oxygen-isotopic study of refractory forsterites from R-chondrite Dar al Gani 013 (R3.5–6), unequilibrated ordinary and carbonaceous chondrites. *Geochim. Cosmochim. Acta* 68, 1135–1157. doi:10.1016/j.gca.2003.07.014
- Petaev, M.I., Wood J.A., 2005. Meteoritic Constraints on Temperatures, Pressures, Cooling Rates, Chemical Compositions and Modes of Condensation in the Solar Nebula, In *Chondrites and the Protoplanetary Disk*, ASP Conference Series, Vol. 341, Proceedings of a workshop held 8-11 November 2004 in Kaua'i, Hawai'i. Edited by Alexander N. Krot, Edward R. D. Scott, and Bo Reipurth. San Francisco: Astronomical Society of the Pacific, p.373
- Piani, L., Marrocchi, Y., Libourel, G., Tissandier, L., 2016. Magmatic sulfides in the porphyritic chondrules of EH enstatite chondrites. *Geochim. Cosmochim. Acta* 195, 84–99. doi:10.1016/j.gca.2016.09.010
- Rambaldi, E.R., 1981. Relict grains in chondrules. *Nature* 293, 558–561. doi:10.1038/293558a0
- Richet, P., Bottinga, Y., Javoy, M., 1977. A Review of Hydrogen, Carbon, Nitrogen, Oxygen, Sulphur, and Chlorine Stable Isotope Fractionation Among Gaseous Molecules. *Annu. Rev. Earth Planet. Sci.* 5, 65–110. doi:10.1146/annurev.ea.05.050177.000433
- Rudraswami, N.G., Ushikubo, T., Nakashima, D., Kita, N.T., 2011. Oxygen isotope systematics of chondrules in the Allende CV3 chondrite: High precision ion microprobe studies. *Geochim. Cosmochim. Acta* 75, 7596–7611. doi:10.1016/j.gca.2011.09.035
- Russell S. S., MacPherson G. J., Leshin L. A., and McKeegan K. D. 2000. ¹⁶O enrichments in aluminum-rich chondrules from ordinary chondrites. *Earth and Planetary Science Letters* 184:57–74.
- Russell, S.S., Krot, A.N., Huss, G.R, Keil K., Itoh S., Yurimoto H., MacPherson G.J., 2005, The genetic relationship between refractory inclusions and chondrules. In *Chondrites and the Protoplanetary Disk*, ASP Conference Series, Vol. 341, Proceedings of a workshop held 8-11 November 2004 in Kaua'i, Hawai'i. Edited by Alexander N. Krot, Edward R. D. Scott, and Bo Reipurth. San Francisco: Astronomical Society of the Pacific, 2005, p.317.
- Ruzicka, A., Floss, C., Hutson, M., 2012. Amoeboid olivine aggregates (AOAs) in the Efremovka, Leoville and Vigarano (CV3) chondrites: A record of condensate evolution in the solar nebula. *Geochim. Cosmochim. Acta* 79, 79–105. doi:10.1016/j.gca.2011.11.043
- Ruzicka, A., Hiyagon, H., Hutson, M., Floss, C., 2007. Relict olivine, chondrule recycling, and the evolution of nebular oxygen reservoirs. *Earth and Planetary Science Letters* 257, 274–289. doi:10.1016/j.epsl.2007.02.037
- Ryerson, F.J., Durham, W.B., Cherniak, D.J., Lanford, W.A., 1989. Oxygen diffusion in olivine: Effect of oxygen fugacity and implications for creep. *Journal of Geophysical Research* 94, 4105–4118. doi:10.1029/JB094iB04p04105

- Sakyi P.A., Tanaka R., Kobayashi K., Nakamura E., 2012. Inherited Pb isotopic records in olivine antecryst-hosted melt inclusions from Hawaiian lavas. *Geochim. Cosmochim. Acta* 95, 169-195.
- Schrader, D.L., Connolly, H.C., Jr, Lauretta, D.S., Nagashima, K., Huss, G.R., Davidson, J., Domanik, K.J., 2013. The formation and alteration of the Renazzo-like carbonaceous chondrites II: Linking O-isotope composition and oxidation state of chondrule olivine. *Geochim. Cosmochim. Acta* 101, 302–327. doi:10.1016/j.gca.2012.09.045
- Schrader, D.L., Connolly, H.C., Jr, Lauretta, D.S., Zega, T.J., Davidson, J., Domanik, K.J., 2015. The formation and alteration of the Renazzo-like carbonaceous chondrites III: Toward understanding the genesis of ferromagnesian chondrules. *Meteorit Planet Sci* 50, 15–50. doi:10.1111/maps.12402
- Schrader, D.L., Nagashima, K., Waitukaitis, S.R., Davidson, J., McCoy, T.J., Connolly, H.C., Lauretta, D.S., 2018. The retention of dust in protoplanetary disks: Evidence from agglomeratic olivine chondrules from the outer Solar System. *Geochim. Cosmochim. Acta* 223, 405–421. doi:10.1016/j.gca.2017.12.014
- Scott, E., Jones, R.H., 1990. Disentangling nebular and asteroidal features of C03 carbonaceous chondrite meteorites. exported from rebase *Geochim. Cosmochim. Acta* 54, 2485–2502. doi:10.1016/0016-7037(90)90235-d
- Sobolev, A.V., Asaflov, E.V., Gurenko, A.A., Arndt, N.T., Batanova, V.G., Portnyagin, M.V., Garbe-Schönberg, D., Krasheninnikov, S.P., 2016. Komatiites reveal a hydrous Archaean deep-mantle reservoir. *Nature* 531, 628–632. doi:10.1038/nature17152
- Soulié, C., Libourel, G., Tissandier, L., 2016. Olivine dissolution in molten silicates: An experimental study with application to chondrule formation. *Meteoritics & Planetary Science* 52, 225–250. doi:10.1111/maps.12792
- Sugiura, N., Petaev, M.I., Kimura, M., Miyazaki A., Hiyagon, H., 2009. Nebular history of amoeboid olivine aggregates. *Meteoritics & Planetary Science* 44, 559–572. doi:10.1111/j.1945-5100.2009.tb00751.x
- Tenner, T.J., Nakashima, D., Ushikubo, T., Kita, N.T., Weisberg, M.K., 2015. Oxygen isotope ratios of FeO-poor chondrules in CR3 chondrites: Influence of dust enrichment and H₂O during chondrule formation. *Geochim. Cosmochim. Acta* 148, 228–250. doi:10.1016/j.gca.2014.09.025
- Tenner, T.J., Ushikubo, T., Kurahashi, E., Kita, N.T., Nagahara, H., 2013. Oxygen isotope systematics of chondrule phenocrysts from the CO3.0 chondrite Yamato 81020: Evidence for two distinct oxygen isotope reservoirs. *Geochim. Cosmochim. Acta* 102, 226–245. doi:10.1016/j.gca.2012.10.034.
- Tenner T.J., Ushikubo T., Nakashima D., Schrader D.L., Weisberg M.K., Kimura M., Kita N.T. (In press) Oxygen Isotope Characteristics of Chondrules from Recent Studies by Secondary Ion Mass Spectrometry. In *Chondrules and the protoplanetary disk*. Cambridge University Press.
- Tissandier, L., Libourel, G., Robert, F., 2002. Gas-melt interactions and their bearing on chondrule formation. *Meteoritics & Planetary Science* 37, 1377–1389. doi:10.1111/j.1945-5100.2002.tb01035.x
- Ushikubo, T., Kimura, M., Kita, N.T., Valley, J.W., 2012. Primordial oxygen isotope reservoirs of the solar nebula recorded in chondrules in Acfer 094 carbonaceous chondrite. *Geochim. Cosmochim. Acta* 90, 242–264. doi:10.1016/j.gca.2012.05.010
- Verdier-Paoletti, M.J., Marrocchi, Y., Avice, G., Roskosz, M., Gurenko, A., Gounelle, M., 2017. Oxygen isotope constraints on the alteration temperatures of CM chondrites. *Earth Planet. Sci. Lett.* 458, 273–281. doi:10.1016/j.epsl.2016.10.055
- Weisberg, M.K., Connolly, H.C., Ebel, D.S., 2004. Petrology and origin of amoeboid olivine aggregates in CR chondrites. *Meteoritics & Planetary Science* 39, 1741–1753. doi:10.1111/j.1945-5100.2004.tb00070.x
- Whattam, S.A., Hewins, R.H., 2009. Granoblastic olivine aggregates as precursors of Type I chondrules: An experimental test. *Geochim. Cosmochim. Acta* 73, 5460–5482. doi:10.1016/j.gca.2009.04.014
- Whattam, S.A., Hewins, R.H., Cohen, B.A., Seaton, N.C., Prior, D.J., 2008. Granoblastic olivine aggregates in magnesian chondrules: Planetesimal fragments or thermally annealed solar nebula condensates? *Earth and Planetary Science Letters* 269, 200–211. doi:10.1016/j.epsl.2008.02.013

Yurimoto, H., Wasson, J.T., 2002. Extremely rapid cooling of a carbonaceous-chondrite chondrule containing very ^{16}O -rich olivine and a ^{26}Mg -excess. *Geochim. Cosmochim. Acta* 66, 4355–4363. doi:10.1016/s0016-7037(02)01218-8