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Oxygen isotope constraints on the alteration temperatures of CM chondrites

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Highlights:

Carbonate O-isotope compositions of 9 CMs define a continuous trend crossing the TFL.

This mass independent trend matches that defined by bulk CM-COs and matrix (BMC trend).

CM water defines a trend (CMW) parallel to the bulk-matrix-carbonate trend (BMC).

The distance between BMC and CMW is directly related to CM alteration temperature.

Carbonates precipitated at higher temperatures than previously inferred (50-300°C).

56 value of Ca-carbonates could be a reliable proxy of the degree of alteration experienced by
57 CM chondrites.

58 **1- Introduction**

59 Some chemically primitive chondrites have recorded intense episodes of hydrothermal
60 alteration that have strongly modified their petrography. This is the case of CM and CI
61 chondrites that are made mostly of secondary minerals such as phyllosilicates, carbonates, and
62 oxides (Brearley, 2006). Though it is widely accepted that hydrothermal alteration occurred
63 on their respective parent-bodies (see however Ciesla, 2003), the physics, chemistry and
64 duration of that process is still poorly understood (Brearley, 2006).

65 Constraining the hydrothermal alteration of water-rich bodies is important for multiple
66 reasons. First, a large number of asteroids have been affected by hydrothermal alteration, as
67 recorded by the ubiquitous detection of spectroscopic hydration features (Rivkin et al., 2002).
68 Second, fluid circulation can potentially modify the nature and abundance of organics
69 (Ehrenfreund et al., 2001; Le Guillou et al., 2012) and can change the L/D ratio of amino
70 acids (Burton et al., 2014). Because water-rich bodies are the source of water and organics on
71 Earth (Marty et al., 2016), hydrothermal alteration of their parent bodies must have played a
72 key role in Earth's evolution by incorporating and deeply stabilizing water in the structure of
73 minerals. In this study, the physicochemical conditions that prevailed during fluid circulation
74 on water-rich parent bodies is constrained by the oxygen isotopic composition of calcium
75 carbonates of a diversity of CM chondrites.

76 In this context, carbonates are of particular interest among secondary minerals,
77 because they: (i) are ubiquitous in CM and CI chondrites (Johnson and Prinz, 1993; Lee et al.,
78 2014), and (ii) directly precipitate from the alteration fluids (Alexander et al., 2015). The
79 oxygen isotopic composition of carbonates therefore represents a valuable proxy of the

80 isotopic evolution of the fluid phase during alteration. In particular, oxygen isotopic
81 compositions are used both as a geothermometer and to track the degree of homogenization of
82 the two dominant oxygen reservoirs present in chondrites, namely minerals and ices.

83 CM chondrites are a target of choice because they represent 25 % of all carbonaceous
84 chondrite falls and may represent the dominant type of mineral matter in the outer Solar
85 System (Gounelle et al., 2005). Despite the fact that they form a well-identified chemical
86 group, CM chondrites record highly variable extents of hydrothermal alteration. Some CM
87 chondrites are almost completely hydrated and have been classified as type 1 (Zolensky et al.,
88 1997) while others retain mineralogies similar to the most primitive (unaltered) chondrites
89 (e.g., Hewins et al., 2014; Marrocchi et al., 2014). Based on several proxies, such as the
90 abundance of secondary minerals or the bulk oxygen isotopic composition, two alteration
91 indexes have been proposed for classifying CM chondrites (Browning et al., 1996; Rubin et
92 al., 2007). In this study we analyzed chondrites spanning the entire alteration index proposed
93 by Rubin et al. (2007). Consequently, an attempt is made to correlate the extent of alteration
94 to the properties of the fluid as recorded by the oxygen isotopic composition of carbonates.

95 Oxygen isotopes are useful for constraining the timing of secondary phase
96 precipitation. For instance, the first *in situ* oxygen isotope analyses of carbonates suggested
97 the existence of two populations of calcites characterized by distinct O-isotopic compositions
98 (Lee et al., 2013; Tyra et al., 2012; 2016). However, additional data later indicated that
99 carbonate O-isotopic compositions form a continuous trend on either side of the terrestrial
100 fractionation line (TFL) in a typical three-isotope plot ($\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$; Horstmann et al., 2014).
101 These observations could reflect continuous changes of the temperature of alteration and/or
102 the composition of the fluid from which the carbonates precipitated. In any case, the alteration
103 conditions of CM chondrites remain largely under-constrained and require more *in situ* data.
104 Here, we report a systematic study of the oxygen isotopic compositions of carbonates in nine

105 CM chondrites with degrees of alteration ranging from the least altered known to date (Paris
106 2.7-2.8; Bourot-Denise et al., 2010; Hewins et al., 2014; Marrocchi et al., 2014; Rubin, 2015)
107 to the most altered (ALH 88045 CM1; Zolensky et al., 1997).

108 **2 - Material and Methods**

109 We studied carbonates in 6 polished thick sections (Paris, Murchison, Cold
110 Bokkeveld, Nogoya, Murray and Jbilet Winselwan) and 3 polished thin sections (QUE93005,
111 ALH88045 and Pollen). Samples were coated with a 20 nm thick carbon layer to avoid
112 charging effects when exposed to an electron beam. Subsequent detailed observations of
113 carbonates of the sections were performed at the Muséum National d'Histoire Naturelle of
114 Paris using a TESCAN Vega 2LSU scanning electron microscope (SEM). Quantitative
115 analyses of the chemical compositions of carbonates were performed using a CAMECA SX-
116 Five electron microprobe (Camparis, Paris, France) at the University of Paris VI. A 10 nA
117 focused beam (~4 µm) accelerated to 15 kV was used for spot analyses of carbonates with 20s
118 analysis time.

119 *In situ* oxygen isotopic measurements were performed at the CRPG-CNRS Nancy
120 using a Cameca 1280HR secondary ion mass spectrometer (SIMS) following previously
121 described procedures (Rollion-Bard and Marin-Carbone, 2011). We used a Cs⁺ primary ion
122 beam (15 keV, ~0.4nA) and an electron flow parallel to the sample surface to neutralize
123 charge excesses. ¹⁶O⁻, ¹⁷O⁻ and ¹⁸O⁻ were detected in multi-collection mode using a Faraday
124 cup (FC) for ¹⁶O⁻ and two Electron Multipliers (EMs) for ¹⁷O⁻ and ¹⁸O⁻. The EMs Dead-time
125 correction was applied to mass ¹⁷O⁻ and ¹⁸O⁻. Each acquisition lasted for 420 s, consisting of
126 300 s of pre-sputtering and 120 s of simultaneous continuous measurement over the three
127 collectors. To prevent the ¹⁶OH interference in the ¹⁷O⁻ peak, the exit slit was adjusted on the
128 central multiplier to obtain a mass resolution of ≈6000 for ¹⁷O⁻. As an additional safeguard

129 against the ^{16}OH interference in the $^{17}\text{O}^-$ peak, we used a N_2 trap to reduce the pressure in the
130 analysis chamber (i.e., $< 3 \times 10^{-9}$ mbar).

131 Instrumental Mass Fractionation (IMF) was determined by replicate analyses of four
132 terrestrial standards: olivine, quartz, magnetite and calcite. The O-isotopic ratios of CM
133 calcites were normalized to that of the terrestrial calcite standard. We also considered a linear
134 deviation of the IMF over time, which enabled us to interpolate its values at the date and time
135 of acquisition of each measurement. Moreover, any measurement showing a column pressure
136 significantly above to 3.10^{-9} mbar in the analysis chamber, or a singular count-rate of the
137 mass $^{16}\text{O}^-$ (generally correlated to an overlapping), was considered biased and therefore
138 excluded from the results reported here.

139 The 2σ errors were 0.2-1.8 ‰ for $\delta^{17}\text{O}$, 0.2-2.4 ‰ for $\delta^{18}\text{O}$, and 0.3-1.2 ‰ for $\Delta^{17}\text{O}$
140 (representing deviation from the TFL, defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$). The error on
141 $\Delta^{17}\text{O}$ was calculated by propagating the errors on $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, and the standard deviation of
142 $\Delta^{17}\text{O}$ values of the four terrestrial standards. After each SIMS measurement session, all
143 analytical spots were observed *via* SEM in order to check if the beam overlapped the matrix
144 or any adjacent silicate; any such measurement was rejected.

145

146 **3- Results**

147 CM chondrites are generally complex breccias with lithologies characterized by
148 significant mineralogical and chemical variations (Zolensky et al., 1997; Brearley, 2006).
149 However, at the exception of the Paris section, all the CM chondrites surveyed in this study
150 did not present brecciations features. Although some rare occurrences of dolomite were
151 observed among the CM chondrites surveyed in this study, the vast majority of carbonates

152 observed were calcium carbonates (Fig. 1). We thus focused our isotopic survey only on
153 calcium carbonates and performed 91 SIMS measurements in the nine different CM
154 chondrites selected for this study. Multiple measurements (up to three) were made on grains
155 of sufficient size allowed it. Results are reported in Table 1.

156

157 - *Paris* (CM 2.7-2.8; $n = 14$)

158 Paris Ca-carbonates exhibit $\delta^{18}\text{O}$ values from 26.5 (± 0.8) to 38.7 (± 0.7) ‰ and $\delta^{17}\text{O}$
159 values from 15.5 (± 0.6) to 23.1 (± 0.6) ‰. All $\Delta^{17}\text{O}$ values plot above the TFL and range from
160 0.9 (± 0.3) to 6.1 (± 0.4) ‰ with an average value of 3.2 (± 1.3) ‰. No distinct populations of
161 calcium carbonates are observed within our data, which rather defines a continuous trend.

162 - *Murchison* (CM 2.5; $n = 9$)

163 Murchison Ca-carbonates exhibit $\delta^{18}\text{O}$ values from 22.6 (± 0.4) to 33.2 (± 0.3) ‰ and
164 $\delta^{17}\text{O}$ values from 12.1 (± 1.0) to 18.5 (± 0.8) ‰ (Fig. 2a). All our measurements display
165 positive $\Delta^{17}\text{O}$ values from 0.4 (± 0.8) to 3.0 (± 0.6) ‰ with a mean value of 1.3 (± 0.9) ‰. As
166 in Paris, no distinct populations of Ca-carbonates emerged from our measurements.

167 - *Murray* (CM 2.4-2.5; $n = 10$)

168 Murray Ca-carbonates exhibit $\delta^{18}\text{O}$ values from 24.3 (± 2.4) to 39.7 (± 2.4) ‰ and $\delta^{17}\text{O}$
169 from 14.2 (± 1.8) to 22.6 (± 1.7) ‰. $\Delta^{17}\text{O}$ values range from 1.3 (± 1.2) to 4.2 (± 1.2) ‰ with an
170 average value of 2.3 (± 1.2) ‰. Ca-Carbonates of Murray present a discontinuous trend with
171 two distinct populations characterized by average O-isotopic compositions of $\delta^{18}\text{O} = 37.0$
172 (± 2.4) ‰ and $\delta^{17}\text{O} = 21.7$ (± 1.8) ‰ ($n = 8$) and $\delta^{18}\text{O} = 25.3$ (± 2.4) ‰ and $\delta^{17}\text{O} = 15.3$ (± 1.8)
173 ‰ ($n = 2$).

174 - *Pollen (CM 2.4; n = 4)*

175 Pollen Ca-carbonates exhibit $\delta^{18}\text{O}$ values from 35.4 (± 0.4) to 37.7 (± 0.4) ‰ and $\delta^{17}\text{O}$
176 values from 16.6 (± 0.7) to 20.0 (± 0.8) ‰. Three of these four measurements are grouped
177 below the TFL with $\Delta^{17}\text{O}$ values ranging from -1.8 (± 0.6) to -1.2 (± 0.6) ‰ whereas one
178 measurement displays a positive $\Delta^{17}\text{O}$ value of 1.6 (± 0.7) ‰.

179 - *Jbilet Winselwan (CM 2.0-2.3; n = 18)*

180 Jbilet Winselwan Ca-carbonates exhibit $\delta^{18}\text{O}$ values from 27.0 (± 0.7) to 38.0 (± 0.7) ‰
181 and $\delta^{17}\text{O}$ from 14.7 (± 0.8) to 19.3 (± 0.7) ‰. Our data defines a trend that crosses the TFL,
182 described by $\Delta^{17}\text{O}$ values that range from -1.1 (± 0.5) to 1.4 (± 0.5) ‰ with a mean value of 0.2
183 (± 0.7) ‰. The whole dataset is centered on a mean O-isotopic composition of $\delta^{18}\text{O} = 33.5$
184 (± 0.6) ‰ and $\delta^{17}\text{O} = 18.0$ (± 0.4) ‰.

185 - *Cold Bokkeveld (CM 2.2; n = 10)*

186 Cold Bokkeveld Ca-carbonates exhibit $\delta^{18}\text{O}$ values from 20.6 (± 1.0) to 28.2 (± 1.0) ‰
187 and $\delta^{17}\text{O}$ values from 10.6 (± 0.7) to 15.7 (± 0.8) ‰. All values plot near the TFL, with
188 $\Delta^{17}\text{O}$ values ranging from -0.7 (± 0.5) to 1.7 (± 0.5) ‰ and an average value of 0.3 (± 0.9) ‰.
189 Our measurements show no evidence for distinct populations of Ca-carbonates.

190 - *Nogoya (CM 2.2; n = 6)*

191 Nogoya Ca-carbonates exhibit $\delta^{18}\text{O}$ values from 21.9 (± 0.6) to 38.9 (± 0.7) ‰ and $\delta^{17}\text{O}$
192 values from 9.1 (± 0.7) to 19.1 (± 0.5) ‰ (Fig. 2b). They plot on both sides of the TFL with
193 $\Delta^{17}\text{O}$ values ranging from -2.3 (± 0.5) to 0.3 (± 0.5) ‰ (average value of -1.1 (± 1.0) ‰). Most
194 of the measurements in Nogoya are similar to a mean O-isotopic composition characterized
195 by $\delta^{18}\text{O} = 35.5$ (± 0.6) ‰ and $\delta^{17}\text{O} = 18.3$ (± 0.4) ‰. However, two measurements display

196 lighter isotopic compositions with $\delta^{18}\text{O} = 21.9 (\pm 0.6) \text{‰}$, $\delta^{17}\text{O} = 9.1 (\pm 0.7) \text{‰}$ and $\delta^{18}\text{O} =$
197 $23.5 (\pm 0.6) \text{‰}$, $\delta^{17}\text{O} = 10.4 (\pm 0.7) \text{‰}$.

198 - *QUE 93005 (CM 2.1; n = 10)*

199 QUE 93005 Ca-carbonates exhibit $\delta^{18}\text{O}$ values from $16.6 (\pm 0.3)$ to $33.4 (\pm 0.4) \text{‰}$ and
200 $\delta^{17}\text{O}$ values from $5.8 (\pm 0.6)$ to $16.5 (\pm 0.7) \text{‰}$. The $\Delta^{17}\text{O}$ falls on both sides of the TFL with
201 values ranging from $-3.4 (\pm 0.6) \text{‰}$ to $0.3 (\pm 0.5) \text{‰}$ (average value of $-1.8 (\pm 1.3) \text{‰}$). The
202 measurements are relatively scattered and show no evidence for the existence of two distinct
203 populations of Ca-carbonates.

204 - *ALH 88045 (CM 1; n = 10)*

205 ALH 88045 Ca-carbonates exhibit $\delta^{18}\text{O}$ values $16.1 (\pm 0.4)$ to $29.6 (\pm 0.4) \text{‰}$ and $\delta^{17}\text{O}$
206 values from $6.6 (\pm 0.6)$ to $13.8 (\pm 0.6) \text{‰}$. The $\Delta^{17}\text{O}$ values range from $-3.7 (\pm 1.2)$ to -1.6
207 $(\pm 1.2) \text{‰}$ with an average value of $-2.7 (\pm 0.8) \text{‰}$. Our data define a continuous trend of O-
208 isotopic compositions.

209

210 **4- Discussion**

211 *4-1 O-isotopic evolution of the alteration fluids*

212 The oxygen isotopic compositions of Ca-carbonates determined for the nine selected
213 CMs in this study define a trend that crosses the TFL, with a general relationship described by
214 $\delta^{17}\text{O} = 0.71 (\pm 0.06) \times \delta^{18}\text{O} - 6.5 (\pm 1.9)$ (2σ , $R^2 = 0.83$, $\text{MSWD} = 5.4$, Fig. 3). This
215 continuous trend does not fall on the slope-1 line defined by chondrule anhydrous minerals in
216 CM chondrites (Clayton & Mayeda, 1984). In addition, it does not follow a mass-dependent
217 fractionation trend (Fig. 3b), implying that the carbonate O-isotopic compositions were not
218 affected by terrestrial alteration (Tyra *et al.*, 2012) and did not result from fluid circulation

219 along a temperature gradient, which would have produced a trend with a slope of 0.52. This
220 trend is similar, within 2σ errors, to regressions reported by other studies (e.g., $\delta^{17}\text{O} = 0.65 (\pm$
221 $0.03) \times \delta^{18}\text{O} - 5.4 (\pm 1.2)$; Horstmann et al., 2014). However, our regression is affected by the
222 significant deviation of the Paris carbonates from the general trend with a slight increase of
223 their $\delta^{17}\text{O}$ at high $\delta^{18}\text{O}$ (Fig. 3). This deviation has been repeatedly observed for other
224 chondrites (i.e., Maribo and LON 94091; see Horstmann et al., 2014; Lee et al., 2013) and
225 may result from the contribution of interstellar $^{17,18}\text{O}$ -enriched water to the alteration fluids
226 from which these specific carbonates precipitated (Horstmann et al., 2014; Vacher et al.,
227 2016). If Paris is excluded, our dataset define a linear relationship [$\delta^{17}\text{O} = 0.66 (\pm 0.05) \times$
228 $\delta^{18}\text{O} - 4.7 (\pm 1.5)$ (2σ , $R^2 = 0.87$, $\text{MSWD} = 3.3$)] that is indistinguishable, within 2σ errors,
229 from the trend defined by the bulk O-isotopic compositions of CM chondrites [$\delta^{17}\text{O} = 0.68 (\pm$
230 $0.02) \times \delta^{18}\text{O} - 3.9 (\pm 0.2)$; Fig. 3; (Clayton and Mayeda, 1999)]. Henceforth, we do not
231 consider Paris when comparing the slope defined by our data with those reported in literature,
232 but we include Paris to determine the temperature of carbonate precipitation. The general
233 trend defined by Ca-carbonates has a slope of 0.66 (excluding Paris) or 0.71 (including Paris)
234 that does not correspond to mass-dependent fractionation defined by a slope of 0.52 in a $\delta^{17}\text{O}$ -
235 $\delta^{18}\text{O}$ diagram due to mass differences between oxygen isotopes. This implies that carbonate
236 O-isotopic compositions were set during alteration by progressive equilibration of a primitive
237 $^{17,18}\text{O}$ -rich fluid with ^{16}O -rich anhydrous minerals (Benedix et al., 2003; Clayton and Mayeda,
238 1999; 1984). This assertion is supported by the continuous trend observed between Ca-
239 carbonates and the bulk O-isotopic compositions of CM chondrites (Fig. 3, Clayton and
240 Mayeda, 1999).

241 In addition to the general Ca-carbonate trend, *in situ* analyses reveal additional oxygen
242 isotopic variations within the different CMs that can be summarized as follow (Table 1):

243 (i) a low variability around an average value (e.g., Pollen), (ii) an important dispersion along a
244 continuous trend (e.g., QUE 93005) and (iii) two distinct populations, each of them showing
245 low O-isotopic variability (e.g., Murray). Our isotopic survey also reveals that no CM shows
246 $\delta^{18}\text{O}$ variations in Ca-carbonates at constant $\Delta^{17}\text{O}$, even those defining a continuous trend
247 with extreme oxygen isotopic variations (e.g., QUE 93005 with $\delta^{18}\text{O}$ ranging from 16.6 to
248 33.4 ‰; Table 1). These results support models in which Ca-carbonates could have recorded
249 either a single continuous precipitation event or successive episodic precipitation events
250 (Benedix et al., 2003; De Leuw et al., 2010). In such schemes, $^{17,18}\text{O}$ -rich Ca-carbonates
251 correspond to early precipitates from primitive fluids that did not suffer significant O-isotopic
252 exchanges with ^{16}O -rich anhydrous silicates (Benedix et al., 2003; Clayton and Mayeda,
253 1999; Lee et al., 2013; Tyra et al., 2016; 2012). Conversely, lighter isotopic compositions
254 indicate that carbonates formed following significant alteration, and as the O-isotopic
255 compositions of fluids converged toward the typical ^{16}O -rich values of anhydrous silicates.
256 Both bulk and *in situ* data (Fig. 2 & 3) thus identify O-isotopic exchange between ^{16}O -rich
257 silicates and $^{17,18}\text{O}$ -rich fluid as the key process that controls the O-isotopic composition of
258 the alteration fluids from which the Ca-carbonates precipitated.

259

260 *4-2 Isotopic trends defined by the components of CM chondrites in the three-isotope plot*

261 The formation temperature of Ca-carbonate in CM chondrites remains disputed, and
262 proposed values have varied significantly over past decades. More generally, the sequence of
263 formation of both carbonates and other secondary phases (e.g., serpentine, tochilinite) is
264 poorly understood. Initially, the temperature of Ca-carbonate precipitation was estimated to
265 be in the range 0-25°C based on the O-isotopic equilibrium between Ca-carbonates and
266 phyllosilicates in the Murchison meteorite (Clayton and Mayeda, 1984). Later measurements

267 suggested instead that most Ca-carbonates in CM chondrites are not in isotopic equilibrium
268 with co-existing phyllosilicates (Benedix et al., 2003). However, a few CM chondrites (i.e.,
269 Nogoya and Murchsion; Baker et al., 2002; Benedix et al., 2003) present mass-dependent
270 relationships between secondary phases that have been used to determine the alteration
271 temperature. This approach led to contrasting results with alteration temperatures ranging
272 from 0-20°C (Benedix et al., 2003) to 80-120°C (Baker et al., 2002). Finally, clumped-isotope
273 thermometry of CO₂ (Δ^{47}) was applied to CM secondary phases, providing formation
274 temperature estimates of 20-70°C for Ca-carbonate precipitation (Guo and Eiler, 2007).

275 Our data do not fall on a mass-dependent line (i.e., slope 0.52). This confirms the lack
276 of general oxygen isotopic equilibrium between Ca-carbonates and phyllosilicates in the
277 matrix (Fig. 2a; Clayton and Mayeda, 1999), even for Nogoya contrary to previous results
278 (slope 0.59; Fig. 2b; Benedix et al., 2003). Therefore, our results confirm that the difference
279 in $\delta^{18}\text{O}$ between coexisting secondary phases cannot be used to estimate a hypothetical single
280 alteration temperature of CM chondrites. On the other hand, considering the entire dataset, a
281 continuous trend is observed between O-isotopic signatures of bulk CO-CM chondrites and
282 Ca-carbonates (Fig. 3 & 4a), which implies that serpentines also broadly align along this trend
283 as they represent the main component of CM chondrites (Brearley, 2006). Previous matrix
284 measurements present $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values along this trend, plotting in-between Ca-carbonates
285 and bulk CO-CM chondrites (Fig. 2 & 4a; Clayton and Mayeda, 1999; 1984). Note that the
286 data dispersion around this line will be discussed in details below (see sub-section 4.3), and
287 may possibly be used to derive a relatively precise timing of phase precipitation.

288 O-isotopic compositions of CM water (hereafter CMW) have been determined either
289 by isotopic mass balance calculations and/or direct measurements (Baker et al., 2002; Clayton
290 and Mayeda, 1999; 1984; Guo and Eiler, 2007). Compilation of all available data defines a

291 line ($R^2 = 0.99$; Fig. 4a) with a slope of 0.69 that is indistinguishable, within error, from the
292 bulk-matrix-carbonates trend (hereafter BMC; slope 0.66 ± 0.05), but has a different intercept
293 (i.e., -2.12 for CMW vs. -4.7 for BMC; Fig. 4a). The meaning of this line is uncertain, but we
294 will now explore the possibility that this line was formed by equilibration between two
295 distinct reservoirs of water and silicates.

296

297 *4-3 Average alteration temperature of CM chondrites and its variability*

298 In the context of closed-system isotopic exchange between two distinct reservoirs,
299 parallel trends in a three-isotope diagram, and the positions of the data points along them, can
300 be interpreted in different ways, as summarized in Fig. 5 (Matsuhisa et al., 1979). At a
301 constant temperature, but variable water/rock ratio or equilibration degree, the isotopic
302 evolution of the fluid and silicate reservoirs will follow parallel lines in a $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ diagram,
303 with the distance between the lines corresponding to the equilibrium isotopic fractionation
304 factor α (Fig. 5a,b). As fractionation depends on temperature, if equilibration occurs at
305 different temperatures but at a fixed water/rock ratio and equilibrium degree, a set of parallel
306 lines will be generated with their respective distances decreasing with increasing equilibration
307 temperature (Fig. 5c). If formation temperature varies between samples, each couple of water
308 and rock data will sit on their own parallel lines and the whole data set will not be seen as
309 parallel straight lines anymore. That the BMC and the CMW trends are straight lines strongly
310 suggests that a single temperature (or a very narrow temperature interval) was recorded by
311 this large dataset. This also implies that we can use the distance between BMC and CMW to
312 estimate the average formation temperatures of secondary phases, as the distance between
313 both lines results from the mass-dependent isotopic fractionation occurring, at low
314 temperature, between carbonates and water and between serpentine and water, respectively

315 (Chacko et al., 2001; Kim and O'Neil, 1997; Matsuhisa et al., 1979). Hence, we first consider
316 the distance between the BMC and CMW trends to obtain an average formation temperature
317 of Ca-carbonates and serpentine. Monte Carlo simulations were then used to account for the
318 statistical scattering of our data points around BMC. Finally, we subsequently address our
319 individual measurements to obtain a range of formation temperatures for CM Ca-carbonates.

320 We assumed that a given phase x (either Ca-carbonate or serpentine) located on the
321 BMC trend (Fig. 4a) formed from a fluid plotting along the CMW line (in other words, that
322 the formation of the secondary phases occurs at equilibrium). Although such an assumption is
323 valid for Ca-carbonates, it represents an approximation in the case of serpentines as they do
324 not precipitate directly from the alteration fluids and could thus present partial isotopic
325 equilibrium. Nonetheless, in the following, we assume complete oxygen isotopic equilibrium
326 for both Ca-carbonates and serpentines. In this case, the O-isotopic compositions of water and
327 the forming mineral are related by a mass-dependent relationship according to:

$$328 \quad \delta^{17}O_x = 0.52 \times \delta^{18}O_x + b \quad (1)$$

329 Hence, each measurement plotting on the BMC trend (phase x) is linked *via* a mass-dependent
330 relationship to a fluid composition given by the intercept with the CMW line (Fig. 4b). This
331 O-isotopic composition represents the fluid from which phase x formed, determined by:

$$332 \quad \delta^{18}O_{H_2O} = \frac{2.12 + \delta^{17}O_x - 0.52 \times \delta^{18}O_x}{0.69 - 0.52} \quad (2)$$

333 with 0.69 and 2.12 being the slope and intercept of the CMW line, respectively (Fig. 4a).
334 Because the O-isotopic fractionations between carbonates and water and between serpentine
335 and water are temperature-dependent (Chacko et al., 2001; Kim and O'Neil, 1997), the
336 determination of the formation temperature of carbonates and serpentine can be fit according
337 to a linear law:

338
$$\Delta^{18}O_{carb-H_2O} = \delta^{18}O_{carb} - \delta^{18}O_{H_2O} = 69.93 - 0.14 \times T_{carb} \quad (3)$$

339
$$\Delta^{18}O_{serp-H_2O} = \delta^{18}O_{serp} - \delta^{18}O_{H_2O} = 52.86 - 0.11 \times T_{serp} \quad (4)$$

340

341 with the formation temperatures (K) of carbonate and serpentine being:

342

343
$$T_{carb}(K) = \frac{69.93 - \delta^{18}O_{carb} + \delta^{18}O_{H_2O}}{0.14} \quad (5)$$

344
$$T_{serp}(K) = \frac{52.86 - \delta^{18}O_{serp} + \delta^{18}O_{H_2O}}{0.11} \quad (6)$$

345 The errors on the average temperature of carbonate formation have been computed by
 346 propagation of the uncertainties on $\delta^{18}O_{carb}$ following a Monte-Carlo method. In this method,
 347 random values of $\delta^{18}O_{carb}$ and $\delta^{18}O_{water}$ are chosen assuming a normal distribution law for the
 348 statistical behavior of these parameters. For each pair of values, a formation temperature was
 349 then computed according to Eqn. (5). This random process was repeated 10^4 times. This
 350 procedure demonstrates that the formation temperatures of Ca-carbonates define normal
 351 distributions with an average formation temperature of $113 \pm 54^\circ\text{C}$ (Fig. 6). Applying such a
 352 method to serpentine data, we determined its average formation temperature at around 75°C
 353 with negligible error as the uncertainties associated with the matrix O-isotopic compositions
 354 are negligible (i.e., errors are smaller than the symbols; Clayton and Mayeda, 1999).

355 This approach gives an average temperature of carbonate precipitation by assuming
 356 that they all fall on the trend defined by the statistic regression calculated from our isotopic
 357 data. However, this first approach is too simplistic as our *in situ* carbonate oxygen isotopic
 358 compositions present significant dispersions on both sides of the carbonate trend (Fig. 3).
 359 Assuming that the CMW line represents the oxygen isotopic composition of the alteration
 360 fluids at the time of the Ca-carbonate precipitation, it is thus possible to determine their

361 precipitation temperatures by connecting the O-isotopic compositions of individual Ca-
362 carbonates to the CMW line according to the mass-dependent isotopic fractionation between
363 carbonate and water (Eqn. 5; see example in Fig. 5a). The underlying assumption here is that
364 the position of the CMW line did not change significantly over the course of the alteration
365 history of the system, which will be discussed below. Application to this method to the
366 carbonates reported in this study provides precipitation temperatures ranging from -50 to
367 275°C with a typical error on temperature estimate of $\pm 44^\circ\text{C}$ (Fig. 7). The important
368 variations in temperature are not related to the errors on the O-isotopic compositions of
369 carbonates as they define a trend with MSWD > 1 (i.e., 3.3). Note that a temperature as low as
370 -50°C appears unrealistic but the important conclusion here is that a significant fraction of the
371 carbonates measured in this study formed at higher temperatures than previously thought. In
372 our sampled CM chondrites, 75% of the carbonates analyzed formed at temperatures higher
373 than 50°C . Moreover, 50% precipitated at temperatures $> 100^\circ\text{C}$ (Fig. 7a). Our data also
374 revealed a positive correlation between the average $\Delta^{17}\text{O}$ and the average temperature of
375 carbonate precipitation per chondrite (Fig. 8). Such a correlation may seem counterintuitive as
376 it is generally proposed that CM1 chondrites were altered at higher temperatures than CM2
377 chondrites (Zolensky et al., 1999). Our results suggest, instead, that all CM chondrites may
378 have experienced high temperature alteration, (at temperature higher than previously thought),
379 and that carbonate precipitation occurred at varying temperatures in the different CMs with
380 CM1 and CM2.1 to CM2.3 having recorded a protracted alteration during the cooling of the
381 parent body to lower temperatures than CM2.4 and higher petrographic grades (Fig. 7b). Such
382 a scheme is consistent with the $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ correlation (Fig. 9) showing that: (i) $^{17,18}\text{O}$ -rich Ca-
383 carbonates correspond to early precipitates from primitive fluids that did not yet suffer
384 significant O-isotopic exchanges with ^{16}O -rich anhydrous silicates and (ii) altered CM
385 chondrites experienced longer water-rock isotopic exchange (Fig. 4). Together, these results

386 thus suggest that O-isotopic exchange between $^{17,18}\text{O}$ -rich fluid and ^{16}O -rich anhydrous
387 silicate took place over a long period of time but that carbonate precipitation in each CM
388 occurred during punctual events in a narrow range of temperatures or, in the case of heavily
389 altered CMs, re-equilibrated over the cooling history of the parent body.

390

391 *4-4 Constraints on the formation sequence of secondary phases of CM chondrites*

392 The precipitation sequence of secondary phases during aqueous alteration of CM
393 chondrites is rather unclear. Our *in situ* dataset can be used to tell whether carbonates or
394 serpentines precipitated first. To do so, we first note that the main component of CM
395 chondrites is serpentine. In this respect, the relative position of the BCM and CMW lines
396 essentially reflects the formation temperature of these hydrous silicates. Second, a single O-
397 isotopic composition for the silicate precursor has been proposed (Clayton and Mayeda,
398 1984). Even if the precise composition of the putative anhydrous solids of each CM may
399 slightly vary, it is reasonable here to assume the single value proposed by Clayton & Mayeda
400 (1984, 1999) as an anchor point (Fig. 4a). Within this framework, the linear regression joining
401 the anhydrous silicate precursor, the bulk matrix, and carbonates will not necessarily be
402 parallel to the CMW line if carbonates formed at a different temperature than the
403 mineralogically dominant serpentine. For carbonates formed at high temperature (before
404 serpentines), the line will intersect the CMW (Fig. S1a). This intersect will provide an
405 estimate of the isotopic composition of the pristine heavy water reservoir (Fig. S1b). For
406 carbonates formed or equilibrated at the same temperature (and time) as serpentines, the two
407 lines will be parallel (Fig. S1a). Finally, for carbonates formed or equilibrated after the
408 precipitation of serpentines, the CMW and BCM lines will diverge (Fig. S1a).

409 These three behaviors are indeed observed in our data set (Fig. S1). Carbonates from
410 Paris and Murchison formed before serpentines (Fig. S1b). Carbonates from Murray and Cold
411 Bokkeveld formed at the same time (or equilibrated at the same temperature) as serpentines
412 (Fig. S1c). Finally, a significant fraction of carbonates from other samples formed after the
413 precipitation of serpentines (or equilibrated with water at lower temperatures than serpentines;
414 Fig. S1d). Our data therefore provide a fairly precise sequence of (re)precipitation of
415 secondary phases. Finally, it is of note that, from our data, the isotopic composition of the
416 heavy water that equilibrated with silicates of CM chondrites ($\delta^{18}\text{O} = 48 \text{ ‰}$, $\delta^{17}\text{O} = 31 \text{ ‰}$;
417 Fig. S1b) is reasonably consistent with, yet slightly heavier than, the initial estimate proposed
418 by (Clayton and Mayeda, 1984a): ($\delta^{18}\text{O} = 30.3 \text{ ‰}$, $\delta^{17}\text{O} = 20.2 \text{ ‰}$). If confirmed, this would
419 imply that the isotopic composition of carbonates from Murchison (and Paris) directly
420 recorded the isotopic composition of the water reservoir that altered CM chondrites.

421

422 *4-5 Implications for the alteration conditions of CM chondrites and concluding remarks*

423 Our data indicate that (i) the Ca-carbonate precipitation occurred at temperature higher
424 than previously thought and (ii) their O-isotopic compositions are a direct proxy of the degree
425 of O-isotopic exchange between ^{16}O -rich anhydrous silicates and the $^{17,18}\text{O}$ -rich fluid. Our
426 data also suggest that both CM1 and CM2 chondrites likely experienced high-temperature
427 hydrothermal alteration. Such a conclusion is in line with the similar structures and chemical
428 compositions of the insoluble organic matter (IOM) in both CM1 and CM2, which require a
429 common temperature peak (assuming similar organic precursors) for both types of chondrites
430 (Alexander and Cody, 2013; Kuga et al., 2015). Furthermore, our results demonstrate that
431 most of Ca-carbonate precipitation likely predates the formation of serpentine (Fig. 6 & 10)
432 consistent with recurring observations of Ca-carbonates pseudomorphosed by tochilinite-

433 serpentine associations (Fujiya et al., 2015; Lee et al., 2013; Marrocchi et al., 2014). For the
434 most altered CM's, a partial or total re-equilibration between carbonates and water may have
435 occurred during cooling of the parent body below temperatures of serpentine formation, as
436 recorded by our *in situ* measurements. Such low-temperature equilibration may not be
437 kinetically favored if the silicate precursor is crystalline. For instance, there is no evidence for
438 O-isotopic exchange between quartz and water up to at least 170°C, regardless of grain size
439 (Clayton et al., 1972). We note, however, that the matrix of the least altered CM, Paris, is
440 mainly composed of amorphous silicates (Leroux et al., 2015) that, relative to crystalline
441 silicates, could have faster O-isotopic exchange rates with water. Moreover, the occurrence of
442 tochilinite-cronstedite intergrowths in Paris with euhedral shapes characteristic of silicates
443 (Pignatelli et al., 2016) confirm that water-mineral interactions also occurred during the
444 alteration of CM matrices. These observations strengthen the conclusion that Ca-carbonates
445 precipitated at high temperature from alteration fluids with varying O-isotopic compositions.
446 In contrast, serpentine did not precipitate directly from the fluid, but resulted from protracted
447 interaction between water and amorphous (Le Guillou et al., 2015; Leroux et al., 2015) and/or
448 crystalline silicates (Pignatelli et al., 2016). Hence, the lower formation temperature
449 determined for serpentine relative to Ca-carbonates (Fig. 7) likely reflects the thermal
450 evolution of the CM parent body during the course of alteration. In this framework, the
451 different degrees of alteration by which CM chondrites are characterized (Fig. 4) are related
452 to (i) different durations of fluid alteration and/or (ii) heterogeneous concentrations of water
453 ice grains within the CM parent bodies.

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465

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592 **Figure caption**

593

594 **Figure 1:** Back-scattered electron micrographs of Ca-carbonates. (a) Porous Ca-carbonate
595 surrounded by a tochilinite-cronstedtite intergrowth (TCI) rim in Jbilet Winselwan (b) Porous
596 irregular Ca-carbonate surrounded by a TCI rim in Paris (c) Ca-carbonate cross-cut by
597 fractures and surrounded by a microporous rim in Cold Bokkeveld (d) Ca-carbonate in Pollen
598 surrounded by a TCI rim.

599

600 **Figure 2:** Oxygen isotopic compositions of Ca-carbonates in Murchison (a) and Nogoya (b),
601 Circles represent single carbonate measurements, while squares and triangles correspond to
602 the matrix and bulk O-isotopic compositions, respectively (Clayton & Mayeda, 1999).

603

604 **Figure 3:** Oxygen three-isotope plot for Ca-carbonates from the nine CM chondrites
605 measured in this study (data in ‰). The light grey area corresponds to the range of bulk O-
606 isotopic compositions determined for CM and CO chondrites (Clayton & Mayeda, 1999), and
607 the dark gray area corresponds to the trend defined by Ca-carbonates (excluding Paris Ca-
608 carbonates, which may reflect interstellar enrichment of alteration fluids). The terrestrial
609 fractionation line (TFL) and the Carbonaceous Chondrite Anhydrous Mineral line (CCAM)
610 are also represented.

611

612 **Figure 4:** (a) Oxygen three-isotope plot showing the general bulk-matrix-carbonate (BMC)
613 trend observed between bulk CM-CO chondrites (Clayton & Mayeda, 1999), matrix
614 phyllosilicates (Clayton *et al.*, 1984; Clayton & Mayeda, 1999) and Ca-carbonates (this
615 study). The CM Water line (CMW) corresponds to the trend defined by the O-isotopic
616 compositions of CM alteration water as determined by isotopic mass balance calculations
617 and/or direct measurements (Clayton *et al.*, 1984; Clayton & Mayeda, 1999; Baker *et al.*,
618 2002, Guo and Eiler, 2007). Both trends are parallel allowing for the determination of the
619 temperature of carbonate precipitation and serpentine formation (see text). (b). Close-up
620 showing that a given carbonate located on the BMC (red point) can be connected to the O-
621 isotopic composition of the fluid from which it precipitated (CMW line) by a mass-dependent
622 relationship. The distance between both compositions ($\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{water}}$, see text) is
623 directly related to temperature, allowing the temperature of carbonate precipitation to be
624 determined.

625

626 **Figure 5:** Theoretical considerations on the oxygen isotopic equilibration between silicates
627 and water. (a) At a fixed temperature and water/rock ratio, the isotopic evolution of the fluid
628 and the silicate reservoirs follow parallel lines in a $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ diagram as a function of the
629 reaction advancement. The distance between the two lines corresponds to the equilibrium
630 isotopic fractionation factor α . □□□ At a fixed temperature and equilibration degree, the
631 isotopic evolution of the fluid and the silicate reservoirs will follow parallel lines in a $\delta^{17}\text{O}$ -
632 $\delta^{18}\text{O}$ diagram as a function of the water/rock ratio. (c) Equilibration at varying temperature
633 but fixed water/rock ratio and equilibration degree will also generate parallel lines but with

634 their respective distances decreasing with increasing equilibration temperature. MDFL
635 corresponds to the mass-dependent fractionation line (i.e., slope 0.52).

636

637 **Figure 6:** Density distribution of the formation temperatures of carbonates (blue) and
638 serpentines (red) determined by the Monte-Carlo method (see text for further detail).

639

640 **Figure 7:** (a) Temperature of carbonate precipitation as a function of the distance between the
641 *in situ* data and the CMW trend. The temperature is calculated as detailed in Fig. 5 (see text
642 for details). The blue areas correspond to the average temperature of carbonates formation and
643 its associated error. (b) Box plots showing median, minimum, maximum, first and last
644 quartile of temperatures computed for each meteorite analyzed during this study.

645

646 **Figure 8:** Average $\Delta^{17}\text{O}$ of Ca-carbonates relative to the average temperature of carbonate
647 precipitation. A general positive trend is observed suggesting that the more altered CMs
648 experienced carbonate precipitation at lower temperature than the least altered CMs.

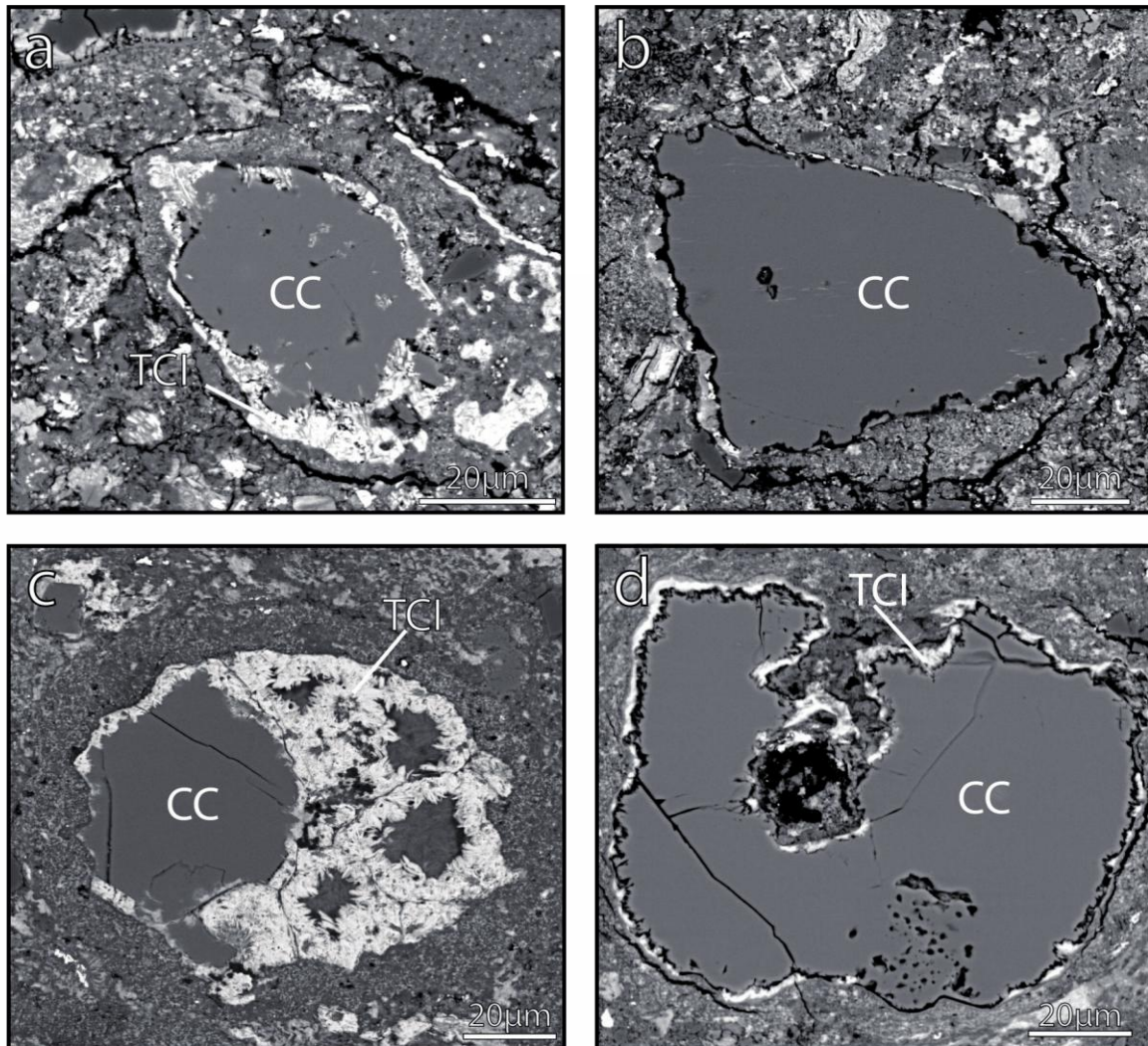
649

650 **Figure 9:** Average $\Delta^{17}\text{O}$ of Ca-carbonates relative to the Rubin's degree of alteration of the
651 CM chondrites (Rubin *et al.*, 2007). A general positive trend is observed suggesting that the
652 average $\Delta^{17}\text{O}$ could represent a valuable proxy of the degree of alteration. Jbilet Winselwan is
653 classified as a CM 2.0-2.3.

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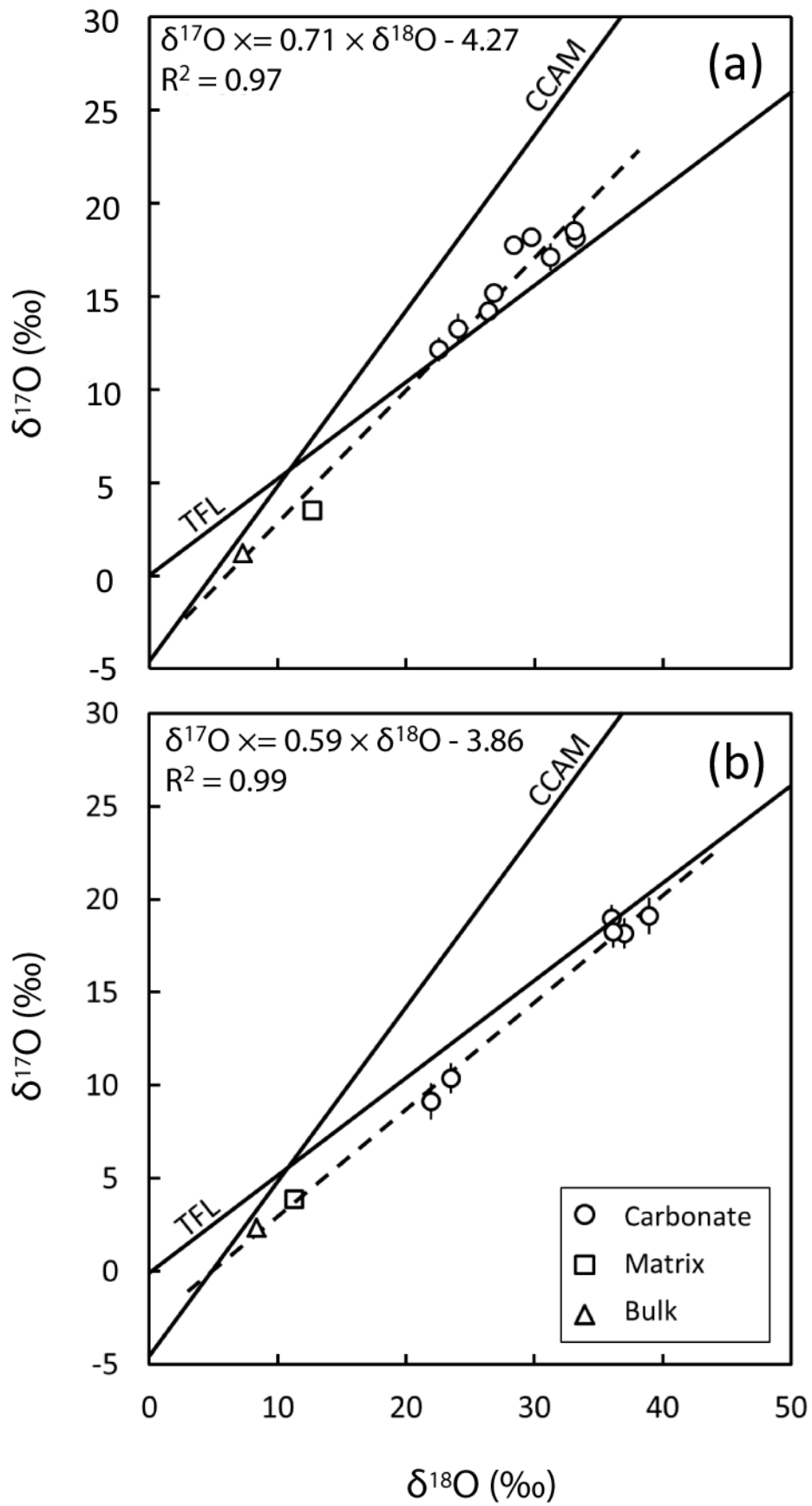


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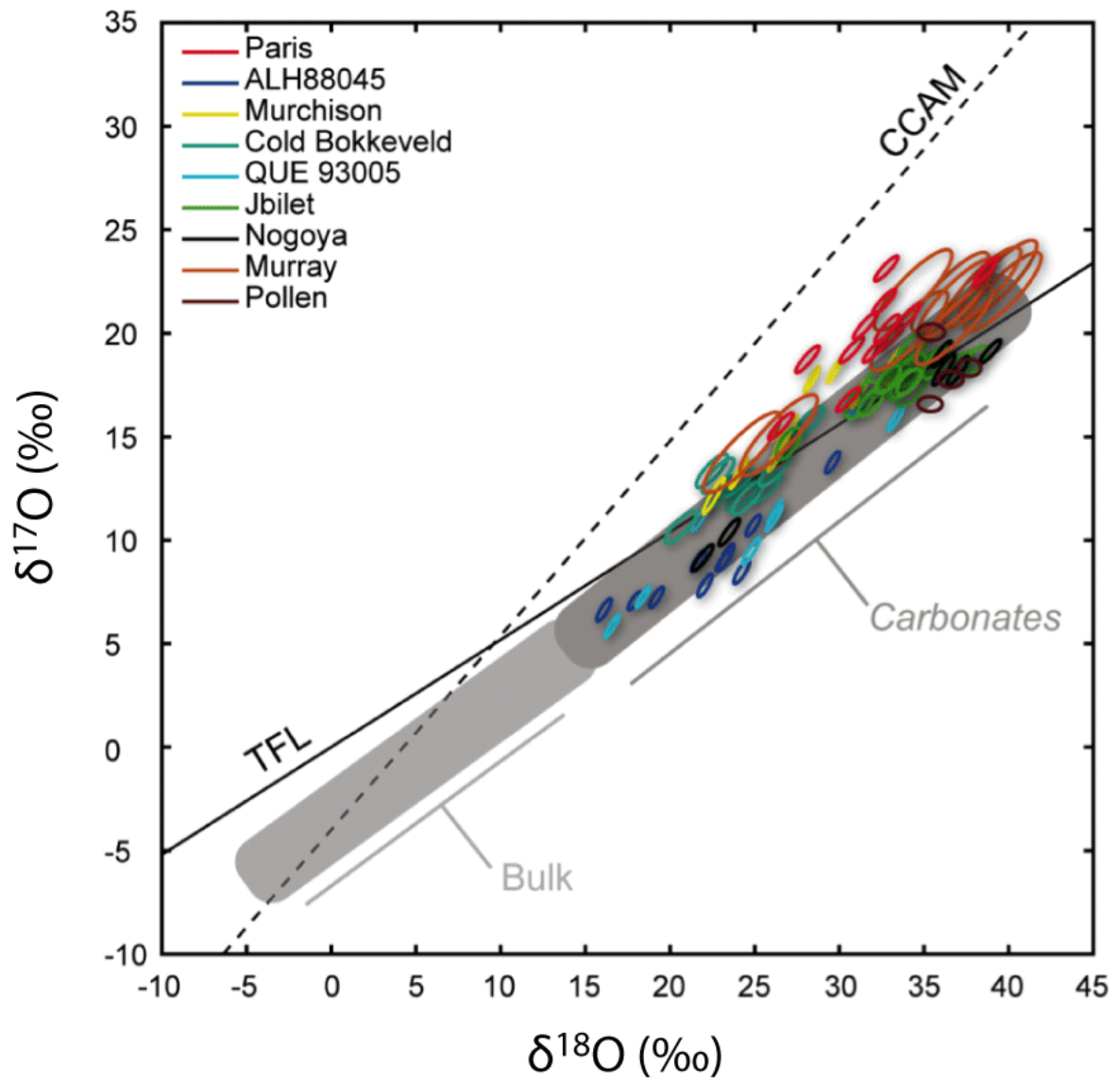
Fig. 1



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Fig. 2



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Fig. 3

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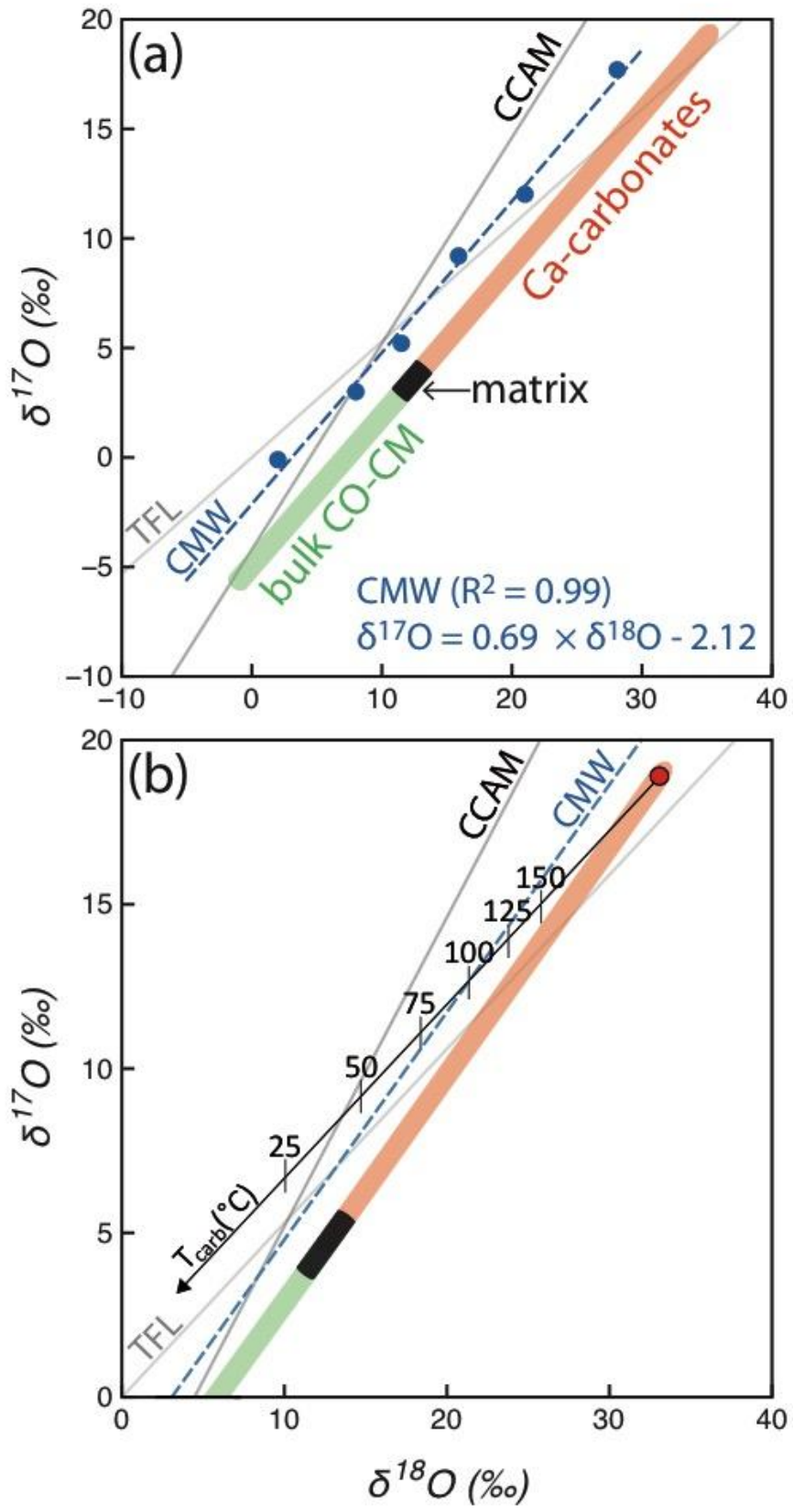
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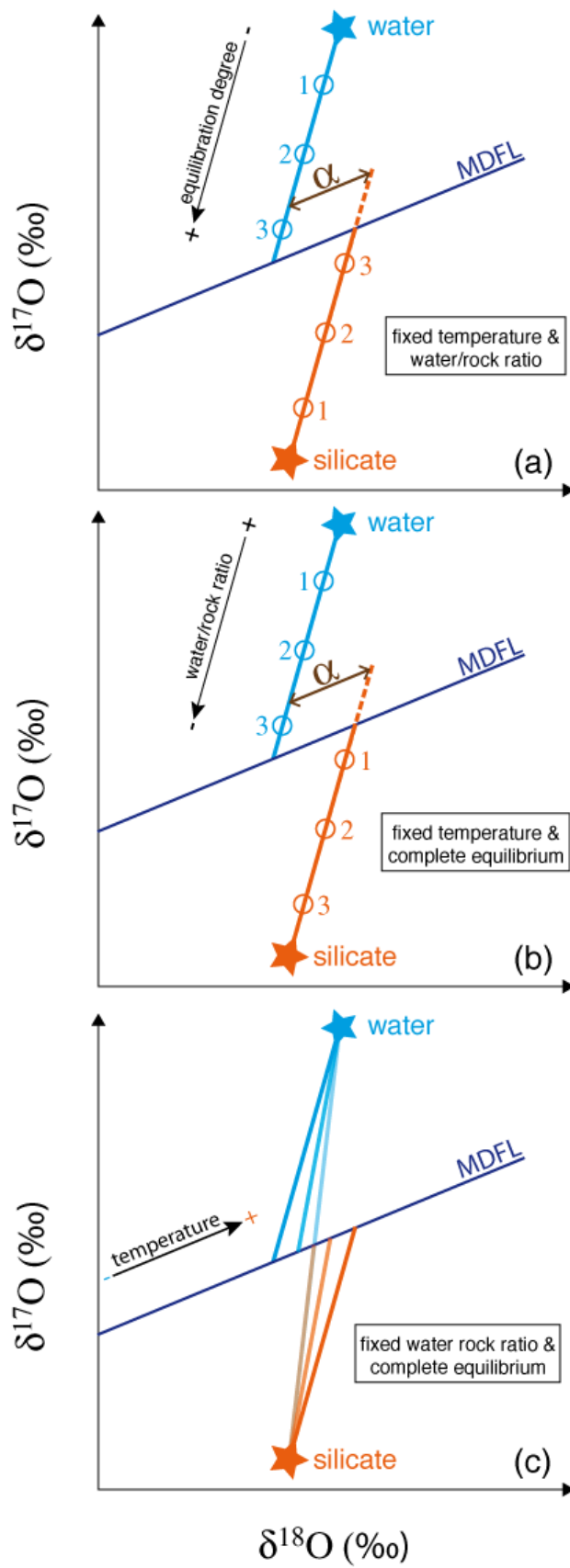


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Fig. 4

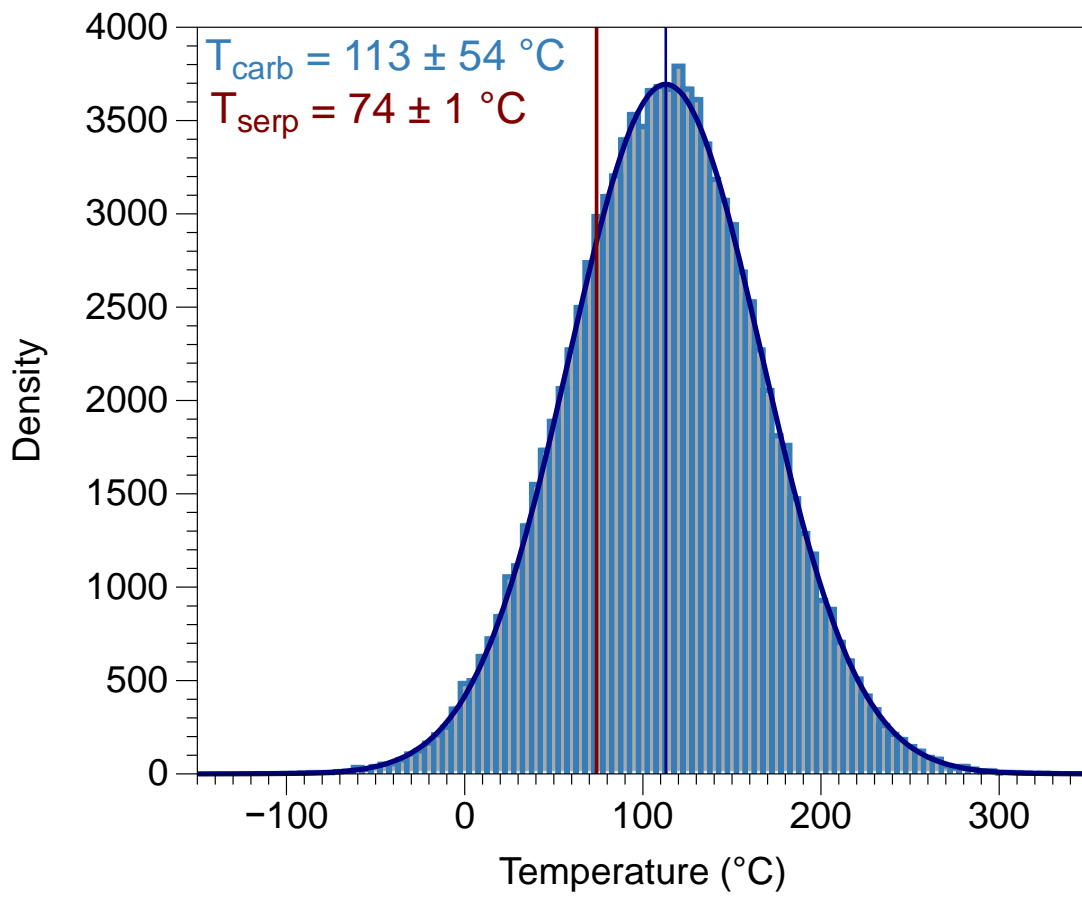


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Fig. 5

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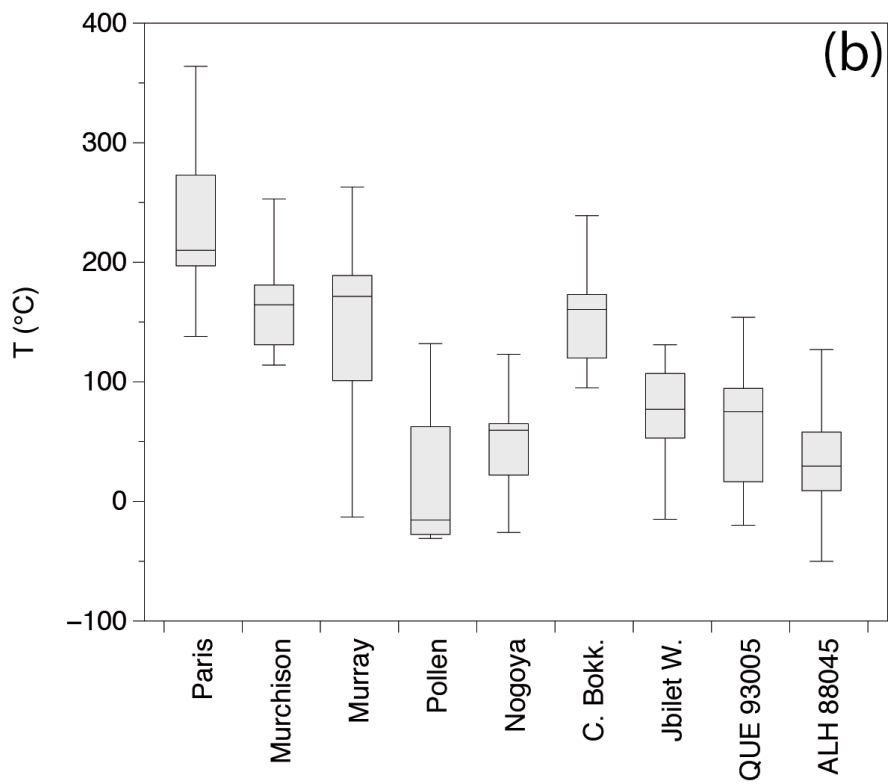
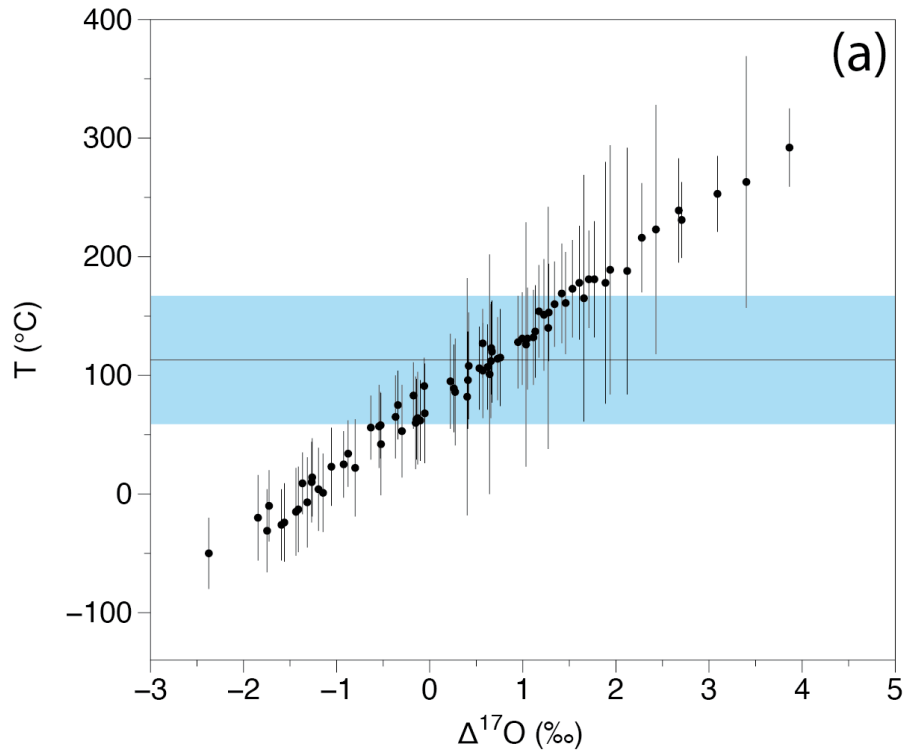
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Fig. 6



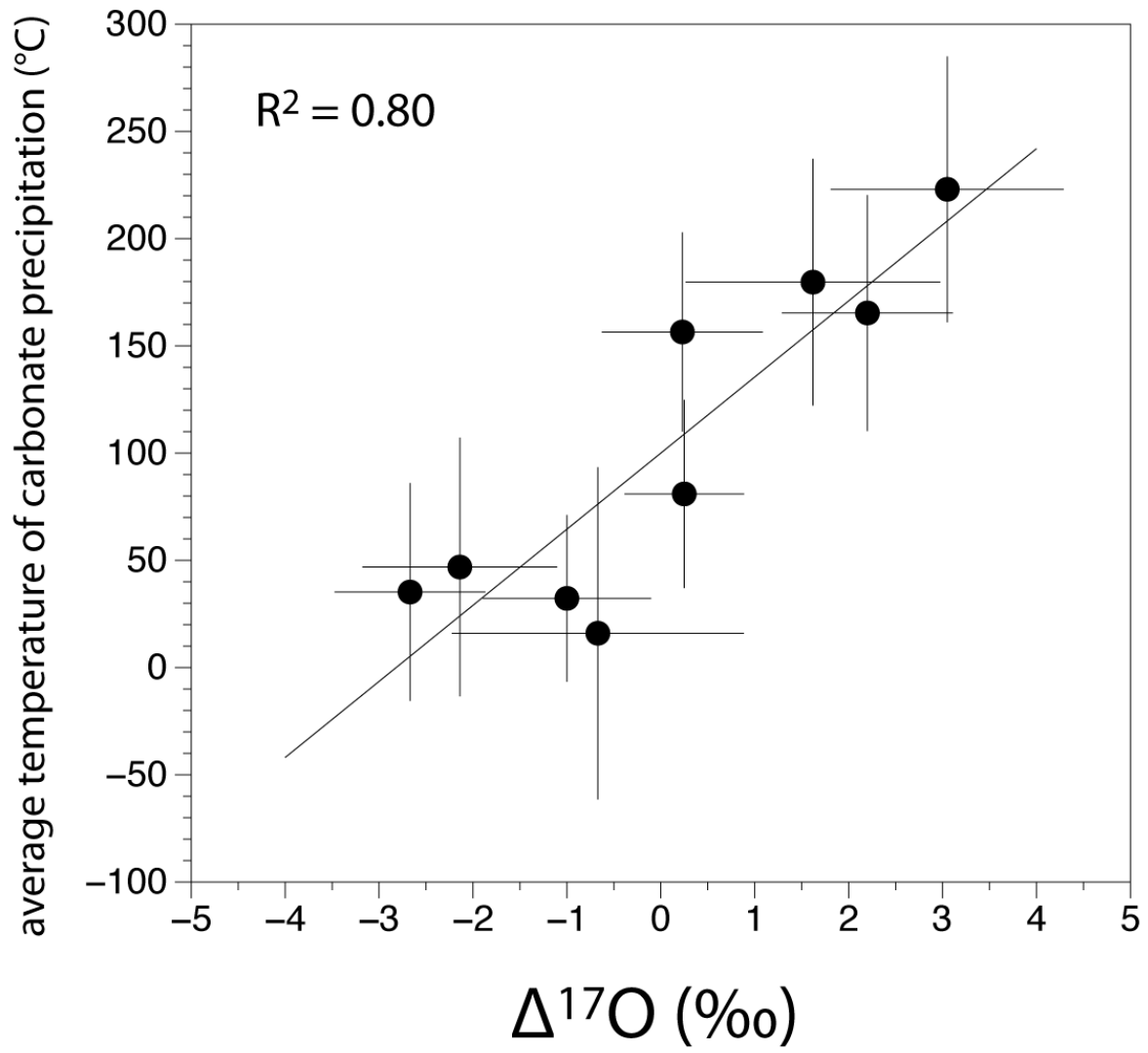
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Fig. 7



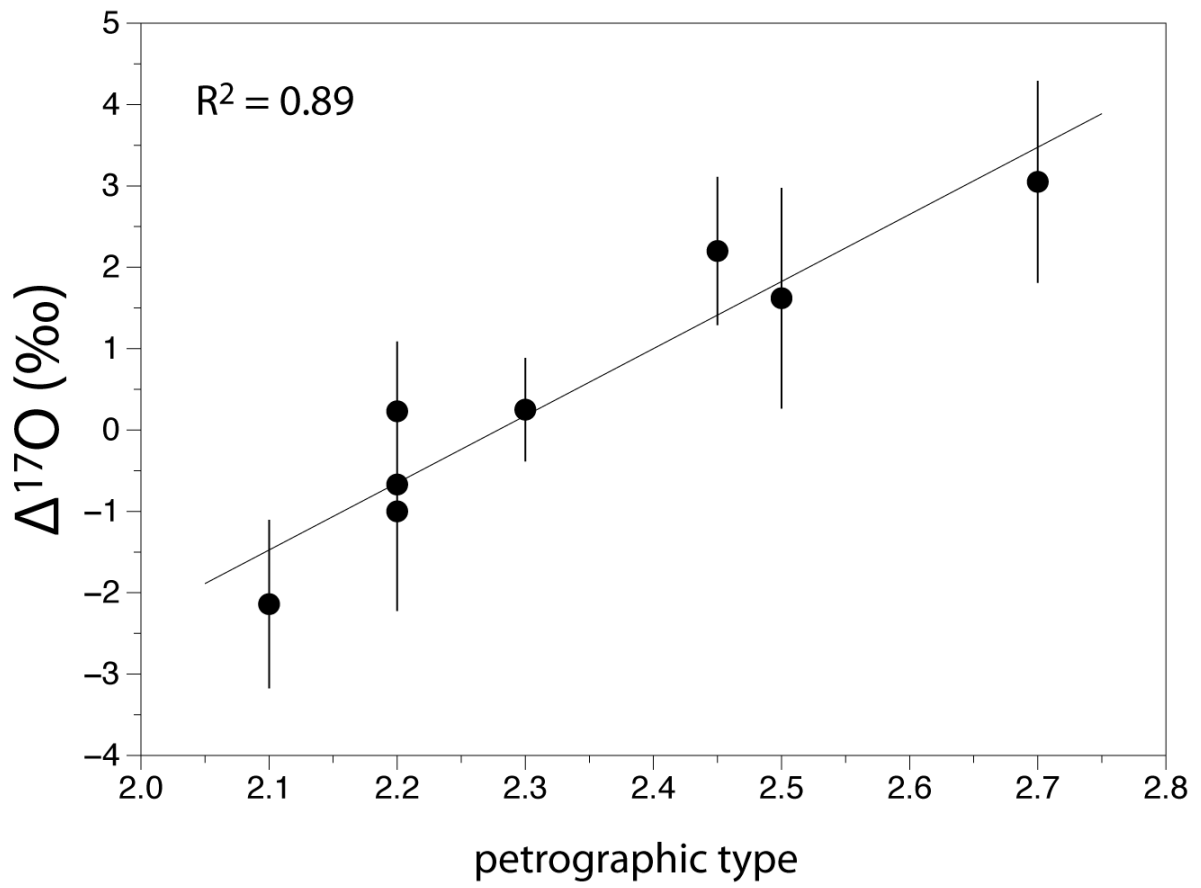
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Fig. 8



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Fig. 9

<i>chondrite</i>		$\delta^{18}\text{O}$	2σ	$\delta^{17}\text{O}$	2σ	$\Delta^{17}\text{O}$	2σ
<i>Paris (CM 2.7)</i>	Ca-Carb1a	30.5	0.7	16.8	0.5	0.9	0.3
	Ca-Carb1b	26.5	0.8	15.5	0.6	1.7	0.4
	Ca-Carb2a	33.1	0.7	19.8	0.5	2.6	0.3
	Ca-Carb2b	32.9	0.7	19.7	0.5	2.6	0.4
	Ca-Carb2b	34.1	0.7	20.8	0.6	3.1	0.4
	Ca-Carb3a	30.7	0.7	19.2	0.6	3.2	0.4
	Ca-Carb4a	32.1	0.7	19.2	0.5	2.5	0.4
	Ca-Carb4b	28.1	0.7	18.7	0.6	4.1	0.4
	Ca-Carb16a	38.6	0.7	22.8	0.6	2.8	0.4
	Ca-Carb19a	32.8	0.7	20.2	0.7	3.2	0.5
	Ca-Carb20a	32.8	0.7	23.1	0.5	6.1	0.4
	Ca-Carb30a	38.7	0.7	23.1	0.6	3.0	0.4
	Ca-Carb33a	31.5	0.7	20.4	0.6	4.0	0.4
	Ca-Carb36a	32.6	0.7	21.5	0.6	4.5	0.4
	<i>average</i>	32.5	0.7	20.1	0.6	3.2	0.4
<i>std. dev.</i>	3.3		2.2		1.3		
<i>Murchison (CM 2.5)</i>	Ca-Carb1a	31.2	0.3	17.1	0.8	0.9	0.7
	Ca-Carb1b	33.2	0.3	18.1	0.7	0.9	0.6
	Ca-Carb1d	33.1	0.3	18.5	0.8	1.3	0.7
	Ca-Carb2a	22.6	0.4	12.1	1.0	0.4	0.8
	Ca-Carb2b	24.1	0.3	13.3	0.9	0.7	0.8
	Ca-Carb2c	26.4	0.4	14.2	1.0	0.5	0.8
	Ca-Carb2d	26.9	0.4	15.2	1.0	1.2	0.9

	Ca-Carb3a	28.4	0.3	17.8	0.7	3.0	0.6	
	Ca-Carb4b	29.7	0.3	18.2	0.7	2.7	0.5	
	<i>average</i>	28.4	0.3	16.1	0.8	1.3	0.7	
	<i>std. dev.</i>	3.8		2.4		0.9		
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<i>Murray (CM 2.4-2.5)</i>	Ca-Carb4a	39.4	2.4	22.6	1.7	2.1	1.2	
	Ca-Carb5a	39.7	2.4	22.0	1.7	1.4	1.1	
	Ca-Carb10a	26.4	2.4	15.1	1.8	1.3	1.2	
	Ca-Carb10b	24.3	2.4	14.2	1.8	1.6	1.2	
	Ca-Carb14a	38.4	2.4	22.2	1.7	2.2	1.2	
	Ca-Carb16a	36.5	2.4	22.0	1.7	3.0	1.2	
	Ca-Carb24a	34.1	2.4	20.1	1.7	2.4	1.2	
	Ca-Carb24b	34.4	2.4	22.1	1.8	4.2	1.2	
	Ca-Carb33a	36.8	2.4	20.4	1.7	1.3	1.2	
	Ca-Carb34a	36.9	2.4	21.7	1.7	2.5	1.2	
		<i>average</i>	33.5	2.4	19.7	1.7	2.3	1.2
		<i>std. dev.</i>	5.2		3.2		1.0	
<hr/>								
<i>Pollen (CM 2.4)</i>	Ca-Carb10a	36.6	0.4	17.8	0.7	-1.2	0.6	
	Ca-Carb10b	37.7	0.4	18.3	0.7	-1.3	0.5	
	Ca-Carb16a	35.4	0.4	20.0	0.8	1.6	0.7	
	Ca-Carb17a	35.4	0.4	16.6	0.7	-1.8	0.6	
		<i>average</i>	36.3	0.4	18.2	0.7	-0.7	0.6
	<i>std. dev.</i>	1.1		1.4		1.6		

<i>Nogoya (CM 2.2)</i>	Ca-Carb7a	37.0	0.6	18.2	0.7	-1.1	0.5
	Ca-Carb10a	36.0	0.6	19.0	0.7	0.3	0.5
	Ca-Carb11a	23.5	0.6	10.4	0.7	-1.8	0.5
	Ca-Carb11b	21.9	0.6	9.1	0.7	-2.3	0.5
	Ca-Carb14a	36.2	0.6	18.2	0.8	-0.6	0.6
	Ca-Carb15a	38.9	0.7	19.1	0.5	-1.1	0.3
	<i>average</i>	31.3	0.6	15.2	0.7	-1.1	0.5
	<i>std. dev.</i>	8.0		5.0		1.0	
<i>Cold Bokkeveld (2.2)</i>	Ca-Carb1a	24.2	1.0	12.1	0.6	-0.5	0.4
	Ca-Carb1b	23.0	1.0	12.3	0.7	0.4	0.4
	Ca-Carb1c	20.6	1.0	10.6	0.7	-0.1	0.5
	Ca-Carb1d	25.6	1.0	12.5	0.7	-0.8	0.4
	Ca-Carb1e	24.0	0.9	12.8	0.5	0.3	0.4
	Ca-Carb2a	22.5	1.0	13.4	0.8	1.7	0.5
	Ca-Carb2b	22.8	1.0	13.1	0.8	1.3	0.5
	Ca-Carb3a	24.6	1.0	12.1	0.8	-0.7	0.5
	Ca-Carb3b	26.2	0.9	13.4	0.7	-0.2	0.5
	Ca-Carb3c	28.2	1.0	15.7	0.8	1.1	0.5
	<i>average</i>	24.2	1.0	12.8	0.7	0.3	0.5
	<i>std. dev.</i>	2.1		1.3		0.9	
<i>Jbilet Winselwan (2.0-2.3)</i>	Ca-Carb1a	27.0	0.7	14.7	0.8	0.6	0.6

Ca-Carb3a	32.0	0.7	17.6	0.7	1.0	0.5
Ca-Carb5a	35.6	0.9	18.7	0.7	0.1	0.4
Ca-Carb8a	34.3	0.9	17.3	0.8	-0.5	0.5
Ca-Carb8b	34.0	0.9	18.3	0.7	0.6	0.4
Ca-Carb11a	33.8	0.9	18.5	0.7	1.0	0.5
Ca-Carb14a	33.2	0.9	17.9	0.7	0.7	0.4
Ca-Carb16a	34.3	0.9	19.3	0.7	1.4	0.5
Ca-Carb20a	34.2	0.9	18.2	0.8	0.4	0.5
Ca-Carb20b	33.7	0.9	17.5	0.7	0.0	0.5
Ca-Carb20c	34.0	0.9	17.6	0.6	-0.1	0.4
Ca-Carb23a	31.3	0.9	16.8	0.9	0.5	0.6
Ca-Carb32a	37.2	0.7	18.5	0.6	-0.8	0.4
Ca-Carb32b	31.9	0.7	16.7	0.6	0.1	0.4
Ca-Carb33a	35.7	0.8	18.5	0.7	0.0	0.5
Ca-Carb34a	32.9	0.7	17.8	0.6	0.7	0.4
Ca-Carb36a	34.1	0.7	17.7	0.6	-0.1	0.4
Ca-Carb37a	38.0	0.7	18.7	0.7	-1.1	0.5
<i>average</i>	34.2	0.8	18.0	0.7	0.2	0.5
<i>std. dev.</i>	1.9		0.7		0.7	

QUE93005 (CM2.1)

Ca-Carb1a	33.4	0.4	15.9	0.7	-1.4	0.6
Ca-Carb2a	16.6	0.3	5.8	0.6	-2.8	0.5
Ca-Carb2b	18.4	0.3	7.3	0.6	-2.3	0.4
Ca-Carb2c	26.2	0.3	11.3	0.7	-2.3	0.6
Ca-Carb2d	26.1	0.4	11.1	0.7	-2.5	0.6
Ca-Carb3a	21.8	0.4	11.1	0.8	-0.2	0.6
Ca-Carb4a	24.8	0.4	9.5	0.7	-3.4	0.6

	Ca-Carb5a	31.1	0.5	16.5	0.7	0.3	0.5	
	<i>average</i>	24.8	0.4	11.1	0.7	-1.8	0.5	
	<i>std. dev.</i>	5.8		3.7		1.3		
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<i>ALH88045 (CM 1)</i>	Ca-Carb1a	23.3	0.4	9.2	0.7	-2.9	1.2	
	Ca-Carb3a	29.6	0.4	13.8	0.6	-1.6	1.2	
	Ca-Carb5a	19.2	0.4	7.2	0.5	-2.8	1.1	
	Ca-Carb5b	23.2	0.5	9.0	0.5	-3.1	1.1	
	Ca-Carb5c	21.7	0.4	9.0	0.6	-2.3	1.1	
	Ca-Carb8a	17.9	0.4	7.1	0.5	-2.2	1.1	
	Ca-Carb8b	16.1	0.4	6.6	0.6	-1.7	1.2	
	Ca-Carb9a	24.2	0.4	8.5	0.6	-4.1	1.2	
	Ca-Carb9b	24.9	0.4	10.7	0.5	-2.2	1.1	
	Ca-Carb9c	22.1	0.4	7.8	0.6	-3.7	1.2	
		<i>average</i>	22.2	0.4	8.9	0.6	-2.7	1.1
		<i>std. dev.</i>	3.8		2.1		0.8	

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Table 1: Oxygen isotopic compositions of Paris Ca-carbonates. $\Delta^{17}\text{O}$ errors were calculated using the errors of the $^{17}\text{O}/^{18}\text{O}$ ratio.

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