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**Miller Range 07687 and its place within the CM-CO clan**

Trygve Prestgard<sup>1\*</sup>, Lydie Bonal<sup>1</sup>, Jolantha Eschrig<sup>1</sup>, Jérôme Gattacceca<sup>2</sup>, Corinne Sonzogni<sup>2</sup>,  
Pierre Beck<sup>1</sup>

<sup>1</sup>Institut de Planétologie et d'Astrophysique de Grenoble, Université Grenoble Alpes, CNRS  
CNES, 38000 Grenoble (France)

<sup>2</sup> CNRS, Aix Marseille Univ, IRD, Coll France, INRA, CEREGE, Aix-en-Provence, France

\* Corresponding author: trygve-johan.prestgard@univ-grenoble-alpes.fr.

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16 **Abstract:**

17 Miller Range (MIL) 07687 is a peculiar carbonaceous chondrite officially classified as  
18 a CO3. However, it has been found to display unique petrographic properties that are atypical  
19 of this group. Moreover, Raman spectra of its polyaromatic carbonaceous matter does not  
20 reflect a structural order consistent with the metamorphic history of a type 3 chondrite. As a  
21 result, it has been suggested to be an ungrouped C2 chondrite with CO affinities, although it  
22 has not been fully excluded as a CO chondrite. The ambiguity of the meteorite's classification  
23 is the motivation behind the present study. We conclude that MIL 07687 is a unique  
24 carbonaceous chondrite with possible affinities to CO, CM and/or some ungrouped  
25 carbonaceous chondrites. The difficulty in classifying this meteorite stems from (i) its heavily  
26 weathered nature, which interferes with the interpretation of our oxygen (O-)isotopic  
27 measurements; (ii) the overlap in the petrographic and O-isotopic descriptions of various COs,  
28 CMs and ungrouped meteorites in the Meteoritical society database. Optical and infrared  
29 spectra are consistent with the meteorite's unequilibrated nature and indicate that it is probably  
30 mildly aqueously altered. Despite traces of aqueous alteration having previously been described  
31 in MIL 07687, this is the first time that the presence of hydrated amorphous silicates is reported.  
32 In fact, our results show that its present hydration is beyond that of most CO3s, less than most  
33 CM2s, and comparable to primitive CR2s. Consequently, we support the meteorite's C2-ung  
34 label, although a CO2 or CM2 classification cannot be fully excluded.

35

36 **1. Introduction**

37 Miller Range (MIL) 07687 is a small (5.5 g) carbonaceous chondrite discovered by the  
38 2007 team of US Antarctic Search for Meteorites program. The meteorite was initially  
39 classified as a CO3 chondrite on the basis of its abundant and small chondrules ( $\leq 1$  mm in  
40 diameter), presence of metal and sulfides occurring within and rimming the chondrules, and  
41 olivine and pyroxene elemental composition (initial petrographic description, available online  
42 on the Meteoritical Society database). However, since its initial classification, Brearley (2012)  
43 was the first to note that MIL 07687 differs significantly from typical CO3 chondrites due to  
44 various distinct features: (i) significantly higher matrix abundance ( $\sim 68$  vol. %: Brearley, 2012;  
45 and 63 vol. %: Vaccaro 2017); (ii) the lack of detectable fine-grained rims; (iii) the low  
46 abundance of refractory inclusions. Therefore, the meteorite is now considered (Antarctic  
47 meteorites classification database:  
48 <https://curator.jsc.nasa.gov/antmet/samples/petdes.cfm?sample=MIL07687>) as an ungrouped  
49 carbonaceous chondrite with affinities to the CO group, as also described by Haenecour et al.

50 (2020). Similarly to MIL 07687, there are various ungrouped chondrites, such as Acfer 094,  
51 Adelaide, and MacAlpine Hills (MAC) 88107, that appear to display some CO-like traits (e.g.  
52 chondrule size, matrix abundance and/or not very hydrated), although many of these have been  
53 considered meteorites with overlapping characteristics, showing possibly affinities with both  
54 the CO and CM chemical groups (Greenwood et al., 2019 and references therein). Unlike the  
55 latter meteorites, which have bulk oxygen (O)-isotopic measurements, to our knowledge, there  
56 appear to be no documented bulk O-isotopic measurements of MIL 07687. Consequently, its  
57 current classification appears to be mainly based on its petrography (Haenecour et al. 2020 and  
58 references therein).

59 In addition to its peculiar petrography, past research suggests MIL 07687 to be a highly  
60 primitive meteorite, notably by its apparently high concentration of amorphous material, <sup>15</sup>N-  
61 enrichment and elevated abundance of presolar grains (Haenecour et al. 2020; McAdam et al.,  
62 2018; Vaccaro 2017). Indeed, amorphous silicates tend to be abundant in primitive chondrite  
63 matrices (Abreu and Brearley., 2010; Brearley, 1993; Dobrică and Brearley, 2020), and high  
64 bulk <sup>15</sup>N content probably reflects material of strong interstellar heritage (Nakamura-Messenger  
65 et al., 2006). Furthermore, the Cr<sub>2</sub>O<sub>3</sub> content in type-II chondrules of MIL 07687 are compatible  
66 with carbonaceous chondrites of petrographic type 3.0, and there is no evidence of zoning of  
67 forsteritic olivine (Brearley 2012), although Haenecour et al. (2020) report slightly lower Cr<sub>2</sub>O<sub>3</sub>  
68 values than Davidson et al. (2014), possibly suggestive of minor thermal metamorphism.

69 Perhaps one of the most notable features about MIL 07687 is the presence of submillimeter-  
70 scale complex Fe-rich and Fe-poor matrix lithologies. The former regions are rich in fibrous  
71 assemblages of ferrihydrite, interpreted as being the result of partial (localized) aqueous  
72 alteration, possibly under highly oxidizing conditions (Brearley 2012, 2013, Haenecour et al.,  
73 2020). The oxidizing conditions are further supported by Ca-sulfates partially replacing Ca-  
74 carbonates (Brearley 2012, Haenecour et al., 2020). The Fe-rich regions appear to be separated  
75 from the primitive Mg-rich matrix by alteration fronts, rather than representing distinct  
76 brecciated lithologies. Interestingly, no phyllosilicates have been detected despite the evidence  
77 of aqueous alteration (Brearley, 2012, 2013, Haenecour et al. 2020). Brearley (2012) and  
78 Haenecour et al. (2020) further note that chondrule mesostasis occasionally appears to have  
79 suffered minor modifications in the regions that are in contact with the matrix. Consequently,  
80 MIL 07687 has been considered as a unique object, potentially providing the opportunity to  
81 study the earliest stages of aqueous alteration on primitive matrix material (Brearley, 2012).

82 The identification and correct assessment of post-accretion processes has not only important  
83 consequences on our understanding of the geological processes themselves, but also on the

84 initial properties and accretion conditions of chondrite parent bodies. Consequently, in order to  
85 provide a primary classification of MIL 07687, we decided to conduct bulk oxygen isotopic  
86 analysis. In regards to its secondary classification, we measured infrared (IR) spectra of bulk  
87 and matrix samples, along with bulk thermogravimetric analysis (TGA), in order to help  
88 provide the best possible constraints on the parent body processes the meteorite experienced.  
89 We additionally did an extensive search through the Meteoritical Society Database for unusual  
90 COs, CMs, and CM-CO clan members, that have similar petrographic descriptions with MIL  
91 07687, and/or that have overlapping petrographic descriptions with the CO3 and CM2 chemical  
92 groups. Those with reported O-isotopic compositions are plotted in gray in Figs. 1 and 2.

93

## 94 **2.1 Sample**

95 A bulk sample (100 mg) of MIL 07687-5 has been provided by the NASA Meteorite Working  
96 Group, initially for the characterization of its metamorphic history through Raman spectroscopy  
97 of its polyaromatic carbonaceous matter (Bonal et al. 2016). As the thermal history of MIL  
98 07687 appears to be different from that of the other CO chondrites considered in this study, we  
99 took advantage of the remaining sample to lead a further spectroscopic characterization and to  
100 characterize its degree of aqueous alteration.

101 The spectral data (of matrix fragments and bulk samples, in transmission and reflectance) of  
102 MIL 07687 are compared to those of CO, CR, CM, CV, CK, CI and ungrouped chondrites. The  
103 comparison data were either acquired in the present work (Prestgard and Bonal, 2019; Prestgard  
104 et al., 2019) or are from previous studies, as stated in Table 1. or are from previous studies, as  
105 stated in Table 1. Most of the spectral data from previous studies are available online on the  
106 GhoSST/SSHADe spectral database (<https://www.sshade.eu/db/ghosst>; Schmitt et al., 2012).

107 We also performed TGA on a series of CO chondrites all listed in Table 2.

108

## 109 **2.2 IR transmission spectra**

110 *Bulk pellets:* a pellet made of KBr and bulk powdered MIL 07867 was prepared following the  
111 same procedure as described in Beck et al. (2014). Several mg of the bulk meteorite were  
112 ground in a dry agate mortar and out of this mass, 1.0 mg was weighed and mixed with 300 mg  
113 of commercial ultrapure KBr powder.

114 IR spectra were measured with a Bruker V70v spectrometer at the Institut de Planétologie et  
115 d'Astrophysique de Grenoble (IPAG, France). Spectra were acquired at 2 cm<sup>-1</sup> spectral  
116 resolution in the 5000 - 400 cm<sup>-1</sup> range under a primary vacuum (P = 10<sup>-3</sup> mbar).

117 *Matrix fragments:* IR spectra were obtained with a BRUKER HYPERION 3000 infrared  
118 microscope (IPAG, France). The IR beam was focused through a 15x objective and the typical  
119 size of the spot on the sample was 40 x 40  $\mu\text{m}^2$ . Spectra were measured at 4  $\text{cm}^{-1}$  spectral  
120 resolution with a MCT detector cooled with liquid nitrogen. Particular care was devoted to  
121 sample preparation, which is a critical issue in IR micro-spectroscopy. Samples must be thin  
122 ( $<20 \mu\text{m}$ ) and their surfaces flat enough to avoid saturation of absorption and scattering  
123 artifacts, respectively (e.g., Raynal et al. 2000). Small matrix fragments (30 - 50  $\mu\text{m}$ ) were  
124 selected under a binocular microscope according to their color and texture. The matrix  
125 fragments were crushed between two diamond windows, allowing access to the 4000 - 650  $\text{cm}^{-1}$   
126 spectral range. The diamond windows were loaded into an environmental cell, designed and  
127 built at IPAG. This cell enables temperatures up to 300 °C to be reached under primary or  
128 secondary dynamic vacuum (from  $10^{-4}$  mbar down to  $10^{-7}$  mbar). Optical access is permitted  
129 from both sides of the cell through ZnS windows, thus enabling measurements in transmission.  
130 Samples were progressively heated up to 250°C or 300°C, with typical steps at 100°C, 200°C,  
131 and spectra were recorded at each temperature step. The transmission spectra were  
132 automatically converted to absorbance ( $A = -\log(T/T_0)$ , where  $T_0$  and  $T$  are the transmittance  
133 without and with the sample, respectively). To remove interferences and scattering effects, a  
134 spline baseline was subtracted from the raw data.

135

### 136 **2.3 Reflectance spectra**

137 The reflectance measurements of MIL 07687 were made by the SHADOWS instrument  
138 (IPAG, France, Potin et al., 2018). The method applied is that described by Eschrig et al. (2020):  
139 (i) we manually prepared 30 - 50 mg of an unsorted powder of sub-millimetre particle size using  
140 a mortar. Contrary to various other works (e.g. Cloutis et al., 2012a,b,c,d), we chose not to sieve  
141 the powder in order to better represent the grain-size heterogeneity expected of asteroidal  
142 regolith. (ii) The sample was secured in an environmental chamber (MIRAGE) under vacuum  
143 ( $P < 1 \times 10^{-4}$  mbar) at ambient temperature. This was done in order to remove weakly bonded  
144 water molecules. The chamber was enclosed by a sapphire window, whose optical contribution  
145 was removed from the raw spectra thanks to an adapted algorithm. (iii) In regards to the  
146 observation geometry, we chose an incidence angle of  $i = 0^\circ$ , and an emergence angle of  $e =$   
147  $30^\circ$ . The spectral resolution used varied from 0.048- $\mu\text{m}$  to 0.39- $\mu\text{m}$  (with a step of 0.02  $\mu\text{m}$ ).  
148 Note that the measurements were normalized to reference surfaces, more specifically by using  
149 a Spectralon<sup>TM</sup> (for wavelengths 0.4 – 2.1  $\mu\text{m}$ ) and an Infragold<sup>TM</sup> (2.1 – 4.2  $\mu\text{m}$ ).

150

## 151 2.4 TGA measurements

152 TGA was used to quantify the amount of hydrogen in the samples by measuring the  
153 mass loss upon heating. The first derivative (DTG) of the TGA curve enables us to determine  
154 the maximum peak temperature of each mass loss and gives an indication of the host mineral  
155 of volatile elements (see Fig. 1 in Garenne et al. 2014). Thermo-Gravimetric measurements  
156 were performed with a TGA-DSC3 Mettler-Toledo at Institut des Sciences de la Terre (ISTerre,  
157 Grenoble - France). A fragment of bulk sample was ground manually (around 50 mg in a  
158 mortar). 30 mg of this powder was extracted for TGA analysis and put inside a 150  $\mu$ L alumina  
159 crucible under a 50 mL/min inert N<sub>2</sub> atmosphere. We included two separate samples of DOM  
160 08006: -21 and -53. The former contained 30 mg, while the second was based on 50 mg of  
161 sample. This was done in order to study the mineralogical heterogeneity of a single meteorite.  
162 The mass loss from each sample was recorded as it was heated from 25°C to 1000°C with a  
163 heating rate of 10 °C/min. The TGA mass resolution is 1  $\mu$ g, which corresponds to an absolute  
164 error of 0.07% for a total mass loss fraction of 5 %. The error on the temperature measurement  
165 is around 0.25 °C.

166 More specifically, the hydrogen in hydrated chondrites is mainly associated with  
167 phyllosilicates. In their work on type-2 chondrites, Garenne et al. (2014) showed that the 400 –  
168 770°C TGA mass loss correlated well with the phyllosilicate content in CIs and CMs. King et  
169 al. (2015) found that mass loss due to serpentines took place between 200 - 800°C, through  
170 dehydration and dehydroxylation. In highly altered CMs, phyllosilicates appear to produce  
171 significant mass loss rates at ~400°C and 500 - 600°C (see Fig. 3 from Garenne et al., 2014).  
172 Carbonates were measured to decompose between 600 - 800°C by King et al., (2015), however  
173 mass loss due to carbonates in CMs has been observed to take place up to 900°C (Garenne et  
174 al., 2014). The breakdown temperatures of carbonates are variable depending on a variety of  
175 parameters, including chemistry, grain size and environment. Temperatures lower than 200°C  
176 correspond to the desorption of weakly bonded water (Garenne et al., 2014), while the 200 –  
177 350°C region is dominated by the effects due to dehydroxylation of oxyhydroxides, most  
178 notably goethite (King et al., 2015).

179 Contrary to CIs and CMs, phyllosilicates appear to be of relatively low abundances, if not  
180 possibly absent, in MIL 07687 and most CO<sub>3</sub>s (Brearley 2006, 2012 and 2013, Haenecour et  
181 al. 2020). Consequently, we can expect the TGA mass loss in the 400 - 770°C interval of MIL  
182 07687 and CO<sub>3</sub>s to be additionally (and significantly) affected by the decompositions of  
183 anhydrous minerals such as sulfides, magnetite and perhaps carbonates (Földvari 2011, King et  
184 al., 2015). Fe-sulfides are present in CO<sub>3</sub>s of all metamorphic grades (e.g. Alexander et al.,

185 2018: ~2-3 vol%), and have also been reported in the matrix of MIL 07687 (~1 vol%: Vaccaro,  
186 2017). In CO<sub>3</sub>s, sulfides do not seem to be the result of aqueous alteration (Brearley 2006). If  
187 we consider that MIL 07687, COs and CVs have comparable concentrations of sulfides  
188 (regardless of metamorphic grade), then, at most, we could possibly expect an additional ~0.4  
189 wt.% mass loss to be associated with this mineral in the TGA 350°C – 700°C interval (Bonal  
190 et al., 2020).

191 Although absent in MIL 07687 (Vaccaro, 2017), magnetite is present to various degrees  
192 in primitive CO<sub>3</sub>s (2 – 8 vol%), and are generally absent in members of higher metamorphic  
193 grade (>3.2) (Rubin and Li, 2019). Minor amounts of magnetite however have been reported  
194 in Moss (>3.6) (Stokke, 2018). CO<sub>3</sub>s appear to be quite poor in carbonates (Brearley 2006), but  
195 these have been reported in MIL 07687 (Davidson et al., 2015).

196 Note that, while carbonates and magnetite are often considered the result of aqueous  
197 alteration (e.g. Brearley 2006, Howard et al., 2014, Rubin and Li, 2019), their abundances are  
198 difficult to determine via TGA. Under oxidizing conditions, the latter is characterized by  
199 significant mass gain between 200 - 800°C (oxidation of magnetite into hematite: Földvari  
200 2011), while the former is affected by a variety of factors, including grain size (e.g. King et al.,  
201 2015). However, as our experiments were done under inert conditions (probably no more than  
202 a few ppm of oxygen), we do not initially expect any mass gain due to magnetite to be highly  
203 significant. However, despite inert conditions, the presence of organics can probably lead to  
204 additional oxidation and/or reduction of certain minerals (e.g. magnetite and hematite),  
205 including at high temperature (e.g. Rudolph et al., 2012, Simmonds and Hayes, 2017), which  
206 may need to be considered when interpreting the TGA results.

207 Organics themselves (at least IOM) are expected to decompose progressively  
208 throughout our studied temperature range (Court and Sephton, 2014). Consequently, in CO<sub>3</sub>s,  
209 the mass loss associated with organics should vary between 0.1 - 0.5 wt.% (Alexander et al.,  
210 2007) within 25°C – 1000°C. However, due to the higher matrix abundance of MIL 07687, the  
211 mass loss contribution due to organics may be higher.

212 Consequently, despite the likely overlap from other minerals, we concluded that the 350  
213 – 700°C range may be the best interval to quantify the phyllosilicate content (if significantly  
214 present) in MIL 07687 and CO<sub>3</sub>s, although we have nonetheless included the 400 – 770°C TGA  
215 values for the purpose of comparison with CMs. Moreover, as Fe-oxyhydroxides may also  
216 appear as parent alteration products in MIL 07687 and CO<sub>3</sub>s (Haenecour et al., 2020; Keller  
217 and Busseck, 1990), we have also chosen to specifically study the 200 - 700°C temperature  
218 interval. All values are summarized in Table 2.



219 In order to more accurately determine the composition of the released gas (i.e. the  
220 composition of the samples), the TGA curves were coupled with an Infrared Spectrograph  
221 (IRS). This is especially useful in regards to our samples, as various minerals (described above)  
222 may significantly contribute to the mass loss across the previously mentioned temperature  
223 ranges (which may hence strongly affect the interpretation of our results).

224

## 225 **2.5 Oxygen isotopes**

226 Measurement of oxygen isotopic compositions of a 1.5 mg aliquot of bulk powdered  
227 MIL 07687 was carried out at the Stable Isotopes Laboratory of CEREGE (Aix-en-Provence,  
228 France) using laser fluorination coupled with isotope ratio mass spectrometry (ir-MS) (see e.g.,  
229 Alexandre et al., 2006; Suavet et al., 2010 for more details about the analytical procedure). The  
230 initial sample mass was 10 mg to ensure that measured aliquot is representative of the bulk  
231 meteorite. The three oxygen isotopic compositions were measured with a dual-inlet mass  
232 spectrometer Thermo-Finnigan Delta Plus. The oxygen isotope results are expressed in ‰  
233 versus the international reference standard V-SMOW:  $\delta^{18}\text{O} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{18}\text{O}/{}^{16}\text{O})_{\text{V-SMOW}} - 1] \times 1000$   
234 and  $\delta^{17}\text{O} = [({}^{17}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{17}\text{O}/{}^{16}\text{O})_{\text{V-SMOW}} - 1] \times 1000$ . The  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values of the  
235 reference gas were calibrated with measurements of NBS28 standard ( $\delta^{18}\text{O} = 9.60\text{‰}$ , (Gröning  
236 2004).  $\Delta^{17}\text{O}$  is computed as  $\Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - \lambda \times \ln(1 + \delta^{18}\text{O})$  with  $\lambda = 0.5247$  (Miller 2002).  
237 The  $\delta^{17}\text{O}$  value of the NBS28 standard ( $\delta^{17}\text{O} = 5.026\text{‰}$ ) was computed so as to give  $\Delta^{17}\text{O} = 0\text{‰}$ .  
238 The measurements of the session when MIL 07687 was measured were corrected on a daily  
239 basis using a 1.5 mg quartz internal laboratory standard “Boulangé” (Alexandre et al. 2006;  
240 Suavet et al. 2010). The analytical uncertainties derived from long term repeated measurement  
241 ( $n = 59$ ) of this internal laboratory standard are 0.076‰, 0.139‰, and 0.013‰ for  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ,  
242 and  $\Delta^{17}\text{O}$ , respectively.

243

## 244 **3. Results**

### 245 **3.1. Oxygen isotopes of MIL 07687**

246 We find that the bulk powder of MIL 07687 has an oxygen isotopic composition of  $\delta^{18}\text{O}$   
247  $= -6.75\text{‰}$  and  $\delta^{17}\text{O} = -7.87\text{‰}$ . This is similar to bulk measurements of CO3 chondrites (Fig.  
248 1), particularly those of some highly weathered Antarctic samples (Alexander et al. 2018): Its  
249  $\delta^{18}\text{O}$  values are slightly lower than typical COs (Figs. 1 and 2). Indeed, CO chondrites generally  
250 plot along and left of the CCAM line, and generally display negative bulk O-isotopic  $\delta^{18}\text{O}$   
251 values, following a fractionation line of  $\sim -0.6$ . Primitive CO3s (e.g. the samples measured by  
252 Alexander et al., 2018) tend to plot nearby the PCM line (Figs. 1 and 2), *although*, some COs

253 listed in the Meteoritical Society Database appear to have positive  $\delta^{18}\text{O}$  values (Fig. 1). CM  
254 chondrites tend to generally have a much heavier O-isotopic compositions ( $\delta^{17}\text{O} > -2 \text{‰}$ ,  $\delta^{18}\text{O}$   
255  $> +4 \text{‰}$ ), however many primitive CMs, and some CO/CM-like ungrouped meteorites are more  
256  $^{16}\text{O}$ -rich, even plotting close to the CO footprint (Greenwood et al. 2019, Kimura et al. 2020,  
257 Lee et al. 2019, Meteoritical Society database: Fig 1 and 2). Anhydrous material from the  
258 Murchison CM2 meteorite also plot within the CO-field (Clayton and Mayeda, 1999: Figs. 1  
259 and 2). In fact, MIL 07687 has a similar O-isotopic composition to EET 83355 (Figs. 1 and 2),  
260 a heated CM-like ungrouped carbonaceous chondrite (King et al., 2021). The O-isotopic  
261 composition of MIL 07687 is distinct from ungrouped CO/CM-like chondrites such as Acfer  
262 094, Adelaide and MAC 88107, which display intermediate bulk isotopic properties of both  
263 typical CM and CO group members (Greenwood et al., 2019 and references therein).

264

### 265 **3.2. IR spectra of matrix fragments**

266 The IR spectra of MIL 07687 matrix fragments (Fig. 3) cover a spectral range that  
267 includes both the  $\text{SiO}_4$  (Si-O) stretching ( $12500 - 800 \text{ cm}^{-1}$  or  $8\text{-}12 \text{ }\mu\text{m}$ , a.k.a. the  $10\text{-}\mu\text{m}$  band)  
268 and the so-called  $3\text{-}\mu\text{m}$  region. The latter is a complex region associated with various vibrational  
269 modes in phyllosilicates and oxyhydroxides ( $\text{X-OH}$  where X is a transition metal), as well as  
270 adsorbed and interfoliar molecular water. With the spectra having been measured at  $250 -$   
271  $300^\circ\text{C}$ , oxyhydroxides and adsorbed molecular water are not expected to significantly  
272 contribute to the  $3\text{-}\mu\text{m}$  band absorption. The peaks at  $3.3 - 3.4 \text{ }\mu\text{m}$  ( $\sim 2900 \text{ cm}^{-1}$ ) are attributed  
273 to organic matter (C-H), and will not be discussed further in this work. We were able to obtain  
274 successful spectra of twelve matrix fragments. All display very common traits, as described  
275 below.

276 The spectral profiles of the  $\text{SiO}_4$  (Si-O) stretching of MIL 07687 matrix fragments (Figs.  
277 3 and 4) appear rounded and asymmetrical. More specifically, they appear to be composed of  
278 broad “bell”-shaped bands with a peak at  $\sim 9.8 \text{ }\mu\text{m}$  ( $1020 \text{ cm}^{-1}$ ), alongside a weaker and narrower  
279 band at  $11.2 \text{ }\mu\text{m}$  ( $890 \text{ cm}^{-1}$ ). The Si-O profile for all matrix fragments measured in this work  
280 are very similar, although the prominence of the  $11.2\text{-}\mu\text{m}$  band does vary slightly (being the  
281 strongest for fragments 1 and 2). Interestingly, the broad  $9.8\text{-}\mu\text{m}$  band displays a similar  
282 morphology to that of saponite (Fig. 4), despite this mineral not having been previously  
283 described in this meteorite. The smooth and broad nature of the band is also indicative of  
284 silicates of low crystallographic order (Fu et al., 2017), hence consistent with amorphous phases  
285 detected by Vaccaro (2017) and McAdam et al. (2018).

286 The Si-O stretching region in MIL 07687 is similar to that observed in matrix fragments of  
287 some (i) CR2 chondrites (Bonal et al., 2013) (Fig. 4), (ii) CM2 chondrites (e.g. NWA 11588),  
288 (iii) low petrologic type 3 CO chondrites DOM 08006 (CO3.00) and LAP 031117 (CO3.05)  
289 (Fig. 4). In regards to the 11.2- $\mu\text{m}$  ( $890\text{ cm}^{-1}$ ) band, its band location and narrow width are  
290 consistent with the presence of olivine.

291 The 3- $\mu\text{m}$  band (measured at 250°C and 300°C, Fig. 4) is broad (2.7 – 3.5  $\mu\text{m}$  or 3750  
292 – 2900  $\text{cm}^{-1}$ ), rounded, asymmetric, with a peak absorption at 2.8  $\mu\text{m}$  ( $3545\text{ cm}^{-1}$ ). The profile  
293 is unlike those observed for CM2 chondrites (e.g. QUE 97990 and NWA 11588), but resemble  
294 those of primitive CR2 matrices (e.g. MET 00426 and QUE 99177). CM2s tend to have  
295 phyllosilicate-rich matrices (Brearley, 2006), while that of CR2s are generally dominated by  
296 hydrated amorphous silicates (Le Guillou et al., 2015). This is again consistent with the  
297 meteorite's amorphous silicate content, and with the lack of phyllosilicates detected in previous  
298 studies. MIL 07687 also seems to share similar 3- $\mu\text{m}$  profiles to primitive CO3s (although much  
299 more intense in appearance). More details regarding the hydrated mineralogy of MIL 07687  
300 will be led in Section 4.2.2.

301 We also observe absorption bands at (i)  $\sim 1600\text{ cm}^{-1}$ , consistent with water; (ii)  $1379\text{ cm}^{-1}$   
302 and  $841\text{ cm}^{-1}$ , consistent with carbonates; (iii)  $1233\text{ cm}^{-1}$ , which might be due to evaporites or  
303 sulphates (Fig. 5). The intensity of each of these bands are highly variable between each  
304 fragment, with the 1233 and  $841\text{ cm}^{-1}$  bands being absent in most spectra.

305

### 306 **3.3 IR spectra of bulk MIL 07687**

307 Bulk measurement probes the combination of matrix, chondrules and CAI/AOA  
308 signatures. The IR spectrum of bulk MIL 07687 (Figs. 6 and 7) covers a spectral range that  
309 includes both the  $\text{SiO}_4$  (Si-O) stretching (8-12  $\mu\text{m}$ , a.k.a. 10- $\mu\text{m}$  band) and bending (15 - 25  
310  $\mu\text{m}$ ) regions, thus providing valuable information on the meteorite's bulk silicate composition.  
311 The spectrum is plotted alongside those of various type 2 carbonaceous chondrites (Fig. 6) and  
312 CO3s (Fig. 7), for comparison. Spectra of individual silicate minerals have also been added  
313 (from Salisbury, 1991). The spectra have been normalized according to the maximum  
314 absorbance of their 10- $\mu\text{m}$  region.

315 We find that the 10- $\mu\text{m}$  stretching band for bulk sample MIL 07687 displays various  
316 absorption peaks: (i) 9.3  $\mu\text{m}$ , consistent with Mg-rich pyroxene; (ii) 11.2  $\mu\text{m}$ , consistent with  
317 Mg-rich olivine; (iii) 9.9- $\mu\text{m}$ : a feature that is consistent with the amorphous silicates observed  
318 in the IR spectra of matrix fragments (Fig. 3 and 4). The Si-O stretching profile is also especially

319 similar to NWA 8631 (CO3.0) and EET 87522 (Heated CM2), probably indicating a similar  
320 silicate make-up between these meteorites.

321 In regards to the SiO<sub>4</sub> bending region (15 – 25 μm), MIL 07687 displays the presence  
322 of broad bands at 16.4 μm and 19.5 μm that are also consistent with the presence of Mg-rich  
323 pyroxene and olivine (e.g., Beck et al. 2014), the latter band likely being a combination of both  
324 minerals. A broad band appears around 23 - 24 μm, which likely represents a convolution  
325 between olivine, pyroxene and amorphous silicates (Figs. 6 and 7). In addition, the bulk spectra  
326 also display various faint absorption features between 13 μm and 16 μm, which are also  
327 observed in enstatite.

328

### 329 **3.4 Reflectance spectra of bulk MIL 07687**

330 The reflectance measurements (Fig. 8) cover a spectral range that extends from 0.4 μm  
331 to 4.0 μm. This includes the range commonly used for asteroid taxonomy (0.4 – 2.5 μm; e.g.,  
332 DeMeo et al., 2009). This region is thought to be affected by a complex combination of  
333 numerous parameters, including the Fe content of various ferromagnesian silicates (e.g. olivine  
334 and phyllosilicates; Cloutis et al., 2011; Beck et al., 2018). The measured spectral range also  
335 includes the 3-μm region (Fig. 8) which is associated with various vibrational modes of  
336 phyllosilicates and oxyhydroxides (Metal-OH bonds), as well as adsorbed molecular water (see  
337 section 3.2).

338 The reflectance spectrum of MIL 07687 displays a red spectral slope (both in the visible and  
339 NIR), a broad 3-μm hydration band, and faint absorption features at 0.86 μm and 2.4 μm (Fig.  
340 8). Otherwise, the spectrum is relatively featureless in the NIR. This spectrum is similar to the  
341 one previously published by McAdam et al. (2018). Poorly defined aliphatic bands are also  
342 detectable at 3.4 μm and 3.5 μm (Fig. 9).

343 With the exception of the visual slope, the 0.4-2.5 μm spectral region of MIL 07687  
344 differs significantly from our CO3 chondrites: (i) the NIR spectral slope of MIL 07687 is redder  
345 than those generally observed in our spectra of CO3s; (ii) CO3 chondrites generally do not  
346 show obvious absorption features centered at 0.86 μm, but rather at 1.05 μm (with the exception  
347 of DOM 08006: narrow band at 0.98 μm) (Fig. 8; Eschrig et al., 2020). In addition, some CO3s  
348 (e.g. MIL 090785 and El Médano 389) also show broad bands at ~0.9-μm, attributable to  
349 oxyhydroxides (similarly to CR2 finds: Fig. 8). These meteorites are hence highly weathered,  
350 as supported by their strong visual slopes. The 0.86-μm feature of MIL 07687 is however  
351 significantly weaker than the 0.9-μm band observed in these weathered CO3s. The NIR  
352 reflectance of MIL 07687, and typical CO3s, also differ significantly from what we measured

353 in our high-matrix abundance COs (NWA 8631 and NWA 11889). While the peculiar spectrum  
354 of NWA 11889 may be due to its high magnetite content (Meteoritical society database), it is  
355 not impossible that the  $\sim 1\text{-}\mu\text{m}$  feature in NWA 8631 is related to oxyhydroxides.

356 Although the  $0.4\text{-}2.5\ \mu\text{m}$  region of MIL 07687 differs from unheated CMs due to  
357 absence of a  $0.7\text{-}\mu\text{m}$  phyllosilicate band (e.g. LEW 85311 and QUE 97990), it does however  
358 share a similar profile to some moderately heated (e.g. Stage II) CM2 chondrites: EET 87522  
359 and MIL 090073 (Fig. 8). The phyllosilicate content in the latter two meteorites are likely  
360 deformed (amorphized) and dehydrated due to thermal metamorphism (Alexander et al., 2018;  
361 King et al., 2021). Overall, the NIR slope of MIL 07687 is comparable to CM chondrites. In  
362 addition to MIL 07687, absorption bands at  $2.4\ \mu\text{m}$  are also apparent in the spectra of some  
363 CMs, CRs and COs (Fig. 8 and Eschrig et al., 2020).

364 In regards to the  $3\text{-}\mu\text{m}$  hydration band, the profile and intensity are similar to that of  
365 CR2 finds and highly weathered CO3s (Fig. 9), hence indicative of oxyhydroxides rather than  
366 phyllosilicates, consistent with matrix transmission spectra (section 3.2 and 3.3).

367

### 368 **3.5 TGA of MIL 07687 and CO3 chondrites**

369 The TGA curve reflects the loss of volatiles from the decomposition of minerals through  
370 increasing temperature, as described in section 2.2. Consequently, the composition of the  
371 meteorite will affect the mass loss curve. The DTG is used to better visualize specific  
372 temperatures of anomalously high mass loss rates. The TGA mass loss values are presented in  
373 Table 2, and the associated curves are displayed in Figs. 10 and 11.

374 In the case of MIL 07687, high rates of mass loss are measured between at  $400\text{--}500^\circ\text{C}$   
375 and  $650\text{--}800^\circ\text{C}$ . We further note that two distinct “peaks” in the DTG curve appear both within  
376 the former ( $400^\circ\text{C}$  and  $440^\circ\text{C}$ ) and latter region ( $670^\circ\text{C}$  and  $765^\circ\text{C}$ ). Below  $350^\circ\text{C}$ , we see  
377 signatures at  $210^\circ\text{C}$  due to Ferrihydrite (Fig. 11), consistent with its detection in previous  
378 studies (e.g. Haenecour et al. (2020)). The narrow DTG peak at  $130^\circ\text{C}$  may be associated with  
379 evaporites (gypsum), if not molecular water. This would be consistent the meteorite’s  
380 description in the Meteoritical Society Database, and possibly with our matrix spectra (section  
381 3.1 and Fig. 5).

382 The overall mass loss of MIL 07687 is significantly higher than those measured for the  
383 CO3s; this statement being applicable to all predefined temperature ranges (Table 2). We note  
384 that the  $400\text{--}770^\circ\text{C}$  mass loss values for MIL 07687 are similar to those of poorly altered CM2  
385 chondrites, such as LEW 85311 and QUE 97990 (Garenne et al., 2014). Moreover, when  
386 normalized according to their matrix abundance, the  $200\text{--}700^\circ\text{C}$ ,  $350\text{--}700^\circ\text{C}$  and  $400\text{--}770^\circ\text{C}$

387 mass loss values for MIL 07687 remain superior to all CO<sub>3</sub>s considered (based on the matrix  
388 abundances in Table 2).

389 Although our CO<sub>3</sub>s present lower mass loss values (Table 2), the morphology of most  
390 CO<sub>3</sub> TGA/DTG curves present broad similarities to that of MIL 07687 (Figs. 10 and 11): (i)  
391 All samples, with the exception of Moss (which presents no obvious mass loss, even a very  
392 mild mass gain), show an especially rapid mass loss between 650 – 900°C. (ii) Furthermore,  
393 DOM 03238, MIL 05104, MIL 07193 and ALHA 77003 also show a similar mass loss feature  
394 between 400 – 500°C (although less pronounced than in MIL 07687). These features are  
395 particularly interesting in the case of ALHA 77003, as it has a similar metamorphic grade to  
396 Moss (>3.6). A small “**inflection**” in the TGA mass loss curve of Moss is apparent at ~890°C.

397 We note obvious similarities between the two DOM 08006 fragments, both in terms of  
398 mass loss values and TGA/DTG curve morphology (Fig. 10). We also observe an overall strong  
399 similarity between MIL 05104, MIL 05024, and MIL 07193, which are all probably paired  
400 (Meteoritical society database, Alexander et al., 2018), which is further supported by their very  
401 similar metamorphic grades (Bonafant et al., 2016). However, small differences appear: (i) MIL  
402 05024 lacks a 400-500°C “peak” in its DTG curve (ii) MIL 07193 displays a distinct mass loss  
403 trend between 650 – 900°C compared to MIL 05104 and MIL 05024. MIL 07193 also has more  
404 mass loss associated with ferrihydrite than the other two.

405 Lastly, in the IRS spectra of all our samples, we observe the presence of two neighboring  
406 bands at 4.6 and 4.75 μm, consistent with carbon monoxide, indicative of carbonates (see  
407 section 4.2.2.). They appear between ~600 and ~950°C (Figs. 10 and 11), and are strongest in  
408 the case of MIL 07687 (Figs. 12 and 13). The peak intensity of the bands coincide with the peak  
409 of the 650-900°C mass loss, as well as the “inflexion” at 890°C in the TGA curve of Moss.  
410 The intensity of the bands is similar between primitive (3.0 - 3.1) CO<sub>3</sub>s (30 mg samples), with  
411 the exception of DOM 03238 in which they appear significantly stronger. The intensity is also  
412 stronger for the 50 mg DOM 08006-53 sample, which is simply due to its higher mass. Those  
413 of ALHA 77003 and Moss are the weakest. The carbon monoxide bands in the DOM 08006  
414 samples appear to have two main peaks of intensity (~650°C and ~790°C: Fig. 12), also  
415 consistent with their TGA/DTG curves.

416 Unfortunately, no absorption band in the IRS spectra was found to match that of the 400  
417 – 500°C feature. We do not believe it to be associated with Fe-sulfides, as Moss does not show  
418 this mass loss feature. However, as noted earlier, the 400 – 500°C DTG peak is absent in DOM  
419 08006, MIL 05024 and Moss. These all appear to be relatively poorly weathered (both the  
420 former have a weathering grade of A/B, and Moss is a recent fall). DOM 08006 and Moss also

421 lack obvious resolvable TGA/DTG signatures of ferrihydrite and other oxyhydroxides (Fig.  
422 11). The feature is most obvious in MIL 07687, DOM 03238 and ALHA 77003, two of  
423 displayed a noticeably “rusty” appearance under optical polarizing light (ALHA 77003 and  
424 MIL 07687). This was however not the case with DOM 03238, where optical observations  
425 suggested the extent terrestrial weathering to be less severe. However, evaporites may be  
426 present based on the narrow DTG peak at 120°C, which could indicate significant terrestrial  
427 weathering. The absence of a 400 – 500°C feature in MIL 05024, despite being present in MIL  
428 07193 and MIL 05104, is also consistent with a terrestrial origin of the host mineral.

429 Moss (a fall), of similar metamorphic grade to ALHA 77003 (a find, significantly  
430 weathered), does not display any significant mass loss. This might suggest that the TGA mass  
431 loss in ALHA 77003 may be due to terrestrial weathering (assuming no post-metamorphic  
432 hydration). Moreover, [seen that](#) all CO<sub>3</sub> finds, and MIL 07687, display similar TGA/DTG  
433 profile, it could be that their TGA mass loss values too are strongly influenced by terrestrial  
434 weathering products. However, despite this, we note that the matrix-normalized TGA 200 –  
435 700°C and 350 – 700°C mass loss decreases with metamorphic grade (Table 2).

436

## 437 **4 Discussion**

### 438 **4.1. MIL 06787 is a weathered chondrite that is difficult to classify**

439 As described in section 3.1. MIL 07687 was found to have a bulk O-isotopic  
440 composition that is most consistent with CO chondrites. In fact, its O-isotopic composition is  
441 within the lighter isotopic range of the CO group. At first glance, this could indicate that MIL  
442 07687 is indeed a true CO chondrite. In fact, three meteorites listed in the Meteoritical Society  
443 database appear to have comparable matrix abundances to MIL 07687: Catalina 008 (58%),  
444 Mdaouer (62%) and NWA 11889 (61%). Both Catalina 008 and NWA 11889 have O-isotopic  
445 measurements consistent with the CO group. Interestingly, over a dozen CO<sub>3</sub> entries are listed  
446 as having a matrix abundance of at least ~50% (e.g. NWA 8631: 53%). Moreover, Davidson et  
447 al. (2019) interestingly noted that DOM 08006 is very poor in refractory inclusions (1%),  
448 especially AOAs, hence again consistent with MIL 07687. The Meteoritical bulletin also lists  
449 NWA11559 (CO>3.6) as not containing any detectable CAIs. We also measured the average  
450 chondrule size of MIL 07687 as being a close match to the CO chondrite average (Table 3).  
451 Lastly, our MIR spectrum of NWA 8631 (CO<sub>3</sub>.0) is similar to MIL 07687, indicating a similar  
452 bulk silicate content. Although these observations may support MIL 07687 as having affinities  
453 with the CO group, they are probably not sufficient to classify it as a true member. Indeed, there  
454 are several points to consider.

455 Firstly, not only does MIL 07687 share petrographic similarities with these unusual  
456 CO3s, but also with the CM group and several ungrouped CM-CO clan members. In fact, the  
457 boundaries between all three taxonomic classes appear to be quite blurry. In average, CM  
458 chondrites have a matrix abundance of 70% (50 – 90%, based on values from the Meteoritical  
459 Society Database), fewer refractory inclusions and similar chondrule sizes to CO chondrites  
460 (Table 3). They are hence, in average, petrographically more alike MIL 07687 than “typical”  
461 CO3s (Table 3). Moreover, the extent of the O-isotopic composition of the CM group has also  
462 been brought into question. Traditionally (other than their bulk elemental composition, and  
463 average petrographic properties: Krot et al., 2014, Weisberg et al., 2006), CM chondrites are  
464 distinguished from COs by their level of hydration (CMs being significantly more hydrated  
465 than COs) and by their O-isotopic composition (gap between  $\delta^{18}\text{O} = 0$  and + 4 ‰: Greenwood  
466 et al., 2019 and references therein). However, this view has been challenged by the discovery  
467 of several mildly altered CM/CO-like objects that populate the O-isotopic “gap” defined by  
468 “typical” COs and CMs (e.g. Greenwood et al., 2019), many of which may actually be primitive  
469 CMs (Kimura et al., 2020). The generally heavier O-isotopic composition of CMs (relative to  
470 COs) may be partially attributed to aqueous alteration (interaction with  $^{16}\text{O}$ -poor fluids), with  
471 the O-isotopic start-point of CM material being similar to that of bulk COs. This is supported  
472 by the CO-like O-isotopic composition of anhydrous CM material and the  $^{16}\text{O}$ -rich composition  
473 of some highly primitive CMs (Figs. 1 and 2., Clayton and Mayeda, 1999, Greenwood et al.,  
474 2014, Kimura et al., 2020). In fact, Lee et al. (2019) measured the mildly altered CM LEW  
475 85311 to have an O-isotopic composition similar to that of CO falls (Figs. 1 and 2). The extent  
476 of the CM field towards lighter O-isotopic compositions is thus not well defined and may  
477 potentially extend into the CO field.

478 We should also note that some CM chondrites have average chondrule sizes that are  
479 closer to MIL 07687 than the CM-average (e.g. LEW 85311 and Winchcombe: Choe et al.  
480 (2010) and Meteoritical Society database). One could thus ask if MIL 07687 actually has closer  
481 affinities with the CM group. Moreover, although MIL 07687 appears to have a significantly  
482 higher  $^{18}\text{O}$  content than CMs, it is likely that its intrinsic O-isotopic composition was closer to  
483 the PCM and CCAM line prior to terrestrial residency (see below). However, fine-grained rims  
484 do seem to be common in CMs (e.g. Metzler and Bischoff, 1987), which is unlike MIL 07687.

485 Lastly, the Meteoritical Society Database lists a large variety of ungrouped chondrites  
486 with properties that are either intermediate, or overlap, with both the CO and CM groups (and  
487 MIL 07687). Like MIL 07687, several ungrouped chondrites appear to have O-isotopic  
488 compositions that are close or consistent with that of the CO group. Some appear to be hydrated



489 (e.g. EET 83226/83355 and NWA 13249, with somewhat similar petrographic descriptions to  
490 CM2s in the Meteoritical bulletin) while others appear relatively anhydrous (e.g. El Médano  
491 200 and NWA 12957). MIL 07687 has a comparable matrix abundance and chondrule size to  
492 several of these (see Table 3). Consequently, MIL 07687 might possibly have closer affinities  
493 with some of these meteorites, despite its lighter O-isotopic composition (which might be due  
494 to terrestrial weathering, see below).

495         Based on the oxygen isotopic composition and petrographic diversity reported for CM-  
496 CO members in the Meteoritical society database (commonly used for classification), the  
497 boundaries between what we consider CO, CM and ungrouped chondrites appears to be quite  
498 blurry (Table 3, Figs. 1 and 2). Due to the overlaps between these groups, it is clear that MIL  
499 07687 cannot be attributed a taxonomic classification simply based on its petrography and O-  
500 isotopic composition.

501         In addition, terrestrial weathering poses a problem when interpreting the O-isotopic  
502 composition. Indeed, as noted in section 3.1, although the O-isotopic composition of MIL  
503 07687 is most consistent with the CO group, it appears slightly more  $^{18}\text{O}$ -poor than “typical”  
504 members, a feature particularly observed by Alexander et al. (2018) in highly weathered CO3  
505 chondrites (e.g. MIL 03442 and MIL 090785). [In fact, overall, it seems that the O-isotopic  
506 composition of CO3 finds tend to be lighter than falls \(e.g. Alexander et al. 2018, Greenwood  
507 and Franchi, 2004 and references therein, Figs. 1 and 2\).](#) Their work concludes that this “offset”  
508 from the typical CO trend is not representative of the original O-isotopic composition of these  
509 meteorites, but instead results from the contribution of Antarctic terrestrial weathering products.  
510 More specifically, the bulk isotopic composition of CO finds may evolve as a result of  
511 progressive interaction with terrestrial water, leading to a  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values that shifts  
512 towards the Terrestrial Fractionation Line (TFL), in vicinity of the Standard Light Antarctic  
513 Precipitation (SLAP) in the case of Antarctic finds (Alexander et al., 2018). Indeed, this can  
514 lead to heavily weathered Antarctic COs displaying relatively light  $^{17}\text{O}$  and  $^{18}\text{O}$  compositions  
515 compared to “typical” COs. An initial analysis by the Johnson Space Center (JSC) found that  
516 MIL 07687 displays a black/brown fusion crust and matrix, including evaporates and the  
517 presence of “rusty” chondrules (initial petrographic description, available online on the  
518 Meteoritical Society database), leading to the attribution of a “Ce” weathering grade (i.e.  
519 strongly weathered, containing evaporates).

520         In addition to many of the TGA features mentioned in section 3.5, the intensely  
521 weathered nature of MIL 07687 is likely supported by various features in our results, including:  
522 *(i)* the TGA mass loss for temperatures lower than 200°C *(ii)* the 3- $\mu\text{m}$  band and *(iii)* the optical

523 slope in the reflectance spectrum. The two former parameters are strongly influenced by  
524 adsorbed molecular H<sub>2</sub>O (although the former also possibly includes the contribution due to  
525 evaporates at 130°C, i.e. gypsum, a weathering product). Indeed, Bonal et al. (2020) found that  
526 low temperature mass loss was a reliable indicator of terrestrial weathering in CV chondrite  
527 samples. More specifically, they found that highly weathered CVs were measured to have  
528 significantly larger TGA < 200°C mass loss values (between 1.2 to 3.5 wt.%, compared to < 1  
529 wt.% for most CVs), hence reflecting strong (or long-term) exposure to terrestrial water. The  
530 absorption feature at 0.86 μm may also represent an excess of oxyhydroxides due to terrestrial  
531 weathering, similar to the feature observed in the highly weathered CO<sub>3</sub>s MIL 090785 and El  
532 Médano 389 at ~0.9 μm (Fig. 8), and in CR<sub>2</sub>s and CH<sub>3</sub>s (Cloutis et al 2012a,d, Fig. 8).

533 McAdam et al. (2018) also suggested that the red NIR slope observed in MIL 07687  
534 due to the influence of terrestrial weathering products, however Eschrig et al. (2020) found that  
535 weathered COs tend to have bluer NIR slopes (with poorly weathered COs and falls being red-  
536 sloped). Moreover, the weathered CO<sub>3</sub> samples presented in Fig. 8 all seem to have neutral or  
537 blue NIR slopes. This raises the question of whether the NIR slope may actually be an intrinsic  
538 spectral feature of the meteorite's parent body, rather than an influence of weathering products.  
539 An in-depth discussion regarding the origin of this feature will be described in section 4.2.2.

540 In order to have a better idea of the pre-weathered O-isotopic composition of MIL  
541 07687, an estimation was made based on the [Lever rule](#). If we consider oxyhydroxides as the  
542 main terrestrial weathering product, we can conclude, based on Lever's rule, that MIL 07687's  
543 original unweathered composition would possibly fall close to the typical range of primitive  
544 CO<sub>3</sub> chondrites, if it was to plot on the PCM line. Although it is difficult to provide an  
545 estimation of the δ<sup>17</sup>O and δ<sup>18</sup>O values, our projection suggests that the original O-isotopic  
546 composition was unlike that of "typical" CM chondrites. We suggest that MIL 07687 should  
547 remain classified as "ungrouped" until further evidence is provided on its nature.

548

## 549 **4.2 Secondary history of MIL 07687**

### 550 **4.2.1 MIL 07687 is a poorly metamorphosed CM-CO clan member**

551 The SiO<sub>4</sub> (Si-O) stretching (~10 μm) and bending (15 – 25 μm) regions of MIL 07687  
552 are dominated by the presence of Mg-rich olivine, pyroxene, and amorphous silicates (see  
553 section 3.3; Figs. 6 and 7). The lack of a 1.05-μm band in the reflectance spectrum of MIL  
554 07687 (Fig. 8) is also consistent with the dominant Mg-rich mineralogy of its olivine. It is  
555 believed that the absorption band at 1.05 μm most likely reflects Fe<sup>2+</sup> crystal field transitions  
556 of olivine, while the band at 2 μm is partially due to Fe<sup>2+</sup> crystal field transitions of spinel

557 (Cloutis et al., 2004; Cloutis et al., 2012b, c). Consequently, chondrites of higher FeO-rich  
558 olivine and spinel concentrations will display stronger 1.05- $\mu\text{m}$  and 2- $\mu\text{m}$  absorption bands.  
559 This is most notably the case of type >3.1 COs (e.g. ALHA 77003 and El Médano 389) and  
560 type 2 heated stage IV chondrites (e.g. PCA 02010) (Fig. 8), suggesting that MIL 07687 has  
561 hence been heated less than these meteorites.

562 Although the bulk Si-O band profile of MIL 07687 has similarities with some primitive  
563 chondrites (e.g. CO3.0 NWA 8631), its reflectance and bulk IR transmission spectra resemble  
564 that of the stage II heated CM2 EET 87522. This is mainly because olivine and amorphous  
565 silicates can be significantly present in both primitive and Stage II/III heated chondrites (e.g.  
566 Abreu and Brearley, 2010; King et al., 2021). With increasing temperatures these poorly-  
567 crystalline silicates (regardless of being primary or secondary in origin) are progressively  
568 crystallized into purely anhydrous minerals, mainly olivine (e.g. King et al., 2021), hence the  
569 higher olivine abundance in CO>3.0 and Stage III/IV chondrites (Figs. 6 and 7). This can also  
570 clearly be observed in our IR spectra of CO3 matrix fragments, where the primary amorphous  
571 silicates decrease in abundance, relative to olivine, in the order of DOM 08006 (3.00), LAP  
572 031117 (3.05) and DOM 03238 (3.1) (Fig. 4).

573 Our matrix and bulk IR spectra show that the abundance of amorphous silicates in the  
574 matrix of MIL 07687 are comparable to that in primitive CR2 matrices, moderately heated  
575 CM2s, and more than in CO3s. Although this could indicate that it has suffered a type-2 thermal  
576 history, our IR spectra alone cannot say whether MIL 07687 is highly primitive or underwent  
577 mild-to-moderate short-term thermal metamorphism. Note however that interpretations of bulk  
578 data are highly influenced by their matrix abundance, hence the importance of matrix-only  
579 measurements.

580 Doubt in regards to the interpretation of the thermal history is removed thanks to Raman  
581 spectroscopy of polyaromatic carbonaceous matter. Indeed, the Raman spectra acquired on  
582 matrix grains of MIL 07687 (Bonal et al., 2016) are characterized by a high fluorescence  
583 background and by a shallow spectral valley between the Raman D- and G-bands (Fig. 14a).  
584 This is typical of type 2 chondrites, and this simple visual inspection allows to distinguish MIL  
585 07687 from primitive CO3 chondrites, such as DOM 08006 (3.0; Bonal et al., 2016). To  
586 characterize the thermal history of type 2 chondrites, the most sensitive spectral parameters are  
587 the ones related to the G-band: its Full Width at Half Maximum and its position (e.g., Quirico  
588 et al., 2018). In particular, Quirico et al. (2018) distinguished 3 Raman groups among 40 CM  
589 and ungrouped chondrites. The R1 group contains chondrites with no detectable structural  
590 modifications by heating. R3 contains chondrites with slight structural modifications induced

591 by a weak heating. The R2 group is characterized by Raman parameters pointing to a higher  
592 degree of structural order than R1 and R3, unambiguously reflecting thermal events. The  
593 Raman parameters describing the spectra of MIL 07687 are plotting among “R1” type 2  
594 chondrites (Fig. 14b). This clearly shows that MIL 07687 escaped any significant thermal  
595 metamorphism.

596

#### 597 **4.2.2 MIL 07687 likely experienced an episode of aqueous alteration**

598 As underlined in section 3.2., the detection of a 3- $\mu\text{m}$  band (broad with a peak intensity  
599 at 2.82  $\mu\text{m}/3545\text{ cm}^{-1}$ ; Figs. 3 and 4) shows that (at least part) of the matrix amorphous silicates  
600 in MIL 07687 are hydrated. This suggests that the meteorite’s matrix possibly suffered  
601 incomplete and incipient **aqueous alteration**, perhaps similarly to primitive CR2s (Le Guillou  
602 et al., 2015). While  $\text{Fe}^{3+}$ oxyhydroxides possibly produced by aqueous alteration have been  
603 detected in MIL 07687 (Brearley 2012, 2013; Haenecour et al., 2020), this appears to be the  
604 first time, to our knowledge, that hydrated amorphous silicates have been reported in this  
605 meteorite. The question is whether these hydrated minerals are of terrestrial or parent-body  
606 origin.

607 As established in section 4.1., MIL 07687 is a highly weathered meteorite. However, if  
608 these minerals were to solely be of terrestrial origin, this would suggest that MIL 07687 would  
609 have been an extremely pristine meteorite prior the onset of Antarctic weathering (thus very  
610 rare). Moreover, the distribution of hydrated amorphous silicates in MIL 07687 seems quite  
611 homogenous throughout the sample, which would unlikely be the case if they were solely due  
612 to terrestrial weathering.

613 The next question is whether our TGA data can also be used as a tracer of the meteorite’s  
614 hydration. At first glance, according to our initial definition (section 2.4), the high-temperature  
615 TGA 350-700°C mass loss (5.8 wt.%) would indicate phyllosilicates being present in this  
616 meteorite. However, as we have observed in our results (section 3.5, Fig. 11), we must note the  
617 overlap with other minerals such as possibly oxyhydroxides at around 400 – 500°C, carbonates  
618 that have an onset at around 650°C, and organics that may decompose throughout the  
619 temperature ranges studied. In fact, MIL 07687 and all CO<sub>3</sub> finds have similar TGA curves,  
620 suggesting that many of the minerals significantly contributing to the TGA mass loss of these  
621 meteorites may actually be of terrestrial origin. Consequently, parent-body phyllosilicates (if  
622 present) are unlikely to significantly contribute to the mass loss, consistent with our IR spectra.

623 However, we do observe a possible trend: (i) the matrix-normalized TGA 200 – 700°C  
624 and 350-700°C mass loss decreases with increasing thermal metamorphism (see Table 2); (ii)

625 the intensity of the carbon monoxide band is weaker in highly metamorphosed CO3s compared  
626 to MIL 07687 and primitive CO3s (Figs. 12 and 13); (iii) although weak, possible signatures of  
627 carbonates are present in the TGA/IRS data of Moss, despite being a fall. Thus, in addition to  
628 hydrated amorphous silicates, our data possibly suggests that a subset of oxyhydroxides and  
629 carbonates are also parent body alteration products in CO3s and MIL 07687. In the case of  
630 oxyhydroxides, “dendritic” ferrihydrite in the matrix of MIL 07687 is already regarded as a  
631 possible aqueous alteration product (e.g. Haenecour et al., 2020). Moreover, oxyhydroxides  
632 have also previously been mentioned as alteration products in COs and CMs (Keller and  
633 Buseck, 1990; Pignatelli et al., 2016), as have carbonates in CMs (e.g. De Leuw et al., 2010).

634 Alternatively, carbon monoxide emissions in our samples may also result from the  
635 interaction between organic matter and magnetite at high temperatures (e.g. Rudolph et al.,  
636 2012). Both organic matter and magnetite are more commonly observed in primitive versus  
637 more metamorphosed CO3s (Alexander et al., 2007; Rubin and Li, 2019). This could explain  
638 the stronger carbon monoxide bands observed in DOM 03238 (a magnetite-enriched CO3.1)  
639 versus the other COs. Vaccaro et al. (2017) did not detect magnetite in the matrix of MIL 07687,  
640 which would suggest that it is significantly richer in carbonates than the CO3s studied in this  
641 work. Both alternatives support the detection of aqueous alteration in MIL 07687 and CO3s  
642 through TGA. A larger number of CO samples studied by TGA should be considered for future  
643 reference.

644 Although the TGA mass loss may be difficult to use in order to quantify the hydration  
645 of MIL 07687 relative to CO3s, the IR transmission spectra of MIL 07687 matrix fragments  
646 support this meteorite as being more hydrated than our CO3s, and comparably so to some CR2s.  
647 As previously mentioned, the MIR matrix spectral profile of MIL 07687 is very similar to  
648 primitive CR2 chondrites, both in terms of their average 3- $\mu\text{m}$  and 10- $\mu\text{m}$  profile and intensity,  
649 indicating that they contain a similar abundance of Fe-rich amorphous hydrated silicates in their  
650 matrices. However, phyllosilicates have been reported in pristine CR2s (Harju et al., 2014; Le  
651 Guillou et al., 2015), unlike MIL 07687, indicating that these CR2s may be slightly more  
652 aqueously altered. Consequently, based on the comparison of the proposed CM petrographic  
653 classification by Kimura et al. (2020), and that by Harju et al. (2014) for primitive CR2s, we  
654 could estimate MIL 07687 as having a petrographic grade of 2.9. This would further be  
655 supported by the type-2 thermal history of this meteorite. We note however that hydrated  
656 amorphous silicates are not detected in the bulk IR transmission spectra of primitive CR2s  
657 (Fig.7), which is most likely due to their lower matrix abundances than in MIL 07687.

658 MIL 07687 is less hydrated than the relatively mildly altered CM2.4-2.7s as shown by  
659 its lack of phyllosilicate absorption bands in its bulk and/or matrix IR spectra (Figs. 4 and 7).  
660 This is despite the comparable TGA 400 – 770°C values between MIL 07687, LEW 85311  
661 (CM2.7) and QUE 97990 (CM2.6), thus showing that this temperature range is not reliable  
662 when quantifying the hydration. This is likely due to the difficulty in quantifying the mass loss  
663 due to carbonates and/or magnetite. The incipient extent of aqueous alteration in MIL 07687 is  
664 further supported by the proximity of the O-isotopic composition to the PCM line (Figs. 1 and  
665 2), as well as the abundance of ferrihydrite, which represents among the first minerals to form  
666 under oxic aqueous conditions (Pignatelli et al., 2017). Again, this assumes that these minerals  
667 do not result from terrestrial weathering, which has yet to be confirmed.

668 Lastly, we propose that the red reflectance NIR slope reflects the content of hydrated  
669 amorphous silicates present in MIL 07687. Indeed, we observe similar slopes in the spectra of  
670 MIL 090073, EET 83355 and EET 87522 (Fig. 8), all which are known to contain deformed  
671 (amorphized) phyllosilicates (Alexander et al., 2018, King et al., 2021), rather than crystalline  
672 phyllosilicates. For comparison, LEW 85311 and QUE 97990 also display similar red NIR  
673 slopes, but are accompanied by distinct 0.7- $\mu\text{m}$  and 2.8- $\mu\text{m}$  features (indicative of significant  
674 crystalline phyllosilicate content). We can rule out metal as the likely cause for their red slopes  
675 (e.g. in CR2s: Cloutis et al. 2012a.), as they are rare in these meteorites (less than 1%), MIL  
676 07687 included (King et al., 2021, Vaccaro, 2017).

677 The 2.4- $\mu\text{m}$  band present in the reflectance spectra of MIL 07687 and various types of  
678 CCs (see section 3.4), might be due to carbonates, based on a comparison with the spectra by  
679 Gaffey (1986), which could also indicate aqueous alteration and/or terrestrial weathering.

680

#### 681 **4.3. What if MIL 07687 is a CO<sub>2</sub> chondrite?**

682 If we were to identify MIL 07687 as a CO<sub>2.9</sub> chondrite, we would extend the known  
683 petrographic range of the CO group, and thus provide new constraints on the geological  
684 processes occurring on their parent body (assuming that our currently recognized CO chondrites  
685 correctly sample one single parent body). The final hydration state of a sample (i.e. presence of  
686 hydrated amorphous silicates) is controlled by the interplay of heat and water. On the CO parent  
687 body, the heat source was likely of radiogenic origin (i.e. long-term metamorphism). If indeed  
688 a CO<sub>2</sub> chondrite, MIL 07687 would possibly have originated from a location within the parent  
689 asteroid that escaped the extent of thermal metamorphism experienced by CO<sub>3</sub>s, while its  
690 relatively hydrated nature would show that it better retained (and/or interacted with) the  
691 surrounding fluids (or did not experienced dehydration thanks to a lower peak metamorphic

692 temperature). This can be explained if MIL 07687 represents a portion of the parent body that  
693 accreted a higher abundance of ice. More specifically, the higher abundance of ice may have  
694 locally buffered the peak metamorphic temperatures (Grimm and McSween, 1989) and also  
695 promote a more extensive interaction of fluid as well as the conservation of hydrated minerals.  
696 Consequently, if it was to be a CO chondrite, MIL 07687 may be evidence that the CO parent  
697 body was heterogeneous, possibly having accreted variable amounts of water ice that was  
698 heterogeneously distributed throughout the parent asteroid.

699 Another possible explanation would be that MIL 07687 formed within a relatively  
700 hydrated region (or layer) close to the parent body surface (perhaps it would have accreted onto  
701 the parent body later than most CO material). Indeed, nearly all the CO3s in the Meteoritical  
702 Society Database (2021) with comparable matrix abundances to MIL 07687 (~50% or more)  
703 all appear to be quite primitive (often listed as CO3.0s), with similar Cr<sub>2</sub>O<sub>3</sub> values to MIL  
704 07687. Thus, if these meteorites are indeed COs (which needs to be verified), and assuming  
705 that this meteorite group only samples one single primary parent body, this would possibly  
706 suggest that MIL 07687, along with these meteorites, would represent a poorly heated, matrix-  
707 enriched, and potentially hydrated, superficial layer of the CO parent body. Unfortunately, to  
708 our knowledge, we were not able to find any noble gas data in the literature that may give  
709 insight into whether or not MIL 07687 was located near the surface of its parent body. In both  
710 cases, not only would it imply that the parent body was petrographically heterogeneous, but  
711 it would further suggest that the overall water content on the CO parent body would likely have  
712 been higher than previously considered. The idea of an unevenly hydrated CO parent  
713 planetesimal may be supported by the discovery of unheated hydrated clasts in NWA 1232, a  
714 brecciated CO3 (Matsumoto et al. 2015), assuming that these are not xenoliths. There are also  
715 several COs that appear to contain phyllosilicates (e.g. Acfer 374, EET 90043 and NWA 11790:  
716 Meteoritical society database).

717 Although it is currently not possible to conclude whether MIL 07687 actually belongs  
718 to the CO group, it is an interesting path to explore as it has important implications on our  
719 understanding of their parent body.

720

## 721 **5. Conclusion**

722 Based on a combination of bulk oxygen isotopic measurements, spectroscopy and  
723 thermogravimetric analysis studies, we are able to conclude that:

724 1. MIL 07687 cannot be provided a primary classification by its O-isotopic composition and  
725 petrography alone, due its overlapping petrographic descriptions and bulk O-isotopic

726 composition with various CO, CM and ungrouped chondrites in Meteoritical Society database.  
727 Significant terrestrial weathering further complicates the interpretation of the O-isotopic  
728 composition. We recommend that this meteorite remains classified as “ungrouped”, although a  
729 CO or CM classification cannot be excluded. We do estimate however that the  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$   
730 values were lower than Acfer 094, Adelaide, MAC 88107 and most CM2s (more alike COs and  
731 some ungrouped CCs).

732 2. MIL 07687 experienced a thermal history similar to type 2 chondrites, as attested by the  
733 structural order of the polyaromatic matter characterized by Raman spectroscopy.

734 3. MIL 07687 has likely experienced more extensive aqueous alteration than most CO3  
735 chondrites, and less than most known CM2s. The hydration probably resulted in hydrated Fe-  
736 rich amorphous silicates, oxyhydroxides, and possibly carbonates. Nevertheless, the alteration  
737 was likely very mild and did not include the entirety of its matrix. Significant nucleation of  
738 phyllosilicates did not likely occur. The extent of aqueous alteration is comparable to that  
739 observed in poorly hydrated CR2s. The red NIR slope of MIL 07687 might be a result of its  
740 hydrated amorphous silicate content. We recommend a petrographic grade of about 2.9, if these  
741 hydrated minerals are indeed pre-terrestrial.

742 4. We explore the hypothetical implications of MIL 07687 being a CO2 chondrite. If true, it  
743 would suggest that the CO parent body was geologically heterogeneous, assuming that all COs  
744 sample a single parent asteroid. It would further suggest that water was unevenly distributed  
745 throughout the planetesimal, leading to localized aqueous alteration, rather than widespread.  
746 Consequently, it is important to have a better understanding of the geochemical and  
747 petrographic limits of the CO group, as meteorites such as MIL 07687 could have strong  
748 implications on our understanding of their parent body(ies).

749

750

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756 **References**

- 757 Abreu N. M., Brearley A. J. 2010. Early solar system processes recorded in the matrices of two  
 758 highly pristine CR3 carbonaceous chondrites, MET 00426 and QUE 99177. *Geochimica*  
 759 *et Cosmochimica Acta* 74(3):1146-1171.
- 760 Abreu N. M., Louro M. D., Friedrich J. M., Schrader D. L., Greenwood R. C. (2018) Elephant  
 761 Moraine (EET) 83226: a clastic, type 2 carbonaceous chondrites with affinities to the  
 762 CO chondrites (abstract #2451). 49th Lunar and Planetary Science Conference.
- 763 Alexandre A., Basile-Doelsch I., Sonzogni C., Sylvestre F., Parron C., Meunier J.-D., and Colin  
 764 F. (2006). Oxygen isotope analyses of fine silica grains using laser-extraction technique:  
 765 Comparison with oxygen isotope data obtained from ion microprobe analyses and  
 766 application to quartzite and silcrete cement investigation. *Geochimica et Cosmochimica*  
 767 *Acta* 70(11):2827–2835.
- 768 Alexander, C. M. O'D., Fogel, M., Yabuta, H., Cody, G. D. 2007. The origin and evolution of  
 769 chondrites recorded in the elemental and isotopic compositions of their macromolecular  
 770 organic matter. *Geochimica et Cosmochimica Acta* 71:4380-4403.
- 771 Alexander C.M.O'D., Greenwood R.C., Bowden R., Gibson J.M., Howard K.T., Franchi I.A.  
 772 2018. A multi-technique search for the most primitive CO chondrites, *Geochimica et*  
 773 *Cosmochimica Acta* 221(15):406-420.
- 774 Beck P. and Garenne A. 2012. MIR transmission spectra at Tamb, 150°C and 300°C of bulk  
 775 CM chondrites in KBr pellets. SSHADE/GhoSST (OSUG Data Center).  
 776 Dataset/Spectral Data.  
 777 [https://doi.org/10.26302/SSHADE/EXPERIMENT\\_LB\\_20170721\\_001](https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20170721_001)
- 778 Beck P., Garenne A., Quirico E., Bonal L., Montes-Hernandez G., Moynier F., and Schmitt B.  
 779 2014. Transmission infrared spectra (2–25µm) of carbonaceous chondrites (CI, CM,  
 780 CV–CK, CR, C2 ungrouped): Mineralogy, water, and asteroidal processes. *Icarus*  
 781 229:263–277.
- 782 Beck P., C., Maturilli, A., Garenne A., Vernazza P., Helbert J., Quirico E., Schmitt B. 2018.  
 783 What is controlling the reflectance spectra (0.35–150 µm) of hydrated (and dehydrated)  
 784 carbonaceous chondrites?. *Icarus* 313:124–138.
- 785 Beck P., Schmitt B., Pommerol A., Potin S., Brissaud O. 2021. Low-phase spectral reflectance  
 786 and equivalent "geometric albedo" of meteorites powders. *Icarus*, submitted for  
 787 publication.
- 788 Bonal L., Bourrot-Denise, M., Quirico, E., Montagnac, G., Lewin, E. 2007. Organic matter and  
 789 metamorphic history of CO chondrites. *Geochimica et Cosmochimica Acta* 71:1605–  
 790 1623.
- 791 Bonal L. 2011a. Mid-IR absorbance spectra of EET92042 matrix grains under vacuum at  
 792 different temperatures) under vacuum at 300°C. SSHADE/GhoSST (OSUG Data  
 793 Center). Dataset/Spectral Data:  
 794 [https://doi.org/10.26302/SSHADE/EXPERIMENT\\_LB\\_20170731\\_004](https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20170731_004)
- 795 Bonal L. 2011b. Raw, normalized and baseline-corrected of MIR transmission spectra of  
 796 GRA95229 matrix grains pressed on diamonds under vacuum at ambient temperature  
 797 and 300C. SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data:  
 798 [https://www.sshade.eu/data/experiment/EXPERIMENT\\_LB\\_20170731\\_003](https://www.sshade.eu/data/experiment/EXPERIMENT_LB_20170731_003)
- 799 Bonal L. 2011c. Raw, normalized and baseline-corrected of MIR transmission spectra of  
 800 MET00426 matrix grains pressed on diamonds under vacuum at ambient temperature  
 801 and 300C. SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data:  
 802 [https://www.sshade.eu/data/experiment/EXPERIMENT\\_LB\\_20170731\\_001](https://www.sshade.eu/data/experiment/EXPERIMENT_LB_20170731_001)
- 803 Bonal L. 2011d. MIR absorbance spectra of pressed QUE99177 matrix grains (CR Chondrite)  
 804 under vacuum at different temperatures. SSHADE/GhoSST (OSUG Data Center).

805 Dataset/Spectral Data :

806 [https://www.sshade.eu/data/experiment/EXPERIMENT\\_LB\\_20170731\\_002](https://www.sshade.eu/data/experiment/EXPERIMENT_LB_20170731_002)

807 Bonal L. 2011e. Mid-IR absorbance spectra of Renazzo matrix grains under vacuum at different

808 temperatures. SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data:

809 [https://doi.org/10.26302/SSHADE/EXPERIMENT\\_LB\\_20170731\\_005](https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20170731_005)

810 Bonal L., Alexander C. M. O., Huss G. R., Nagashima K., Quirico E., and Beck P. 2013.

811 Hydrogen isotopic composition of the water in CR chondrites. *Geochimica et*

812 *Cosmochimica Acta* 106(1):111–133.

813 Bonal L., Quirico E., Flandinet L., and Montagnac G. 2016. Thermal history of type 3

814 chondrites from the Antarctic meteorite collection determined by Raman spectroscopy

815 of their polyaromatic carbonaceous matter. *Geochimica et Cosmochimica Acta*

816 189:312–337.

817 Brearley A. J. 1993. Matrix and fine-grained rims in the unequilibrated CO3 chondrite,

818 ALHA77307: origins and evidence for diverse, primitive nebular dust components.

819 *Geochimica et Cosmochimica Acta* 57(7):1521–1550

820 Brearley A. J. 2006. The action of water. In *Meteorites and the Early Solar System II*, University

821 of Arizona Press. Tucson: D.S. Lauretta and H.Y. McSween Jr. pp. 584–624.

822 Brearley A. J. 2012. MIL 07687 - An intriguing, very low petrologic type 3 carbonaceous

823 chondrite with a unique style of aqueous alteration. The Woodlands, Texas: LPI

824 Contribution. p. 1233.

825 Brearley A. J. 2013. Miller Range MIL 07687: A unique carbonaceous chondrite with a

826 complex record of partial aqueous alteration (abstract #5206). *Meteoritics & Planetary*

827 *Science* 47 (Suppl.).

828 Choe W. H., Huber H., Rubin A.E., Kallemeyn G. W., and Wasson J. T. 2010. Compositions

829 and taxonomy of 15 unusual carbonaceous chondrites. *Meteoritics & Planetary Science*.

830 45(4):531 - 554.

831 Clayton R.N. and Mayeda T.K. 1999. Oxygen isotope studies of carbonaceous chondrites.

832 *Geochimica et Cosmochimica Acta* 63(13-14), 2089-2104.

833 Cloutis E. A., Sunshine J. M., Morris R. V. 2004. Spectral reflectance-compositional properties

834 of spinels and chromites: Implications for planetary remote sensing and

835 geothermometry. *Meteoritics & Planetary Science* maps 39(4):545-565.

836 Cloutis E., Hudon P., Hiroi T., Gaffey M., Mann P. 2011. Spectral reflectance properties of

837 carbonaceous chondrites 2. CM chondrites. *Icarus*, 216(1):309-346

838 Cloutis E., Hudon P., Hiroi T., Gaffey M., Mann P. 2012a. Spectral reflectance properties of

839 carbonaceous chondrites – 3: CR chondrites. *Icarus*, 217(1):389-407

840 Cloutis E., Hudon P., Hiroi T., Gaffey M., Mann P. 2012b. Spectral reflectance properties of

841 carbonaceous chondrites – 5: CO chondrites. *Icarus*, 220(2):466-486

842 Cloutis E., Hudon P., Hiroi T., Gaffey M., Mann P. 2012c. Spectral reflectance properties of

843 carbonaceous chondrites – 6: CV chondrites. *Icarus*, 221(1):328-358

844 Cloutis E., Hudon P., Hiroi T., Gaffey M., Mann P. 2012d. Spectral reflectance properties of

845 carbonaceous chondrites: 8. “Other” carbonaceous chondrites: CH, ungrouped,

846 polymict, xenolithic inclusions, and R chondrites. *Icarus*, 221(1):984-1001.

847 Court R. W., Sephton M. A. 2014. New estimates of the production of volatile gases from

848 ablating carbonaceous micrometeoroids at Earth and Mars during an E-belt-type Late

849 Heavy Bombardment. *Geochimica et Cosmochimica Acta* 145:175-205.

850 Davidson J., Nittler L. R., Alexander C. M. O., and Stroud R. M. 2014. Petrography of very

851 primitive CO3 chondrites: Dominion Range 08006, Miller Range 07687, and four others

852 (abstract #1384). 45th Lunar and Planetary Science Conference.

853 Davidson J., Nittler L. R., Stroud R. M., Takigawa, A., De Gregorio, B. T., Alexander C. M.

854 O., Kilcoyne, A. L. D., Cody, G. D. 2015. Organic matter in the unique carbonaceous

855 chondrite Miller Range 07687: a coordinated in situ nanosims, FIB-TEM, and XANES  
856 study (abstract #1609). 46th Lunar and Planetary Science Conference.

857 Davidson J., Alexander C.M.O'D., Stroud R. D., Busemann H., Nittler L. R. 2019. Mineralogy  
858 and petrology of Dominion Range 08006: A very primitive CO<sub>3</sub> carbonaceous  
859 chondrite. *Geochemica et Cosmochimica Acta* 265:259-278.

860 DeMeo F.E., Binzel R.P., Slivan S.M., Bus S.J. 2009. An extension of the Bus asteroid  
861 taxonomy into the near-infrared. *Icarus*, 202(1):160-180

862 De Leuw S., Rubin A. E., Wasson J. T. 2010. Carbonates in CM chondrites: Complex  
863 formational histories and comparison to carbonates in CI chondrites. *Meteoritics &*  
864 *Planetary Science* maps. 45(4), 513-530.

865 Dobircă E., Brearley A. J. 2020. Amorphous silicates in the matrix of Semarkona: The first  
866 evidence for the localized preservation of pristine matrix materials in the most  
867 unequilibrated ordinary chondrites. *Meteoritics & Planetary Science* maps. 55(3), 649-  
868 668.

869 Eschrig J., Bonal L., Beck P., Prestgard T. 2019. NIR reflectance spectrum (i= 0°, e= 30°) of  
870 bulk CO chondrites under vacuum at T= 80°C.  
871 [https://doi.org/10.26302/SSHADE/EXPERIMENT\\_LB\\_20191220\\_002](https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20191220_002)

872 Eschrig J., Bonal L., Beck P. 2019. NIR reflectance spectrum (i= 0°, e= 30°) of bulk CR  
873 chondrites under vacuum at T= 80°C.  
874 [https://doi.org/10.26302/SSHADE/EXPERIMENT\\_LB\\_20191220\\_003](https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20191220_003)

875 Eschrig J., Bonal L., Beck P., Prestgard T. J. 2020. Spectral reflectance analysis of type 3  
876 carbonaceous chondrites and search for their asteroidal parent bodies. *Icarus*  
877 354:114034.

878 Földvari M. 2011. Handbook of thermogravimetric system of minerals and its use in geological  
879 practice. Geological Inst. of Hungary, Budapest.

880 Gaffey S. J. 1986. Spectral reflectance of carbonate minerals in the visible and near infrared  
881 (0.35-2.55 microns); calcite, aragonite, and dolomite. *American Mineralogist* 71(1-  
882 2):151-162.

883 Garenne A., Beck P., Montes-Hernandez G., Chiriac R., Toche F., Quirico E., Bonal L., and  
884 Schmitt B. 2014. The abundance and stability of “water” in type 1 and 2 carbonaceous  
885 chondrites (CI, CM and CR). *Geochimica et Cosmochimica Acta* 137:93–112.

886 Greenwood R. C., Franchi I. A. 2004. Alteration and metamorphism of CO<sub>3</sub> chondrites:  
887 Evidence from oxygen and carbon isotopes. *Meteoritics & Planetary Science* maps.  
888 39(11), 1823-1838.

889 Greenwood R. C., Howard K. T., Franchi I. A., Zolensky, M. E., Buchanan, P. C., Gibson, J.  
890 M. 2014. Oxygen isotope evidence for the relationship between CM and CO chondrites:  
891 Could they both coexist on a single asteroid?. (abstract #2610). 45th Lunar and Planetary  
892 Science Conference.

893 Greenwood R. C., Howard K. T., King A. J., Lee M. R., Burbine T. H., Franchi I. A., Anand  
894 M., Findlay R., Gibson J. M. 2019. Oxygen isotope evidence for multiple CM parent  
895 bodies: what will we learn from the Hayabusa 2 and OSIRIS-REx return missions?  
896 (abstract #2191). 50th Lunar and Planetary Science Conference.

897 Grimm R. E. and McSween H. Y. 1989. Water and the thermal evolution of carbonaceous  
898 chondrite parent bodies. *Icarus* 82:244–280.

899 Gröning M. (2004) Chapter 40 – International Stable Isotope Reference Materials. In *Handbook*  
900 *of Stable Isotope Analytical Techniques*. pp. 874–906.

901 Haenecour P., Floss C., Brearley A. J., and Zega T. J. 2020. The effects of secondary processing  
902 in the unique carbonaceous chondrite Miller Range 07687. *Meteoritics & Planetary*  
903 *Science* maps.13477.

904 Harju E. R., Rubin A. E., Ahn I., Choi B., Ziegler K., Wasson J. T. 2014. Progressive aqueous

- 905 alteration of CR carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 139:267–  
 906 292.
- 907 Howard K. T., Alexander C. M. O'D., Dyl K. A. 2014. PSD-XRD Modal Mineralogy of Type  
 908 3.0 CO Chondrites: Initial Asteroidal Water Mass Fractions and Implications for CM  
 909 Chondrites. The Woodlands, Texas: LPI Contribution. p. 1830.
- 910 Howard K. T., Alexander C. M. O'D., Schrader D. L., Dyl K. A. 2015. Classification of hydrous  
 911 meteorites (CR, CM and C2ungrouped) by phyllosilicate fraction: PSD-XRD modal  
 912 mineralogy and planetesimal environments. *Geochimica et Cosmochimica Acta*  
 913 149:206–222.
- 914 Keller L. P., Buseck P. R. 1990. Matrix mineralogy of the Lancé CO3 carbonaceous chondrite:  
 915 A transmission electron microscope study. *Geochimica et Cosmochimica Acta* 54:1155–  
 916 1163.
- 917 Kimura M., Imae N., Komatsu M., Barrat J. A., Greenwood R. C., Yamaguchi A., Noguchi T.  
 918 2020. The most primitive CM chondrites: Asuka 12085, 12169, and 12236, of subtypes  
 919 3.0 – 2.8: Their characteristics features and classification. *Polar science* 26:100565.
- 920 King A. J., Schofield P. F., Russell S. S. 2021. Thermal alteration of CM carbonaceous  
 921 chondrites: Mineralogical changes and metamorphic temperatures. *Geochimica et*  
 922 *Cosmochimica Acta* 298:167-190.
- 923 King A. J., Solomon J. R., Schofield P. F., Russell S. S. 2015. Characterising the CI and CI-  
 924 like carbonaceous chondrites using thermogravimetric analysis and infrared  
 925 spectroscopy. *Earth, Planets and Space* 67:198.
- 926 Krot A. N., Keil K., Scott E. R. D., Goodrich C. A., and Weisberg M. K. 2014. Classification  
 927 of meteorites and their genetic relationships. In *Treatise on Geochemistry* (2nd ed.),  
 928 edited by Turekian H. D. H. K. Oxford, UK: Elsevier. pp. 1–63.
- 929 Lee M. R., Cohen B. E., King A. J., Greenwood R. C. 2019. The diversity of CM carbonaceous  
 930 chondrite parent bodies explored using Lewis Cliff 85311. *Geochimica et*  
 931 *Cosmochimica Acta* 264:224–244.
- 932 Le Guillou C., Changela H. G., Brearley A. J. 2015. Widespread oxidized and hydrated  
 933 amorphous silicates in CR chondrites matrices: Implications for alteration conditions  
 934 and H<sub>2</sub> degassing of asteroids. *Earth and Planetary Science Letters* 420(15), 162-173.
- 935 Matsumoto M., Tomeoka K., Seto Y., et al. 2015. Hydrated, Unmetamorphosed Clasts in the  
 936 NWA 1232 CO3 Carbonaceous Chondrite (abstract). *Meteoritics & Planetary Science*  
 937 78(Suppl.): 1856.pdf.
- 938 Metzler K. and Bischoff A. (1987) Accretionary dark rims in  
 939 CM chondrites. *Meteoritics* 22, 458-459
- 940 McAdam M.M., Sunshine J.M., Howard K.T., Alexander C.M.O'D., McCoy T.J., Bus S.J.  
 941 2018. Spectral evidence for amorphous silicates in least-processed CO meteorites and  
 942 their parent bodies. *Icarus* 306(15):32-49.
- 943 Miller M. F. 2002. Isotopic fractionation and the quantification of 17 O anomalies in the oxygen  
 944 three-isotope system. *Geochimica et Cosmochimica Acta* 66(11):1881–1889.
- 945 Nakamura-Messenger K., Messenger S., Keller L. P., Clemette S. J., Zolensky E. M. 2006.  
 946 Organic Globules in the Tagish Lake Meteorite: Remnants of the Protosolar Disk.  
 947 *Nature* 314(5804):1439-805.
- 948 Pignatelli I., Marrocchi Y., Vacher L. G., Delon R., Gounelle M. 2016. Multiple precursors of  
 949 secondary mineralogical assemblages in CM chondrites. *Meteoritics & Planetary*  
 950 *Science* maps 51(4):785-805.
- 951 Pignatelli I., Marrocchi Y., Mugnaioli E., Bourdelle F., Gounelle M. 2017. Mineralogical,  
 952 crystallographic and redox features of the earliest stages of fluid alteration in CM  
 953 chondrites. *Geochimica et Cosmochimica Acta* 209:106-122.

- 954 Potin S., Brissaud O., Beck P., Schmitt B., Magnard Y., Correia J.-J., Rabou P., Jocoü L. 2018.  
 955 SHADOWS: a spectro-gonio radiometer for bidirectional reflectance studies of dark  
 956 meteorites and terrestrial analogs: design, calibrations, and performances on challenging  
 957 surfaces. *Appl. Opt.*, 57(28):8279-8296
- 958 Potin S., Beck P., Usui F., Bonal L., Vernazza P., Schmitt B. 2020. Style and intensity of  
 959 hydration among C-complex asteroids: A comparison to desiccated carbonaceous  
 960 chondrites. *Icarus* 348:113826.
- 961 Prestgard T., Bonal L. 2019. Raw MIR transmission spectra of matrix fragments of CO  
 962 chondrites, pressed on diamonds under vacuum and at several temperatures.  
 963 SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data.
- 964 Quirico E., Montagnac G., Rouzaud J.-N., Bonal L., Bourot-Denise M., Duber S., Reynard B.  
 965 2009. Precursor and metamorphic condition effects on Raman spectra of poorly ordered  
 966 carbonaceous matter in chondrites and coals. *Earth Planet. Sci. Lett.*, 287(1):185-193
- 967 Quirico E., Bonal L., Beck P., Alexander C.M.O'D., Yabuta H., Nakamura T., Nakato A.,  
 968 Flandinet L., Montagnac G., Schmitt-Kopplin P., Herd C.D.K. 2018. Prevalence and  
 969 nature of heating processes in CM and C2-ungrouped chondrites as revealed by  
 970 insoluble organic matter. *Geochimica et Cosmochimica Acta* 241:17–37.
- 971 Raynal P. I., Quirico E., Borg J., Deboffle D., Dumas P., d'Hendecourt L., Bibring J.-P., and  
 972 Langevin Y. 2000. Synchrotron infrared microscopy of micron-sized extraterrestrial  
 973 grains. *Planetary and Space Science* 48:1329–1339.
- 974 Rubin A. E., Trigo-Rodríguez J. M., Huber H., Wasson J. T. 2007. Progressive aqueous  
 975 alteration of CM carbonaceous chondrites. *Geochimica et Cosmochimica Acta*  
 976 71(9):2361-2382.
- 977 Rubin A. E., Li, Y. 2019. Formation and destruction of magnetite in CO3 chondrites and other  
 978 chondrite groups. *Geochemistry* 79(4):125528
- 979 Rudolph M., Erler J., Peuker U. A. 2012. A TGA-FTIR perspective of fatty acid adsorbed on  
 980 magnetite nanoparticles – Decomposition steps and magnetite reduction. *Colloids and*  
 981 *Surfaces A: Physicochem. Eng. Aspects*.397:16–23
- 982 Salisbury J.W., Walter L.S., Vergo N., D'Aria D., 1991. Infrared (2.1–25 $\mu$ m) Spectra of  
 983 Minerals. Johns Hopkins University Press, Baltimore.
- 984 Schmitt B., Bollard P., Albert D., Bonal L. 2012. SSHADE/GhoSST: "Grenoble astroPhysics  
 985 and planetOlogy Solid Spectroscopy and Thermodynamics" database. SSHADE  
 986 (OSUG Data Center). Service/Database. doi:10.26302/SSHADE/GHOSST
- 987 Simmonds T., Hayes P. C. 2017. Reduction of Hematite to Magnetite in CO/CO2 Gas Mixtures  
 988 Under Carbon Looping Combustion Conditions. *Metallurgical and Materials*  
 989 *Transactions E*. 4:101-113.
- 990 Stokke A. 2018. Compositional and Topographical Characterization of Carbonaceous  
 991 Chondritic Meteorites Moss and Murray Using micro-Raman Spectroscopy and  
 992 SEM/EDS. Thesis. Minnesota State University.
- 993 Suavet C., Alexandre A., Franchi I. A., Gattacceca J., Sonzogni C., Greenwood R. C., Folco L.,  
 994 and Rochette P. 2010. Identification of the parent bodies of micrometeorites with high-  
 995 precision oxygen isotope ratios. *EPSL* 293:313-320.
- 996 Torrano Z. A., Schrader D. L., Davidson J., Greenwood R. C., Dunlap D. R., Wadhwa, M.  
 997 2021. The relationship between CM and CO chondrites: Insights from combined  
 998 analyses of titanium, chromium, and oxygen isotopes in CM, CO, and ungrouped  
 999 chondrites. *Geochimica et Cosmochimica Acta* 301(15):70–90.
- 1000 Ushikubo T., Makoto K., Kita N. T., Valley J. W. 2012. Primordial oxygen isotope reservoirs  
 1001 of the solar nebula recorded in chondrules in Acfer 094 carbonaceous chondrite.  
 1002 *Geochimica et Cosmochimica Acta* 90(1):242-264.
- 1003 Vaccaro E. 2017. Physical and chemical properties of matrix in primitive chondrites. PhD

- 1004 Thesis. The Open University.  
1005 Weisberg M. K., McCoy, T., Krot, A. N. 2006. Systematics and evaluation of meteorite  
1006 classification In Meteorites and the Early Solar System II, edited by Lauretta DS and  
1007 McSween HY Jr. University of Arizona Press, Tucson, pp. 19–54.  
1008