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

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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 (≤ 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 (~ 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, ^{15}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 ^{15}N content probably reflects material of strong interstellar heritage (Nakamura-Messenger
65 et al., 2006). Furthermore, the Cr_2O_3 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_2O_3
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⁻¹ spectral
116 resolution in the 5000 - 400 cm⁻¹ range under a primary vacuum (P = 10⁻³ 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 μm^2 . Spectra were measured at 4 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 μm) 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 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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ or 300 $^{\circ}\text{C}$, with typical steps at 100 $^{\circ}\text{C}$, 200 $^{\circ}\text{C}$,
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° . The spectral resolution used varied from 0.048- μm to 0.39- μm (with a step of 0.02 μm).
148 Note that the measurements were normalized to reference surfaces, more specifically by using
149 a SpectralonTM (for wavelengths 0.4 – 2.1 μm) and an InfragoldTM (2.1 – 4.2 μm).

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 μ L alumina
159 crucible under a 50 mL/min inert N₂ 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 μ 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 CO₃s (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 CO₃s 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 CO₃s 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 CO₃s, 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 CO₃s (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). CO₃s 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 CO₃s,
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 CO₃s, 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 CO₃s (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 ~ -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}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 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 (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°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 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 cm^{-1}), alongside a weaker and narrower
279 band at $11.2\text{ }\mu\text{m}$ (890 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- μm (890 cm^{-1}) band, its band location and narrow width are
290 consistent with the presence of olivine.

291 The 3- μm band (measured at 250°C and 300°C, Fig. 4) is broad (2.7 – 3.5 μm or 3750
292 – 2900 cm^{-1}), rounded, asymmetric, with a peak absorption at 2.8 μm (3545 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- μm 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 cm^{-1}
302 and 841 cm^{-1} , consistent with carbonates; (iii) 1233 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 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 SiO_4 (Si-O) stretching (8-12 μm , a.k.a. 10- μm band) and bending (15 - 25
310 μm) 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- μm region.

315 We find that the 10- μm stretching band for bulk sample MIL 07687 displays various
316 absorption peaks: (i) 9.3 μm , consistent with Mg-rich pyroxene; (ii) 11.2 μm , consistent with
317 Mg-rich olivine; (iii) 9.9- μm : 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 SiO₄ 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°C and 440°C) and latter region (670°C and 765°C). Below 350°C , we see
377 signatures at 210°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°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 CO₃s considered (based on the matrix
388 abundances in Table 2).

389 Although our CO₃s present lower mass loss values (Table 2), the morphology of most
390 CO₃ 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 (Bonal 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) CO₃s (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 CO₃ 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 CO₃ 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_{3.0}) 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}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}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}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}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}O and ^{18}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- μm band and *(iii)* the optical

523 slope in the reflectance spectrum. The two former parameters are strongly influenced by
524 adsorbed molecular H₂O (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 CO₃s MIL 090785 and El
532 Médano 389 at ~0.9 μm (Fig. 8), and in CR₂s and CH₃s (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 CO₃ 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 CO₃ chondrites, if it was to plot on the PCM line. Although it is difficult to provide an
545 estimation of the δ¹⁷O and δ¹⁸O 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 SiO₄ (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 Fe²⁺ crystal field transitions
556 of olivine, while the band at 2 μm is partially due to Fe²⁺ 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- μm and 2- μm 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- μm 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 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 CO₃ 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- μm and 10- μm 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- μm and 2.8- μm 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- μm 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 CO₂ chondrite?**

682 If we were to identify MIL 07687 as a CO_{2.9} 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 CO₂ chondrite, MIL 07687 would possibly have originated from a location within the parent
689 asteroid that escaped the extent of thermal metamorphism experienced by CO₃s, 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 Cr₂O₃ 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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