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

Trygve Prestgard, Lydie Bonal, Jolantha Eschrig, J. Gattacceca, Corinne Sonzogni, Pierre Beck

► To cite this version:

Trygve Prestgard, Lydie Bonal, Jolantha Eschrig, J. Gattacceca, Corinne Sonzogni, et al.. Miller Range 07687 and its place within the CM-CO clan. *Meteoritics and Planetary Science*, 2021, 56 (9), pp.1758-1783. 10.1111/maps.13736 . insu-03517358

HAL Id: insu-03517358

<https://hal-insu.archives-ouvertes.fr/insu-03517358>

Submitted on 18 Jan 2022

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

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

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

Trygve Prestgard^{1*}, Lydie Bonal¹, Jolantha Eschrig¹, Jérôme Gattacceca², Corinne Sonzogni²,
Pierre Beck¹

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

² CNRS, Aix Marseille Univ, IRD, Coll France, INRA, CEREGE, Aix-en-Provence, France

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

To be submitted to Meteoritics & Planetary Science

Abstract:

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

1. Introduction

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

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

In addition to its peculiar petrography, past research suggests MIL 07687 to be a highly primitive meteorite, notably by its apparently high concentration of amorphous material, ^{15}N -enrichment and elevated abundance of presolar grains (Haenecour et al. 2020; McAdam et al., 2018; Vaccaro 2017). Indeed, amorphous silicates tend to be abundant in primitive chondrite matrices (Abreu and Brearley., 2010; Brearley, 1993; Dobrică and Brearley, 2020), and high bulk ^{15}N content probably reflects material of strong interstellar heritage (Nakamura-Messenger et al., 2006). Furthermore, the Cr_2O_3 content in type-II chondrules of MIL 07687 are compatible with carbonaceous chondrites of petrographic type 3.0, and there is no evidence of zoning of forsteritic olivine (Brearley 2012), although Haenecour et al. (2020) report slightly lower Cr_2O_3 values than Davidson et al. (2014), possibly suggestive of minor thermal metamorphism.

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

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

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

2.1 Sample

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

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

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

2.2 IR transmission spectra

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

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

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

2.3 Reflectance spectra

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

2.4 TGA measurements

TGA was used to quantify the amount of hydrogen in the samples by measuring the mass loss upon heating. The first derivative (DTG) of the TGA curve enables us to determine the maximum peak temperature of each mass loss and gives an indication of the host mineral of volatile elements (see Fig. 1 in Garenne et al. 2014). Thermo-Gravimetric measurements were performed with a TGA-DSC3 Mettler-Toledo at Institut des Sciences de la Terre (ISTerre, Grenoble - France). A fragment of bulk sample was ground manually (around 50 mg in a mortar). 30 mg of this powder was extracted for TGA analysis and put inside a 150 μ L alumina crucible under a 50 mL/min inert N₂ atmosphere. We included two separate samples of DOM 08006: -21 and -53. The former contained 30 mg, while the second was based on 50 mg of sample. This was done in order to study the mineralogical heterogeneity of a single meteorite. The mass loss from each sample was recorded as it was heated from 25°C to 1000°C with a heating rate of 10 °C/min. The TGA mass resolution is 1 μ g, which corresponds to an absolute error of 0.07% for a total mass loss fraction of 5 %. The error on the temperature measurement is around 0.25 °C.

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

Contrary to CIs and CMs, phyllosilicates appear to be of relatively low abundances, if not possibly absent, in MIL 07687 and most CO3s (Brearley 2006, 2012 and 2013, Haenecour et al. 2020). Consequently, we can expect the TGA mass loss in the 400 - 770°C interval of MIL 07687 and CO3s to be additionally (and significantly) affected by the decompositions of anhydrous minerals such as sulfides, magnetite and perhaps carbonates (Földvari 2011, King et al., 2015). Fe-sulfides are present in CO3s of all metamorphic grades (e.g. Alexander et al.,

2018: ~2-3 vol%), and have also been reported in the matrix of MIL 07687 (~1 vol%: Vaccaro, 2017). In CO₃s, sulfides do not seem to be the result of aqueous alteration (Brearley 2006). If we consider that MIL 07687, COs and CVs have comparable concentrations of sulfides (regardless of metamorphic grade), then, at most, we could possibly expect an additional ~0.4 wt.% mass loss to be associated with this mineral in the TGA 350°C – 700°C interval (Bonal et al., 2020).

Although absent in MIL 07687 (Vaccaro, 2017), magnetite is present to various degrees in primitive CO₃s (2 – 8 vol%), and are generally absent in members of higher metamorphic grade (>3.2) (Rubin and Li, 2019). Minor amounts of magnetite however have been reported in Moss (>3.6) (Stokke, 2018). CO₃s appear to be quite poor in carbonates (Brearley 2006), but these have been reported in MIL 07687 (Davidson et al., 2015).

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

Organics themselves (at least IOM) are expected to decompose progressively throughout our studied temperature range (Court and Sephton, 2014). Consequently, in CO₃s, the mass loss associated with organics should vary between 0.1 - 0.5 wt.% (Alexander et al., 2007) within 25°C – 1000°C. However, due to the higher matrix abundance of MIL 07687, the mass loss contribution due to organics may be higher.

Consequently, despite the likely overlap from other minerals, we concluded that the 350 – 700°C range may be the best interval to quantify the phyllosilicate content (if significantly present) in MIL 07687 and CO₃s, although we have nonetheless included the 400 – 770°C TGA values for the purpose of comparison with CMs. Moreover, as Fe-oxyhydroxides may also appear as parent alteration products in MIL 07687 and CO₃s (Haenecour et al., 2020; Keller and Busseck, 1990), we have also chosen to specifically study the 200 - 700°C temperature interval. All values are summarized in Table 2.

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

2.5 Oxygen isotopes

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

3. Results

3.1. Oxygen isotopes of MIL 07687

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

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

3.2. IR spectra of matrix fragments

The IR spectra of MIL 07687 matrix fragments (Fig. 3) cover a spectral range that 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) and the so-called $3\text{-}\mu\text{m}$ region. The latter is a complex region associated with various vibrational modes in phyllosilicates and oxyhydroxides (X-OH where X is a transition metal), as well as adsorbed and interfoliar molecular water. With the spectra having been measured at $250 - 300^\circ\text{C}$, oxyhydroxides and adsorbed molecular water are not expected to significantly 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 to organic matter (C-H), and will not be discussed further in this work. We were able to obtain successful spectra of twelve matrix fragments. All display very common traits, as described below.

The spectral profiles of the SiO_4 (Si-O) stretching of MIL 07687 matrix fragments (Figs. 3 and 4) appear rounded and asymmetrical. More specifically, they appear to be composed of broad “bell”-shaped bands with a peak at $\sim 9.8\text{ }\mu\text{m}$ (1020 cm^{-1}), alongside a weaker and narrower band at $11.2\text{ }\mu\text{m}$ (890 cm^{-1}). The Si-O profile for all matrix fragments measured in this work are very similar, although the prominence of the $11.2\text{-}\mu\text{m}$ band does vary slightly (being the strongest for fragments 1 and 2). Interestingly, the broad $9.8\text{-}\mu\text{m}$ band displays a similar morphology to that of saponite (Fig. 4), despite this mineral not having been previously described in this meteorite. The smooth and broad nature of the band is also indicative of silicates of low crystallographic order (Fu et al., 2017), hence consistent with amorphous phases detected by Vaccaro (2017) and McAdam et al. (2018).

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

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

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

3.3 IR spectra of bulk MIL 07687

Bulk measurement probes the combination of matrix, chondrules and CAI/AOA signatures. The IR spectrum of bulk MIL 07687 (Figs. 6 and 7) covers a spectral range that includes both the SiO_4 (Si-O) stretching ($8\text{--}12\text{ }\mu\text{m}$, a.k.a. $10\text{-}\mu\text{m}$ band) and bending ($15 - 25\text{ }\mu\text{m}$) regions, thus providing valuable information on the meteorite's bulk silicate composition. The spectrum is plotted alongside those of various type 2 carbonaceous chondrites (Fig. 6) and CO3s (Fig. 7), for comparison. Spectra of individual silicate minerals have also been added (from Salisbury, 1991). The spectra have been normalized according to the maximum absorbance of their $10\text{-}\mu\text{m}$ region.

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

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

In regards to the SiO₄ bending region (15 – 25 μ m), MIL 07687 displays the presence of broad bands at 16.4 μ m and 19.5 μ m that are also consistent with the presence of Mg-rich pyroxene and olivine (e.g., Beck et al. 2014), the latter band likely being a combination of both minerals. A broad band appears around 23 - 24 μ m, which likely represents a convolution between olivine, pyroxene and amorphous silicates (Figs. 6 and 7). In addition, the bulk spectra also display various faint absorption features between 13 μ m and 16 μ m, which are also observed in enstatite.

3.4 Reflectance spectra of bulk MIL 07687

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

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

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

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

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

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

3.5 TGA of MIL 07687 and CO3 chondrites

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

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

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

mass loss values for MIL 07687 remain superior to all CO₃s considered (based on the matrix abundances in Table 2).

Although our CO₃s present lower mass loss values (Table 2), the morphology of most CO₃ TGA/DTG curves present broad similarities to that of MIL 07687 (Figs. 10 and 11): (i) All samples, with the exception of Moss (which presents no obvious mass loss, even a very mild mass gain), show an especially rapid mass loss between 650 – 900°C. (ii) Furthermore, DOM 03238, MIL 05104, MIL 07193 and ALHA 77003 also show a similar mass loss feature between 400 – 500°C (although less pronounced than in MIL 07687). These features are particularly interesting in the case of ALHA 77003, as it has a similar metamorphic grade to Moss (>3.6). A small “inflection” in the TGA mass loss curve of Moss is apparent at ~890°C.

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

Lastly, in the IRS spectra of all our samples, we observe the presence of two neighboring bands at 4.6 and 4.75 μm , consistent with carbon monoxide, indicative of carbonates (see section 4.2.2.). They appear between ~600 and ~950°C (Figs. 10 and 11), and are strongest in the case of MIL 07687 (Figs. 12 and 13). The peak intensity of the bands coincide with the peak of the 650-900°C mass loss, as well as the “inflexion” at 890°C in the TGA curve of Moss.

The intensity of the bands is similar between primitive (3.0 - 3.1) CO₃s (30 mg samples), with the exception of DOM 03238 in which they appear significantly stronger. The intensity is also stronger for the 50 mg DOM 08006-53 sample, which is simply due to its higher mass. Those of ALHA 77003 and Moss are the weakest. The carbon monoxide bands in the DOM 08006 samples appear to have two main peaks of intensity (~650°C and ~790°C: Fig. 12), also consistent with their TGA/DTG curves.

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

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

Moss (a fall), of similar metamorphic grade to ALHA 77003 (a find, significantly weathered), does not display any significant mass loss. This might suggest that the TGA mass loss in ALHA 77003 may be due to terrestrial weathering (assuming no post-metamorphic hydration). Moreover, [seen that](#) all CO₃ finds, and MIL 07687, display similar TGA/DTG profile, it could be that their TGA mass loss values too are strongly influenced by terrestrial weathering products. However, despite this, we note that the matrix-normalized TGA 200 – 700°C and 350 – 700°C mass loss decreases with metamorphic grade (Table 2).

4 Discussion

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

As described in section 3.1. MIL 07687 was found to have a bulk O-isotopic composition that is most consistent with CO chondrites. In fact, its O-isotopic composition is within the lighter isotopic range of the CO group. At first glance, this could indicate that MIL 07687 is indeed a true CO chondrite. In fact, three meteorites listed in the Meteoritical Society database appear to have comparable matrix abundances to MIL 07687: Catalina 008 (58%), Mdaouer (62%) and NWA 11889 (61%). Both Catalina 008 and NWA 11889 have O-isotopic measurements consistent with the CO group. Interestingly, over a dozen CO₃ entries are listed as having a matrix abundance of at least ~50% (e.g. NWA 8631: 53%). Moreover, Davidson et al. (2019) interestingly noted that DOM 08006 is very poor in refractory inclusions (1%), especially AOAs, hence again consistent with MIL 07687. The Meteoritical bulletin also lists NWA11559 (CO>3.6) as not containing any detectable CAIs. We also measured the average chondrule size of MIL 07687 as being a close match to the CO chondrite average (Table 3). Lastly, our MIR spectrum of NWA 8631 (CO₃.0) is similar to MIL 07687, indicating a similar bulk silicate content. Although these observations may support MIL 07687 as having affinities with the CO group, they are probably not sufficient to classify it as a true member. Indeed, there are several points to consider.

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

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

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

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

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

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

In addition to many of the TGA features mentioned in section 3.5, the intensely weathered nature of MIL 07687 is likely supported by various features in our results, including: (i) the TGA mass loss for temperatures lower than 200°C (ii) the 3- μm band and (iii) the optical

slope in the reflectance spectrum. The two former parameters are strongly influenced by adsorbed molecular H₂O (although the former also possibly includes the contribution due to evaporates at 130°C, i.e. gypsum, a weathering product). Indeed, Bonal et al. (2020) found that low temperature mass loss was a reliable indicator of terrestrial weathering in CV chondrite samples. More specifically, they found that highly weathered CVs were measured to have significantly larger TGA < 200°C mass loss values (between 1.2 to 3.5 wt.%, compared to < 1 wt.% for most CVs), hence reflecting strong (or long-term) exposure to terrestrial water. The absorption feature at 0.86 µm may also represent an excess of oxyhydroxides due to terrestrial weathering, similar to the feature observed in the highly weathered CO₃s MIL 090785 and El Médano 389 at ~0.9 µm (Fig. 8), and in CR₂s and CH₃s (Cloutis et al 2012a,d, Fig. 8).

McAdam et al. (2018) also suggested that the red NIR slope observed in MIL 07687 due to the influence of terrestrial weathering products, however Eschrig et al. (2020) found that weathered COs tend to have bluer NIR slopes (with poorly weathered COs and falls being red-sloped). Moreover, the weathered CO₃ samples presented in Fig. 8 all seem to have neutral or blue NIR slopes. This raises the question of whether the NIR slope may actually be an intrinsic spectral feature of the meteorite's parent body, rather than an influence of weathering products. An in-depth discussion regarding the origin of this feature will be described in section 4.2.2.

In order to have a better idea of the pre-weathered O-isotopic composition of MIL 07687, an estimation was made based on the [Lever rule](#). If we consider oxyhydroxides as the main terrestrial weathering product, we can conclude, based on Lever's rule, that MIL 07687's original unweathered composition would possibly fall close to the typical range of primitive CO₃ chondrites, if it was to plot on the PCM line. Although it is difficult to provide an estimation of the δ¹⁷O and δ¹⁸O values, our projection suggests that the original O-isotopic composition was unlike that of "typical" CM chondrites. We suggest that MIL 07687 should remain classified as "ungrouped" until further evidence is provided on its nature.

4.2 Secondary history of MIL 07687

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

The SiO₄ (Si-O) stretching (~10 µm) and bending (15 – 25 µm) regions of MIL 07687 are dominated by the presence of Mg-rich olivine, pyroxene, and amorphous silicates (see section 3.3; Figs. 6 and 7). The lack of a 1.05-µm band in the reflectance spectrum of MIL 07687 (Fig. 8) is also consistent with the dominant Mg-rich mineralogy of its olivine. It is believed that the absorption band at 1.05 µm most likely reflects Fe²⁺ crystal field transitions of olivine, while the band at 2 µm is partially due to Fe²⁺ crystal field transitions of spinel

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

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

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

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

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

4.2.2 MIL 07687 likely experienced an episode of aqueous alteration

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

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

The next question is whether our TGA data can also be used as a tracer of the meteorite’s hydration. At first glance, according to our initial definition (section 2.4), the high-temperature TGA 350-700°C mass loss (5.8 wt.%) would indicate phyllosilicates being present in this meteorite. However, as we have observed in our results (section 3.5, Fig. 11), we must note the overlap with other minerals such as possibly oxyhydroxides at around 400 – 500°C, carbonates that have an onset at around 650°C, and organics that may decompose throughout the temperature ranges studied. In fact, MIL 07687 and all CO3 finds have similar TGA curves, suggesting that many of the minerals significantly contributing to the TGA mass loss of these meteorites may actually be of terrestrial origin. Consequently, parent-body phyllosilicates (if present) are unlikely to significantly contribute to the mass loss, consistent with our IR spectra.

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

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

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

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

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

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

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

4.3. What if MIL 07687 is a CO₂ chondrite?

If we were to identify MIL 07687 as a CO_{2.9} chondrite, we would extend the known petrographic range of the CO group, and thus provide new constraints on the geological processes occurring on their parent body (assuming that our currently recognized CO chondrites correctly sample one single parent body). The final hydration state of a sample (i.e. presence of hydrated amorphous silicates) is controlled by the interplay of heat and water. On the CO parent body, the heat source was likely of radiogenic origin (i.e. long-term metamorphism). If indeed a CO₂ chondrite, MIL 07687 would possibly have originated from a location within the parent asteroid that escaped the extent of thermal metamorphism experienced by CO₃s, while its relatively hydrated nature would show that it better retained (and/or interacted with) the surrounding fluids (or did not experienced dehydration thanks to a lower peak metamorphic

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

Another possible explanation would be that MIL 07687 formed within a relatively hydrated region (or layer) close to the parent body surface (perhaps it would have accreted onto the parent body later than most CO material). Indeed, nearly all the CO3s in the Meteoritical Society Database (2021) with comparable matrix abundances to MIL 07687 (~50% or more) all appear to be quite primitive (often listed as CO3.0s), with similar Cr₂O₃ values to MIL 07687. Thus, if these meteorites are indeed COs (which needs to be verified), and assuming that this meteorite group only samples one single primary parent body, this would possibly suggest that MIL 07687, along with these meteorites, would represent a poorly heated, matrix-enriched, and potentially hydrated, superficial layer of the CO parent body. Unfortunately, to our knowledge, we were not able to find any noble gas data in the literature that may give insight into whether or not MIL 07687 was located near the surface of its parent body. In both cases, not only would it imply that the parent body was petrographically heterogeneous, but it would further suggest that the overall water content on the CO parent body would likely have been higher than previously considered. The idea of an unevenly hydrated CO parent planetesimal may be supported by the discovery of unheated hydrated clasts in NWA 1232, a brecciated CO3 (Matsumoto et al. 2015), assuming that these are not xenoliths. There are also several COs that appear to contain phyllosilicates (e.g. Acfer 374, EET 90043 and NWA 11790: Meteoritical society database).

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

5. Conclusion

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

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

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

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

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

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

Acknowledgements

We wish to thank Valérie Magnin and Alejandro Fernandez-Martinez (ISTerre) for having managed the TGA and IRS measurements. We also wish to thank the reviewers for their insightful and constructive comments. [This work was funded by the European Research Council under the H2020 framework program/ERC grant agreement no. 771691 \(Solarys\)](#)

References

- Abreu N. M., Brearley A. J. 2010. Early solar system processes recorded in the matrices of two highly pristine CR3 carbonaceous chondrites, MET 00426 and QUE 99177. *Geochimica et Cosmochimica Acta* 74(3):1146-1171.
- Abreu N. M., Louro M. D., Friedrich J. M., Schrader D. L., Greenwood R. C. (2018) Elephant Moraine (EET) 83226: a clastic, type 2 carbonaceous chondrites with affinities to the CO chondrites (abstract #2451). 49th Lunar and Planetary Science Conference.
- Alexandre A., Basile-Doelsch I., Sonzogni C., Sylvestre F., Parron C., Meunier J.-D., and Colin F. (2006). Oxygen isotope analyses of fine silica grains using laser-extraction technique: Comparison with oxygen isotope data obtained from ion microprobe analyses and application to quartzite and silcrete cement investigation. *Geochimica et Cosmochimica Acta* 70(11):2827–2835.
- Alexander, C. M. O'D., Fogel, M., Yabuta, H., Cody, G. D. 2007. The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. *Geochimica et Cosmochimica Acta* 71:4380-4403.
- Alexander C.M.O'D., Greenwood R.C., Bowden R., Gibson J.M., Howard K.T., Franchi I.A. 2018. A multi-technique search for the most primitive CO chondrites, *Geochimica et Cosmochimica Acta* 221(15):406-420.
- Beck P. and Garenne A. 2012. MIR transmission spectra at Tamb, 150°C and 300°C of bulk CM chondrites in KBr pellets. SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data.
https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20170721_001
- Beck P., Garenne A., Quirico E., Bonal L., Montes-Hernandez G., Moynier F., and Schmitt B. 2014. Transmission infrared spectra (2–25µm) of carbonaceous chondrites (CI, CM, CV–CK, CR, C2 ungrouped): Mineralogy, water, and asteroidal processes. *Icarus* 229:263–277.
- Beck P., C., Maturilli, A., Garenne A., Vernazza P., Helbert J., Quirico E., Schmitt B. 2018. What is controlling the reflectance spectra (0.35–150 µm) of hydrated (and dehydrated) carbonaceous chondrites?. *Icarus* 313:124–138.
- Beck P., Schmitt B., Pommerol A., Potin S., Brissaud O. 2021. Low-phase spectral reflectance and equivalent "geometric albedo" of meteorites powders. *Icarus*, submitted for publication.
- Bonal L., Bourrot-Denise, M., Quirico, E., Montagnac, G., Lewin, E. 2007. Organic matter and metamorphic history of CO chondrites. *Geochimica et Cosmochimica Acta* 71:1605–1623.
- Bonal L. 2011a. Mid-IR absorbance spectra of EET92042 matrix grains under vacuum at different temperatures) under vacuum at 300°C. SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data:
https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20170731_004
- Bonal L. 2011b. Raw, normalized and baseline-corrected of MIR transmission spectra of GRA95229 matrix grains pressed on diamonds under vacuum at ambient temperature and 300C. SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data:
https://www.sshade.eu/data/experiment/EXPERIMENT_LB_20170731_003
- Bonal L. 2011c. Raw, normalized and baseline-corrected of MIR transmission spectra of MET00426 matrix grains pressed on diamonds under vacuum at ambient temperature and 300C. SSHADE/GhoSST (OSUG Data Center). Dataset/Spectral Data:
https://www.sshade.eu/data/experiment/EXPERIMENT_LB_20170731_001
- Bonal L. 2011d. MIR absorbance spectra of pressed QUE99177 matrix grains (CR Chondrite) 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	
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	
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. <i>Geochimica et</i>	
812	<i>Cosmochimica Acta</i> 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. <i>Geochimica et Cosmochimica Acta</i>	
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	<i>Geochimica et Cosmochimica Acta</i> 57(7):1521–1550	
820	Brearley A. J. 2006. The action of water. In <i>Meteorites and the Early Solar System II</i> , 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). <i>Meteoritics & Planetary</i>	
827	<i>Science</i> 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. <i>Meteoritics & Planetary Science</i> .	
830	45(4):531 - 554.	
831	Clayton R.N. and Mayeda T.K. 1999. Oxygen isotope studies of carbonaceous chondrites.	
832	<i>Geochimica et Cosmochimica Acta</i> 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. <i>Meteoritics & Planetary Science</i> 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. <i>Icarus</i> , 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. <i>Icarus</i> , 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. <i>Icarus</i> , 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. <i>Icarus</i> , 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. <i>Icarus</i> , 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. <i>Geochimica et Cosmochimica Acta</i> 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	

- chondrite Miller Range 07687: a coordinated in situ nanosims, FIB-TEM, and XANES study (abstract #1609). 46th Lunar and Planetary Science Conference.
- Davidson J., Alexander C.M.O'D., Stroud R. D., Busemann H., Nittler L. R. 2019. Mineralogy and petrology of Dominion Range 08006: A very primitive CO₃ carbonaceous chondrite. *Geochimica et Cosmochimica Acta* 265:259-278.
- DeMeo F.E., Binzel R.P., Slivan S.M., Bus S.J. 2009. An extension of the Bus asteroid taxonomy into the near-infrared. *Icarus*, 202(1):160-180
- De Leuw S., Rubin A. E., Wasson J. T. 2010. Carbonates in CM chondrites: Complex formational histories and comparison to carbonates in CI chondrites. *Meteoritics & Planetary Science* maps. 45(4), 513-530.
- Dobircă E., Brearley A. J. 2020. Amorphous silicates in the matrix of Semarkona: The first evidence for the localized preservation of pristine matrix materials in the most unequilibrated ordinary chondrites. *Meteoritics & Planetary Science* maps. 55(3), 649-668.
- Eschrig J., Bonal L., Beck P., Prestgard T. 2019. NIR reflectance spectrum (i= 0°, e= 30°) of bulk CO chondrites under vacuum at T= 80°C. https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20191220_002
- Eschrig J., Bonal L., Beck P. 2019. NIR reflectance spectrum (i= 0°, e= 30°) of bulk CR chondrites under vacuum at T= 80°C. https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20191220_003
- Eschrig J., Bonal L., Beck P., Prestgard T. J. 2020. Spectral reflectance analysis of type 3 carbonaceous chondrites and search for their asteroidal parent bodies. *Icarus* 354:114034.
- Földvari M. 2011. Handbook of thermogravimetric system of minerals and its use in geological practice. Geological Inst. of Hungary, Budapest.
- Gaffey S. J. 1986. Spectral reflectance of carbonate minerals in the visible and near infrared (0.35-2.55 microns); calcite, aragonite, and dolomite. *American Mineralogist* 71(1-2):151-162.
- Garenne A., Beck P., Montes-Hernandez G., Chiriac R., Toche F., Quirico E., Bonal L., and Schmitt B. 2014. The abundance and stability of “water” in type 1 and 2 carbonaceous chondrites (CI, CM and CR). *Geochimica et Cosmochimica Acta* 137:93–112.
- Greenwood R. C., Franchi I. A. 2004. Alteration and metamorphism of CO₃ chondrites: Evidence from oxygen and carbon isotopes. *Meteoritics & Planetary Science* maps. 39(11), 1823-1838.
- Greenwood R. C., Howard K. T., Franchi I. A., Zolensky, M. E., Buchanan, P. C., Gibson, J. M. 2014. Oxygen isotope evidence for the relationship between CM and CO chondrites: Could they both coexist on a single asteroid?. (abstract #2610). 45th Lunar and Planetary Science Conference.
- Greenwood R. C., Howard K. T., King A. J., Lee M. R., Burbine T. H., Franchi I. A., Anand M., Findlay R., Gibson J. M. 2019. Oxygen isotope evidence for multiple CM parent bodies: what will we learn from the Hayabusa 2 and OSIRIS-REx return missions? (abstract #2191). 50th Lunar and Planetary Science Conference.
- Grimm R. E. and McSween H. Y. 1989. Water and the thermal evolution of carbonaceous chondrite parent bodies. *Icarus* 82:244–280.
- Gröning M. (2004) Chapter 40 – International Stable Isotope Reference Materials. In *Handbook of Stable Isotope Analytical Techniques*. pp. 874–906.
- Haenecour P., Floss C., Brearley A. J., and Zega T. J. 2020. The effects of secondary processing in the unique carbonaceous chondrite Miller Range 07687. *Meteoritics & Planetary Science* maps.13477.
- Harju E. R., Rubin A. E., Ahn I., Choi B., Ziegler K., Wasson J. T. 2014. Progressive aqueous

- alteration of CR carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 139:267–292.
- Howard K. T., Alexander C. M. O'D., Dyl K. A. 2014. PSD-XRD Modal Mineralogy of Type 3.0 CO Chondrites: Initial Asteroidal Water Mass Fractions and Implications for CM Chondrites. The Woodlands, Texas: LPI Contribution. p. 1830.
- Howard K. T., Alexander C. M. O'D., Schrader D. L., Dyl K. A. 2015. Classification of hydrous meteorites (CR, CM and C2ungrouped) by phyllosilicate fraction: PSD-XRD modal mineralogy and planetesimal environments. *Geochimica et Cosmochimica Acta* 149:206–222.
- Keller L. P., Buseck P. R. 1990. Matrix mineralogy of the Lancé CO3 carbonaceous chondrite: A transmission electron microscope study. *Geochimica et Cosmochimica Acta* 54:1155–1163.
- Kimura M., Imae N., Komatsu M., Barrat J. A., Greenwood R. C., Yamaguchi A., Noguchi T. 2020. The most primitive CM chondrites: Asuka 12085, 12169, and 12236, of subtypes 3.0 – 2.8: Their characteristics features and classification. *Polar science* 26:100565.
- King A. J., Schofield P. F., Russell S. S. 2021. Thermal alteration of CM carbonaceous chondrites: Mineralogical changes and metamorphic temperatures. *Geochimica et Cosmochimica Acta* 298:167-190.
- King A. J., Solomon J. R., Schofield P. F., Russell S. S. 2015. Characterising the CI and CI-like carbonaceous chondrites using thermogravimetric analysis and infrared spectroscopy. *Earth, Planets and Space* 67:198.
- Krot A. N., Keil K., Scott E. R. D., Goodrich C. A., and Weisberg M. K. 2014. Classification of meteorites and their genetic relationships. In *Treatise on Geochemistry* (2nd ed.), edited by Turekian H. D. H. K. Oxford, UK: Elsevier. pp. 1–63.
- Lee M. R., Cohen B. E., King A. J., Greenwood R. C. 2019. The diversity of CM carbonaceous chondrite parent bodies explored using Lewis Cliff 85311. *Geochimica et Cosmochimica Acta* 264:224–244.
- Le Guillou C., Changela H. G., Brearley A. J. 2015. Widespread oxidized and hydrated amorphous silicates in CR chondrites matrices: Implications for alteration conditions and H₂ degassing of asteroids. *Earth and Planetary Science Letters* 420(15), 162-173.
- Matsumoto M., Tomeoka K., Seto Y., et al. 2015. Hydrated, Unmetamorphosed Clasts in the NWA 1232 CO3 Carbonaceous Chondrite (abstract). *Meteoritics & Planetary Science* 78(Suppl.): 1856.pdf.
- Metzler K. and Bischoff A. (1987) Accretionary dark rims in CM chondrites. *Meteoritics* 22, 458-459
- McAdam M.M., Sunshine J.M., Howard K.T., Alexander C.M.O'D., McCoy T.J., Bus S.J. 2018. Spectral evidence for amorphous silicates in least-processed CO meteorites and their parent bodies. *Icarus* 306(15):32-49.
- Miller M. F. 2002. Isotopic fractionation and the quantification of ¹⁷O anomalies in the oxygen three-isotope system. *Geochimica et Cosmochimica Acta* 66(11):1881–1889.
- Nakamura-Messenger K., Messenger S., Keller L. P., Clemette S. J., Zolensky E. M. 2006. Organic Globules in the Tagish Lake Meteorite: Remnants of the Protosolar Disk. *Nature* 314(5804):1439-805.
- Pignatelli I., Marrocchi Y., Vacher L. G., Delon R., Gounelle M. 2016. Multiple precursors of secondary mineralogical assemblages in CM chondrites. *Meteoritics & Planetary Science* maps 51(4):785-805.
- Pignatelli I., Marrocchi Y., Mugnaioli E., Bourdelle F., Gounelle M. 2017. Mineralogical, crystallographic and redox features of the earliest stages of fluid alteration in CM 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 μ 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