AUTHOR QUERY FORM

ELSEVIER	**Journal:** EPSL **Article Number:** 117149	**Please e-mail your responses and any corrections to:** **E-mail:** **corrections.esch@elsevier.vtex.lt**

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof. **It is crucial that you NOT make direct edits to the PDF using the editing tools as doing so could lead us to overlook your desired changes.** Rather, please request corrections by using the tools in the Comment pane to annotate the PDF and call out the changes you would like to see. To ensure fast publication of your paper please return your corrections within 48 hours.
For correction or revision of any artwork, please consult *http://www.elsevier.com/artworkinstructions*

Any queries or remarks that have arisen during the processing of your manuscript are listed below and highlighted by flags in the proof.

Location in article	**Query / Remark: Click on the Q link to find the query's location in text** **Please insert your reply or correction at the corresponding line in the proof**
Q1	Your article is registered as a regular item and is being processed for inclusion in a regular issue of the journal. If this is NOT correct and your article belongs to a Special Issue/Collection please contact <v.bellanjoghi@elsevier.com> immediately prior to returning your corrections. (p. 1/ line 1)
Q2	The author names have been tagged as given names and surnames (surnames are highlighted in teal color). Please confirm if they have been identified correctly and are presented in the desired order. (p. 1/ line 15)
Q3	Figure(s) will appear in black and white in print and in color on the web. The figure(s) contains references to color or the colors are mentioned in the main text. Based on this, the explanatory text about the interpretation of the colors has been added. Please check, and correct if necessary. (p. 3/ line 29)
Q4	Please check if sponsor names have been identified correctly and correct if necessary. (p. 11/ line 1)

Please check this box or indicate your approval if you have no corrections to make to the PDF file ☐

Thank you for your assistance.

Earth and Planetary Science Letters ••• (••••) ••••••

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Heterogeneity within refractory organic matter from CM2 Carbonaceous Chondrites: Evidence from Raman spectroscopy

Christian Potiszil [1],*, Wren Montgomery [2], Mark A. Sephton

Impacts and Astromaterials Research Centre, Department of Earth Science and Engineering, Imperial College London, SW7 2AZ, United Kingdom

A R T I C L E I N F O

Article history:
Received 24 May 2021
Received in revised form 18 July 2021
Accepted 3 August 2021
Available online xxxx
Editor: F. Moynier

Keywords:
carbonaceous chondrite
Raman spectroscopy
refractory organic matter
heterogeneity
alteration

A B S T R A C T

CM2 chondrites experienced widespread aqueous and short term thermal alteration on their parent bodies. Whilst previous Raman spectroscopic investigations have investigated insoluble organic matter (IOM), they have not taken into account the binary nature of IOM. Studies employing mass spectrometry have indicated that IOM also known as macromolecular organic matter (MOM) is in fact composed of two distinct fractions: labile organic matter (LOM) and refractory organic matter (ROM). The ROM component represents the aromatic rich and heteroatom poor component of IOM/MOM, whilst the LOM fraction represents a more heteroatom and aliphatic rich component. Here we report Raman 2D maps and spectroscopic data for Murchison and Mighei, both before and after chemical degradation, which attacks and liberates LOM. The removal of LOM simulates the effects of aqueous alteration, where ester and ether bonds are broken and is thought to release some components to the soluble organic matter (SOM) fraction, also known as the free organic matter fraction (FOM). Raman spectroscopy can be used to reveal the nature of bonding (sp^2 and sp^3) within carbonaceous materials such as meteoritic organic matter, through evaluation of the D and G band peak centres and FWHM values from the recorded data. The presence of sp^3 orbitals indicates that the organic materials contain aliphatic linkages and/or heteroatoms. Statistical analysis of the Raman parameters obtained here indicates that the organic matter originating the Raman response is indistinguishable between the bulk (chemically untreated) and chemically degraded (treated with KOH and HI) samples. Such an observation indicates that the ROM fraction is the major contributor to the Raman response of meteoritic organic matter and thus Raman spectroscopy is unlikely to record any aqueous alteration processes that have affected meteoritic organic matter. Therefore, studies which use Raman to probe the IOM are investigating just one of the components of IOM and not the entire fraction. Studies that aim to investigate the effects of aqueous alteration on meteoritic organic matter should use alternate techniques to Raman spectroscopy. Furthermore, the indistinguishable nature of the Raman response of ROM from Murchison and Mighei suggests these meteorites inherited a ROM component that is chemically similar, reflecting either a common process for the formation of CM2 meteoritic ROM and/or that these meteorites probed the same ROM reservoir.

1. Introduction

CM2 chondrites contain organic matter, which was exposed to the conditions present on meteorite parent bodies shortly after the formation of the solar system <4567.30 ± 0.16 Ma (Connelly et al., 2012). These extraterrestrial objects and their organic cargo can reveal much about the processes which operated during this period of abiotic chemistry, directly preceding the delivery of large quantities of meteoritic material to Earth and the subsequent origin of life (Sephton, 2013).

Meteoritic organic matter, such as that found in CM2 chondrites, is composed of different fractions. Approximately 70% is insoluble/macromolecular organic matter (IOM/MOM) and only ∼30% is present as solvent soluble/free organic matter (SOM/FOM) (Sephton, 2013). SOM/FOM has been studied more extensively than IOM/MOM and a great diversity of solvent soluble organic compounds have been identified (Glavin et al., 2018; Martins and Sephton, 2009; Pizzarello and Shock, 2010; Sephton, 2013). IOM/MOM is composed of two fractions: labile organic matter

---

* Corresponding author.
E-mail address: cpotiszil@okayama-u.ac.jp (C. Potiszil).

[1] Permanent address: Pheasant Memorial Laboratory, Institute for Planetary Materials, Okayama University, Yamada 827, Misasa, Tottori 682-0193, Japan.

[2] Permanent address: Imaging and Analysis Centre, The Natural History Museum, London SW7 5BD, United Kingdom.

https://doi.org/10.1016/j.epsl.2021.117149

Please cite this article as: C. Potiszil, W. Montgomery and M.A. Sephton, Heterogeneity within refractory organic matter from CM2 Carbonaceous Chondrites: Evidence from Raman spectroscopy, Earth and Planetary Science Letters, https://doi.org/10.1016/j.epsl.2021.117149

(LOM) and refractory organic matter (ROM) (Sephton et al., 2003). Whilst ROM is relatively resistant to pyrolysis techniques, LOM is liberated by processes such as hydrous pyrolysis (Oba and Naraoka, 2006), a laboratory simulation of parent body aqueous alteration.

Aqueous fluids have been implicated in both the alteration and synthesis of organic matter in carbonaceous chondrites. Hydrous pyrolysis of the MOM present within CM2 and CI1 chondrites was shown to liberate aromatic moieties, which were attached by ester and ether linkages (Sephton et al., 2000, 1999). The liberated compounds possessed near identical $\delta^{13}C$ values to their FOM counterparts, indicating that LOM may be the originator of these FOM components (Sephton et al., 1998). Furthermore, the released compounds demonstrated alteration-dependent genetic relationships. A decreasing abundance of products from the liberation of ether linkages and condensed aromatic networks was observed with increasing levels of aqueous alteration (Sephton et al., 2000).

Previous studies have also investigated the effects of aqueous alteration on the generation of meteoritic organic matter using interstellar or cometary starting compositions. Kebukawa et al. (2017) used simple chemical starting compositions, consisting of cometary or interstellar analogues, to produce compounds indicative of carbonaceous chondrite compositions. Meanwhile, Vinogradoff et al. (2018) studied the effects of aqueous alteration on a common organic interstellar ice analogue, hexamethylenetetramine (HMT). The experiment demonstrated that a large variety (>150) of compounds and an insoluble residue could be produced from this one starting material, under hydrothermal conditions. Subsequently, Danger et al. (2021) use hydrothermal experiments to chart how meteorite SOM might form from material that was originally present as ice housed within dense molecular clouds.

Anhydrous or thermal alteration is also recorded by meteoritic organic matter. Quirico et al. (2003) used Raman spectroscopy to study the organic matter of 6 unequilibrated ordinary chondrites (UOCs) and concluded that parent body thermal metamorphism is the major control on the maturity of meteoritic organic matter among examples of this meteorite class, as opposed to nebula heating. Similar conclusions were drawn by studies of CV3 chondrites (Bonal et al., 2006) and CO3 chondrites (Bonal et al., 2007), with the former introducing quantification of the thermal metamorphic grade and the latter employing a geothermometer.

Busemann et al. (2007) studied 51 chondrites of different classes through Raman spectroscopy and concluded that they are representative of different processes. Contrasting styles of metamorphism were responsible for the differences in ordinary, CO and oxidised and reduced CV chondrites, whilst the presence of amorphous carbon in more primitive meteorites (CI, CM and CR) was the result of sputtering, UV or particle irradiation. Busemann et al. (2007) also calibrated a geothermometer, which related the full width at half maximum (FWHM) of the D bands to the Raman spectroscopy based peak metamorphic temperatures (PMT) of Huss et al. (2006). However, Quirico et al. (2009) suggested that the Raman response of organic matter is not as well correlated with thermal metamorphism as previously thought. Instead, the level of confinement (free volume), pressure and precursor composition are also major factors, especially among the chondrites containing more primitive organic matter. Nevertheless, subsequent studies have highlighted the different effects of prolonged (radiogenic heating in the case of >type 3) versus short term heating (most likely impact-related in the case of type 1 and 2) on the Raman response of meteoritic organic matter (Busemann et al., 2007; Quirico et al., 2018, 2014; Starkey et al., 2013).

Raman spectroscopy has a proven history for studying macromolecular materials and provides information concerning the type of carbon bonding present in meteorite organic matter. Raman spectroscopy can indicate whether organic matter is closer to ordered graphite-like carbon (containing mostly sp^2 orbitals) or whether it is more similar to disordered amorphous carbon (containing a larger amount of sp^3 orbitals) (Beyssac et al., 2003; Busemann et al., 2007; Ferrari and Robertson, 2000; Tuinstra and Koenig, 1970).

Whilst investigations of bulk meteorite organic matter and FOM and LOM have been undertaken, few studies have probed the ROM fraction. The ROM fraction is depleted in the heavy isotopes ^{13}C and ^{15}N (Sephton et al., 2003) and is seemingly unaffected by hydrous pyrolysis and, therefore, analogous processing associated with parent body aqueous alteration. However, to date a Raman spectroscopic investigation of isolated ROM and a comparison with bulk meteorite organic matter has not been undertaken. This is likely in part because of the assumption that IOM/MOM is a single component, despite experimental evidence that suggests it is composed of two distinct fractions (LOM and ROM) in terms of composition, structure and isotopes (Kitajima et al., 2002; Sephton et al., 2003, 1999, 1998).

Chemical degradation can be used to target functionalities similar to aqueous alteration, such as ether and ester linkages. However, chemical degradation, unlike hydrous pyrolysis, avoids the introduction of phenolic groups by interaction with water (at >250 °C) (Sephton et al., 1999). Experiments involving KOH and HI have been performed previously in order to liberate units from terrestrial samples (Höld et al., 1998; Schouten et al., 1998). Here we extract FOM compounds and liberate LOM via the use of potassium hydroxide (KOH) and hydroiodic acid (HI) to isolate the ROM component. Raman spectroscopy has enabled a detailed investigation of heterogeneity between different fractions of the same meteorite and between complementary fractions of different meteorites. We discuss the potential processes that could yield the relationships observed and present these in the wider context of extraterrestrial organic matter.

2. Methodology

The Murchison and Mighei meteorites (CM2) were selected because they represent a class of carbonaceous chondrites that have experienced aqueous alteration and contain the primitive organic matter of interest to the current study. Interior samples of the Murchison (171.5 mg) and Mighei (187.6 mg) meteorites were ground using an agate pestle and mortar and extracted with deionised water for 22 hours at 100 °C. Subsequently, the supernatant was removed, the residue left to dry overnight and the meteorite samples subjected to chemical degradation. The samples were first treated with KOH in water for 1 hour at 65 °C and then, after supernatant removal and drying overnight, to HI for 2 hours at 130 °C. After chemical treatment the mineral matrix of the samples was still visible, indicating that the majority of the inorganic material was not removed by the procedure. Additional raw samples of Murchison and Mighei were only ground and not extracted or degraded.

Raman spectroscopy was undertaken using a Thermo Fisher DXR microscope at the SMIS beamline, SOLEIL Synchrotron, France. The Raman microscope was fitted with a 532 nm laser, a 100x objective and a 0.8 numerical aperture with a spot size of 0.8 µm, a resolution of 4 cm^{-1} and a 25 µm slit. The 2D maps were taken as grids with 0.5 µm spacing, each point consisting of 2 acquisitions recorded over 30 s. A low laser power of 0.2 mW was used to ensure that laser induced heating did not alter the meteoritic organic matter. The chemically degraded and undegraded meteorite samples were placed onto separate glass slides and grains with flat surfaces and spectra that displayed a good signal to noise ratio were selected.

Three spectra were selected for each sample, Fityk version 0.9.8 (Wojdyr, 2010) was used to baseline correct, normalise and fit the peaks for all samples. Two Lorentzian peaks were chosen after

Table 1
A comparison of the Lorentzian and Gaussian standard deviations for the peak parameters of the Murchison grain 1 spectra.

	Peak Centre		FWHM	
Peak Fit	D	G	D	G
Lorentzian	1356.48 ± 2.19	1591.23 ± 0.46	178.42 ± 2.48	76.26 ± 3.46
Gaussian	1362.18 ± 4.35	1592.05 ± 0.08	238.09 ± 4.45	88.98 ± 4.59

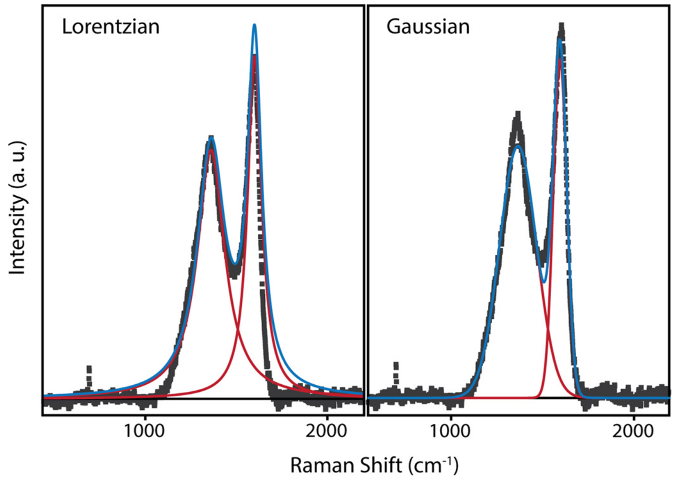

Fig. 1. Lorentzian and Gaussian peak fits for a Raman spectrum from the Murchison grain 1 sample. The data is shown in grey, the peak fits in red and the convolution of the fitted peaks is shown in blue. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

fitting of the spectra with Gaussian functions gave no consistent improvement in the standard deviations of the peak parameters (Table 1). Lorentzian peaks were used by Busemann et al. (2007), who also employed a 532 nm laser. The Gaussian peaks gave a visibly better fit for the lower areas of the peaks, but the main parameters studied here are reliant on the middle (FWHM) and upper (peak height) portions of the peaks, which were fitted better by the Lorentzian peaks (Fig. 1). P-values were obtained via the GraphPad online unpaired T-test calculator (Motulsky, 2017), the current study defines a statistically significant difference as one where the P-value calculated is <0.05.

3. Results

Prior to Raman spectroscopic analysis, chemical degradation was used to remove ester and ether functionalities through treatment with KOH and HI. Raman spectroscopy was then used to probe and compare the signature of the bulk organic matter to that of the ROM fraction, left behind after chemical degradation. Further comparisons were then possible between these fractions within the two CM2 carbonaceous chondrites studied here, Murchison and Mighei.

3.1. Peak parameters

Organic matter can be described by the amount of disorganised, or amorphous, carbon versus ordered, or crystalline, carbon it contains. In perfectly crystalline organic matter, the G band is the only peak found within the first order region and arises from stretching vibrations found within layers of graphite-like material (containing mostly sp^2 orbitals) and is present at ~1580 cm^{-1} (Beyssac et al., 2003; Tuinstra and Koenig, 1970). The D band represents defects in the crystal lattice of aromatic organic matter, introduced by amorphisation (incorporation of sp^3 orbitals) and is found at ~1350 cm^{-1} (Busemann et al., 2007; Ferrari and Robertson, 2000). The FWHM of the D band (Table 2) is also linked to the level of disorder in organic matter and has been used as an indicator of meteoritic organic matter maturity by numerous studies (Bonal et al., 2007, 2006; Busemann et al., 2007; Matrajt et al., 2004; Quirico et al., 2009, 2003). Studies have linked lower peak centres of G bands and the presence of further D bands, in the first order region, to high levels of disorder, which can arise from irradiation (Baratta et al., 1996; Ferini et al., 2004; Strazzulla et al., 2001), although these were not observed in the current study. D and G bands were detected in all the samples reported here as shown in Fig. 2 and Table 2. Busemann et al. (2007) found the G band parameters to be associated with a higher spread of values than those of the D band and suggested the G band is less useful for indicating the maturity of organic matter, although this was not the case with the data presented here.

The results from the current study show very few variations in peak centres. Most samples contained organic matter which displayed peak centres that were statistically indistinguishable (T-test results given in Table 3). Only Murchison grain 1 displayed identifiable mineral bands; peaks centred at 247 and 317 cm^{-1} were present, which are consistent with the iron oxyhydroxide goethite (Bouchard and Smith, 2003; de Faria et al., 1997).

3.2. Peak ratios

Two commonly used ratios to measure the degree of disorder present in organic matter are: i) R_1 (intensity [peak height] of D/G) and ii) R_2 (area of D/[G+D]) (Beyssac et al., 2003). R_2 is useful for more organised organic matter, becoming more or less constant at a value above 0.6. At this point the R_1 ratio becomes more useful (Beyssac et al., 2003), although it is often associated with higher uncertainties than the R_2 ratio (Beyssac et al., 2002a; Beyssac et al., 2002b). The higher uncertainties likely originate from the difficulty in fitting a baseline for such poorly organised organic matter (Beyssac et al., 2003; O. Beyssac et al., 2002b). In cases where organic matter is very poorly organised the R_1 ratio can become almost zero (Ferrari and Robertson, 2000); however, this was not observed in the current study.

The R_2 values reported here for both the chemically degraded and undegraded samples of Murchison and Mighei are >0.60 (Table 4), indicating that this ratio is not a useful parameter for the organic matter found in these CM2 meteorites. The R_1 values ranged between 0.69 for chemically degraded Mighei grain 1 and 0.77 for chemically degraded Murchison grain 1 and 2, with P-values that indicated no statistically significant differences between the organic matter measured (Table 5).

3.3. 2D spectroscopic maps

The spatial relationships present in the 2D Raman spectroscopic maps (Fig. 3) indicate that the D and G and bands were common responses from organic material found within the grains analysed by the current study. The organic material displaying a Raman response was also distributed heterogeneously within the grains, giving a more intense Raman response in certain localities within a given grain.

Table 2
Numerical values for the peak centres and FWHM of the Raman shift bands (Δ cm^{-1}) assigned to the spectra in Fig. 2. The assignments relate to organic matter present in both the chemically degraded and undegraded meteorite samples.

	Peak Centre		FWHM	
Sample	D	G	D	G
Murchison Gr 1	1356.48 ± 2.19	1591.23 ± 0.46	178.42 ± 2.48	76.26 ± 3.46
Murchison Gr 3	1351.37 ± 2.12	1593.39 ± 0.69	167.96 ± 5.58	67.30 ± 2.74
Mighei Gr 4	1350.15 ± 3.81	1592.32 ± 0.95	151.80 ± 18.76	69.92 ± 3.49
Murchison (Degraded) Gr 1	1352.21 ± 1.43	1590.81 ± 2.04	159.00 ± 3.87	73.30 ± 2.87
Murchison (Degraded) Gr 2	1344.76 ± 2.70	1595.94 ± 0.90	143.57 ± 5.46	60.62 ± 3.49
Mighei (Degraded) Gr 1	1341.68 ± 1.25	1595.80 ± 0.32	148.47 ± 14.45	57.17 ± 0.92
Mighei (Degraded) Gr 2	1346.47 ± 2.37	1595.71 ± 1.05	150.27 ± 14.21	61.33 ± 3.65

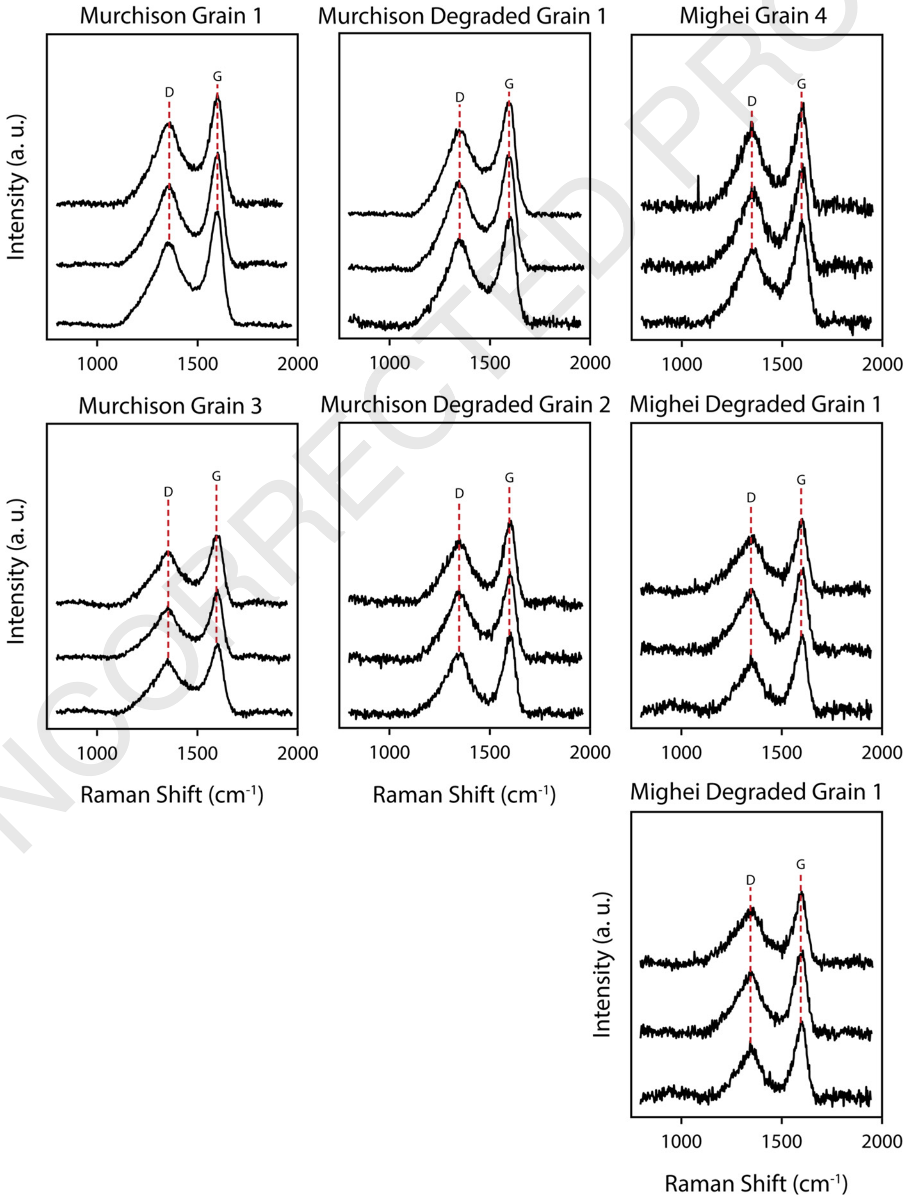

Fig. 2. Raman spectra of undegraded and chemically degraded Murchison and Mighei meteorite material. All the spectra show the D and G bands found within the first order region. Three spectra were included to highlight the similarity of the Raman spectra obtained for each grain.

Table 3
The P-values relating to the peak centres and FWHM of the D and G band in Table 2. Values with an asterisk are statistically significant (P-value <0.05), indicating that there are differences in the bands and thus the organic matter of the meteorite grains being compared. Murch. = Murchison, Mig. = Mighei, Gr. = Grain, Deg. = Chemically Degraded.

Sample	Peak Centre D	Peak Centre G	FWHM D	FWHM G
Murch. Gr. 1 vs. Gr. 3	0.169	0.060	0.159	0.420
Murch. Gr. 1 vs. Murch. Deg. Gr. 1	0.178	0.851	0.013*	0.674
Murch. Gr. 1 vs. Murch. Deg. Gr. 2	0.028*	0.010*	0.004*	0.096
Murch. Gr. 3 vs. Murch. Deg. Gr. 1	0.759	0.297	0.258	0.205
Murch. Gr. 3 vs. Murch. Deg. Gr. 2	0.127	0.088	0.035*	0.207
Murch. Deg. Gr. 1 vs. Murch. Deg. Gr. 2	0.071	0.083	0.082	0.049*
Mig. Gr. 4 vs. Mig. Deg. Gr. 1	0.102	0.026*	0.726	0.017*
Mig. Gr. 4 vs. Mig. Deg. Gr. 2	0.458	0.075	0.695	0.147
Mig. Deg. Gr. 1 vs. Mig. Deg. Gr. 2	0.148	0.939	0.934	0.331
Murch. Deg. Gr. 1 vs. Mig. Gr. 4	0.223	0.360	0.232	0.787
Murch. Deg. Gr. 3 vs. Mig. Gr. 4	0.794	0.414	0.455	0.560
Murch. Deg. Gr. 1 vs. Mig. Deg. Gr. 1	0.005*	0.073	0.520	0.006*
Murch. Deg. Gr. 1 vs. Mig. Deg. Gr. 2	0.107	0.100	0.585	0.062
Murch. Deg. Gr. 2 vs. Mig. Deg. Gr. 1	0.359	0.891	0.767	0.393
Murch. Deg. Gr. 2 vs. Mig. Deg. Gr. 2	0.659	0.230	0.683	0.895

Table 4
Band ratios calculated for the assignments in Table 2. The R_1 ratio is an intensity ratio (peak height) of the D_1 and G bands, whilst the R_2 ratio is an area ratio of the D band over the sum of the G and D bands.

Sample	R_1	R_2
Murchison Gr 1	0.76 ± 0.01	0.65 ± 0.01
Murchison Gr 3	0.74 ± 0.01	0.65 ± 0.01
Mighei Gr 4	0.73 ± 0.03	0.61 ± 0.02
Murchison (Degraded) Gr 1	0.77 ± 0.02	0.65 ± 0.00
Murchison (Degraded) Gr 2	0.77 ± 0.01	0.63 ± 0.01
Mighei (Degraded) Gr 1	0.69 ± 0.05	0.64 ± 0.04
Mighei (Degraded) Gr 2	0.73 ± 0.06	0.64 ± 0.04

Table 5
The P-values relating to the ratios R_1 and R_2 in Table 4. All calculated values are statistically indistinguishable (P-value >0.05). Murch. = Murchison, Mig. = Mighei, Gr. = Grain, Deg. = Chemically Degraded.

Sample	R_1	R_2
Murch. Gr. 1 vs. Gr. 3	0.230	1.000
Murch. Gr. 1 vs. Murch. Deg. Gr. 1	0.519	0.230
Murch. Gr. 1 vs. Murch. Deg. Gr. 2	0.678	1.000
Murch. Gr. 3 vs. Murch. Deg. Gr. 1	0.101	0.230
Murch. Gr. 3 vs. Murch. Deg. Gr. 2	0.251	1.000
Murch. Deg. Gr. 1 vs. Murch. Deg. Gr. 2	1.000	0.137
Mig. Gr. 4 vs. Mig. Deg. Gr. 1	0.530	0.539
Mig. Gr. 4 vs. Mig. Deg. Gr. 2	1.000	0.539
Mig. Deg. Gr. 1 vs. Mig. Deg. Gr. 2	0.636	1.000
Murch. Deg. Gr. 1 vs. Mig. Gr. 4	0.397	0.148
Murch. Deg. Gr. 3 vs. Mig. Gr. 4	0.768	0.148
Murch. Deg. Gr. 1 vs. Mig. Deg. Gr. 1	0.192	0.820
Murch. Deg. Gr. 1 vs. Mig. Deg. Gr. 2	0.547	0.820
Murch. Deg. Gr. 2 vs. Mig. Deg. Gr. 1	0.212	0.816
Murch. Deg. Gr. 2 vs. Mig. Deg. Gr. 2	0.516	0.816

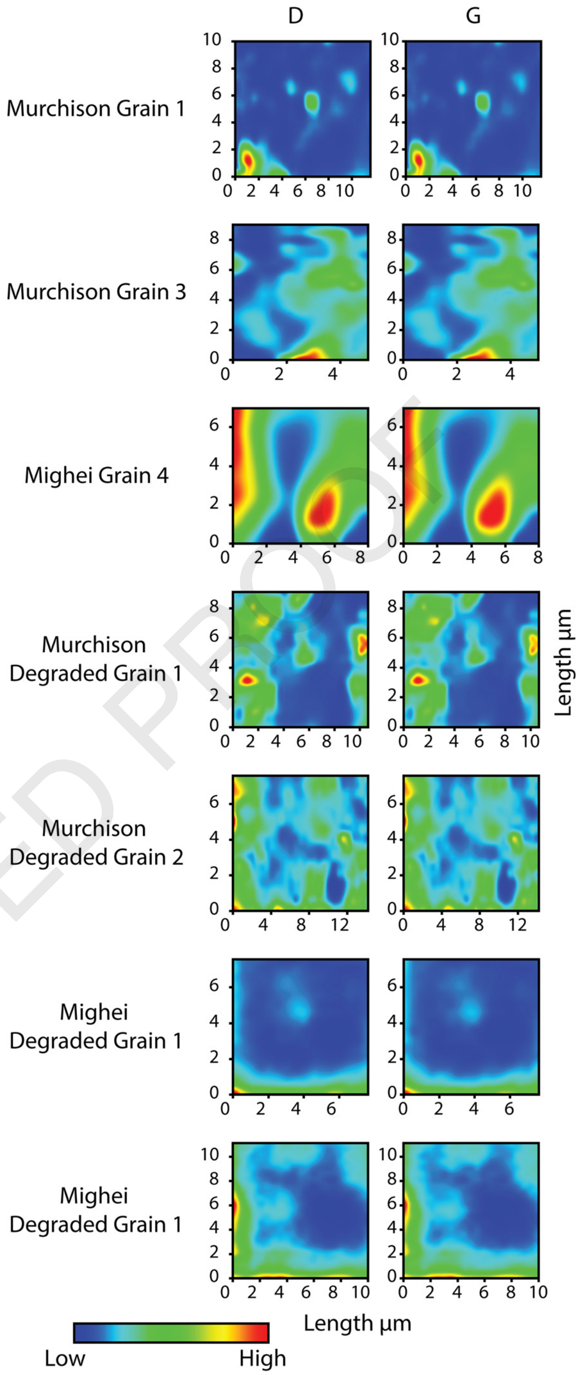

Fig. 3. 2D Raman spectroscopic maps of chemically degraded and undegraded meteorite samples. Colour indicates the intensity of the Raman shift recorded for a given material. The colours are, in the order from highest to lowest intensity: red, orange, yellow, green and blue. The maps are separated into columns depending on the Raman band analysed (refer to Fig. 2): D (defect band) and G (graphite band). The x and y axes represent the distance over which the maps were taken, the scale is in μm. Note that the R1 and R2 ratios were plotted as maps, because the R1 and R2 values from the current study are all statistically indistinguishable ~~and that this~~ means the maps would not show any meaningful information.

4. Discussion

4.1. Chemical degradation

Treatment of terrestrial kerogen-like material with KOH and HI releases ester and ether bound units (Höld et al., 1998). Therefore, a similar chemical degradation of Murchison and Mighei should lead to the removal of LOM via the cleavage of ester functionalities, which are known to be present within MOM (Cody et al., 2002; Watson et al., 2010).

The ROM component consists of mostly aromatic material (Sephton et al., 2003). Raman spectroscopy of meteorite organic matter probes the aromatic component as the D band can only arise from aromatic ring-containing compounds and the G band is the response of the stretching vibrations of graphite-like layers. Thus, the ROM fraction is likely to contribute the bulk of the Raman response of the meteorite organic matter. Both the undegraded and chemically degraded samples demonstrate peak positions for the D and G band and record FWHM values that are nearly all statistically indistinguishable, as demonstrated by the P-values (Table 3). Furthermore, the significant values (except in the case of Murch. Gr. 1 vs. Murch. Deg. Gr. 2, Table 3) do not appear to show obvious relationships, such as being consistently present in either meteorite or pre- or post-chemically degraded samples. Nevertheless, the significant p-values, for Murchison grain 1 vs. chemically degraded Murchison grain 2, could arise if the LOM fraction of Murchison grain 1 was sufficiently aromatic in nature that its liberation could affect the Raman response of the degraded sample. In such a scenario, the loss of aromatic material, with heteroatoms and a greater quantity of in-plane defects, could lead to an increase in the order of the remaining organic matter. In turn this could lead to an increase in the G band position and an altered Raman response. Indeed, studies that have induced disorder in organic matter have demonstrated decreases in the peak centres of their G bands (Baratta et al., 1996; Beyssac et al., 2003; Ferini et al., 2004).

However, an alternate explanation is that these values may be recording either heterogeneity or errors introduced by peak fitting or background removal. If the significant values are indeed anomalous then the Raman parameters would all be statistically indistinguishable. Such a finding would be in agreement with Busemann et al. (2007), who cited the similarity of the G and D bands of CI, CM and CR chondrites as evidence that aqueous alteration had little effect on the organic matter which yields a Raman response. Nevertheless, in the case of Murchison grain 1 compared to Murchison degraded grain 2, a significant p-value is recorded for both the G and D band peak centres. Therefore, in some cases aqueous alteration may affect the Raman response of meteorite organic matter, although this appears to be limited in effect.

4.2. Heterogeneity in Refractory Organic Matter (ROM)

Both the current study and that of Busemann et al. (2007) used a 532 nm laser and fitted the D and G bands with Lorentzian curves, which allows for direct comparison of the peak parameters. The data presented here show D and G band FWHM values that are all statistically significant (Table 6) when compared to those of Busemann et al. (2007), with the D band FWHM values of the current study being smaller by roughly 50%. However, the D and G peak centre positions of Busemann et al. (2007) and the current study are statistically indistinguishable (Table 6). Plots of the D and G peak centres against D and G FWHM demonstrate this relationship (Fig. 4). The standard deviations recorded by Busemann et al. (2007), for their D and G band peak centres, are large and overlap with the peak centre values of the current study, but their FWHM values are smaller and do not. Starkey et al. (2013) also analysed Murchison, but they used a 514 nm laser and a Gaussian-Lorentzian fitting procedure. When compared to the current study, the FWHM values are statistically significant, but the D and G peak centres show a more complex relationship. The D peak centre for Murchison grain 1 and the G peak centre for Murchison grain 3 are statistically indistinguishable from the values reported for Murchison by Starkey et al. (2013), but the other peak centres reported here are statistically significant when compared to the data of this previous study.

Meteorite organic matter has been indicated as heterogeneous below the µm scale (Carter and Sephton, 2013; Changela et al., 2018; Le Guillou et al., 2014; Vollmer et al., 2014) and this characteristic should be evident in the Raman response, reflecting differences in the primary constituents available at the time of accretion or formation, or the alteration of the meteorite organic matter. Such heterogeneity might account for the differences observed between the Raman parameters of the current study and those of the previous studies mentioned above. Indeed, Starkey et al. (2013) reported that the Raman response of type 1 and 2 chondrites is heterogeneous in comparison to those of type 3 or higher. Alternatively, there might be a contribution to the Raman response of meteorite organic matter by non-organic graphitic components, which can be present as µm sized grains in meteorites, including Murchison (Anders and Zinner, 1993; El Amri et al., 2005; Le Guillou et al., 2012).

Table 6
The P-values relating to the peak centres and FWHM of the D and G bands of the data from the current study and that of Busemann et al. (2007) and Starkey et al. (2013). Values with an asterisk are statistically significant (P-value <0.05), indicating that there are differences in the bands, and thus the organic matter of the meteorite grains being compared. Murch. = Murchison, Mig. = Mighei, Gr. = Grain, Deg. = Chemically Degraded and Mur II and III and Mig are samples of Murchison and Mighei, respectively, from the study of Busemann et al. (2007). Mur 514 nm is from the study of Starkey et al. (2013).

Sample	Peak Centre		FWHM	
	D	G	D	G
Murch. Gr. 1 vs. Mur II	0.122	0.599	0.000^{*}	0.000^{*}
Murch. Gr. 1 vs. Mur III	0.650	0.974	0.000^{*}	0.000^{*}
Murch. Gr. 3 vs. Mur II	0.877	0.265	0.000^{*}	0.000^{*}
Murch. Gr. 3 vs. Mur III	0.889	0.869	0.000^{*}	0.000^{*}
Mig. Gr. 4 vs. Mig	0.985	0.419	0.000^{*}	0.000^{*}
Murch. Gr. 1 vs. Mur 514 nm	0.193	0.002^{*}	0.000^{*}	0.000^{*}
Murch. Gr. 3 vs. Mur 514 nm	0.000^{*}	0.493	0.000^{*}	0.000^{*}

Nevertheless, neither µm scale heterogeneity or µm sized graphitic grains can explain the consistency in ROM observed within this study, which was the case even between different carbonaceous chondrites. The data presented in Fig. 4 demonstrates the variation in the Raman parameters for Murchison and Mighei from different studies (Busemann et al., 2007; Quirico et al., 2018, 2014; Starkey et al., 2013), with the data for particular authors tending to plot together, suggesting that some component of either the experimental setup or data treatment may be influencing the overall distribution of the data.

The removal of backgrounds, which can be very different depending on the level of fluorescence experienced (Quirico et al., 2005), could introduce errors in the peak shapes that might explain the difference in FWHM values recorded by Busemann et al. (2007), Starkey et al. (2013) and the current study. Furthermore, the presence or lack of minerals during analysis could potentially change the level or expression of fluorescence and thus effect the values reported by the current study and those of Busemann et al. (2007) and Starkey et al. (2013), both of which demineralised their samples. It may be that the minerals present in the current study influenced the fluorescence and thus induced a different background to the aforementioned studies. Accordingly, a different background may yield different peak shapes that can influence the peak fitting process and thus the FWHM and peak centre values. Interestingly there was almost no statistically significant variation between the peak centre values of the current study and those of Busemann et al. (2007) and Starkey et al. (2013), which suggests that any differences in the background are likely to only affect the FWHM values and not the peak centre values. Another difference to consider is the large standard deviations of Busemann et al. (2007). The large standard deviations are likely due to the large number of spectra used (>1000 in many cases), which prohibits the checking of individual spectra and thus likely leads to the inclusion of data with a low intensity compared to the fluorescence background (Quirico et al., 2018). However, further assessment of the heterogeneity of meteorite organic matter and the distribution of graphitic grains over µm scales, within different carbonaceous chondrites, would allow for the determination of which factors are most important.

Whilst some significant p-values were observed for the D and G band peak centres and FWHM values from the current study, the R_1 values are statistically indistinguishable (Table 5). Such a finding further suggests that ROM is the organic fraction responsible for the Raman response in meteoritic organic matter and indicates an

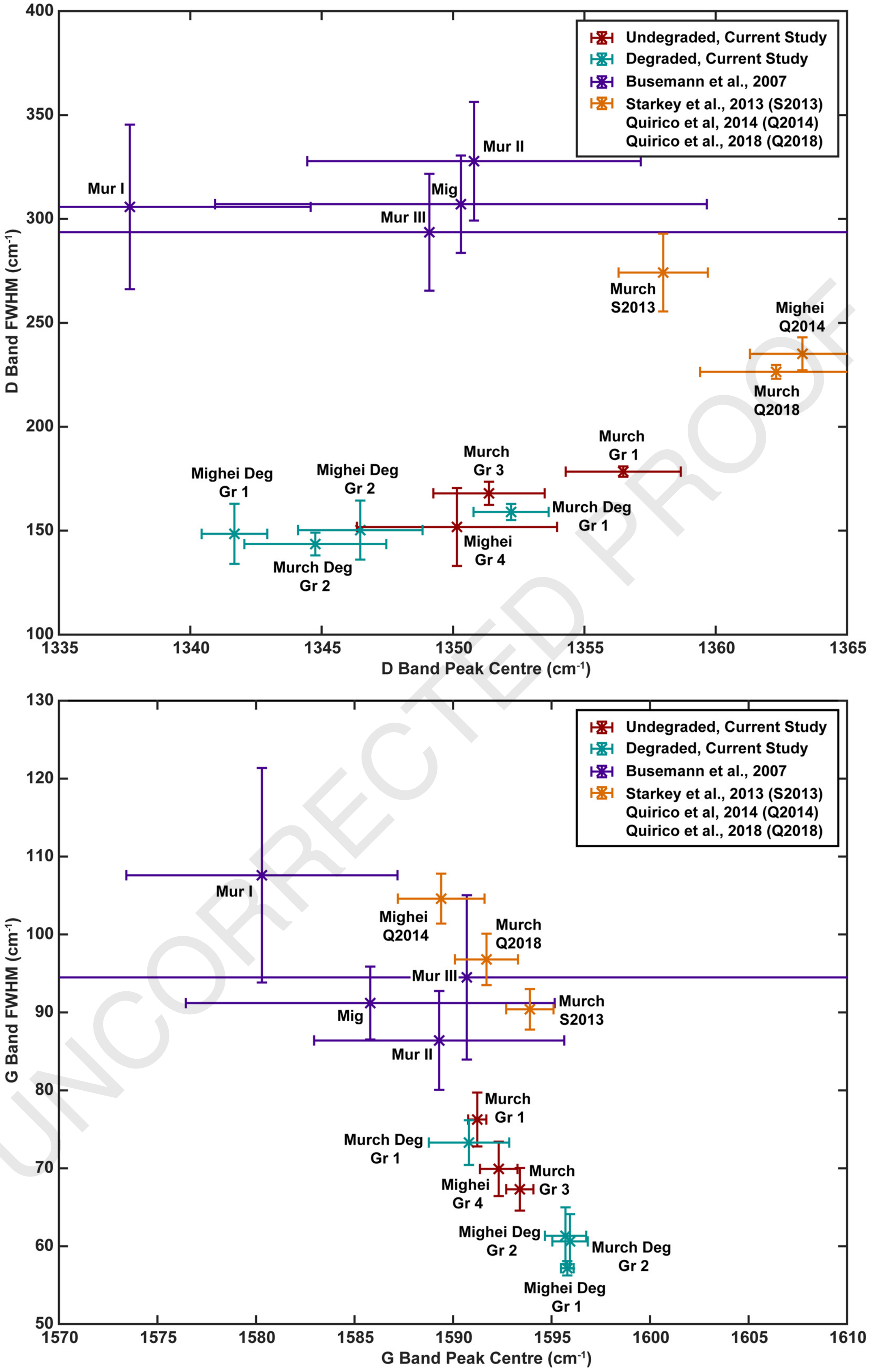

Fig. 4. The D and G band peak centre positions plotted against D and G FWHM values for Murchison and Mighei from the current study and that of Busemann et al. (2007), Starkey et al. (2013), Quirico et al. (2014) and Quirico et al. (2018). Error bars are 1σ standard deviations of the mean.

inherent similarity among the ROM fractions within the same meteorite sample and between different CM2 chondrites. Therefore, it may be the case that Murchison and Mighei had the same parent body or that the ROM fraction represents a common organic progenitor accreted by at least the CM2 chondrites. Indeed, Alexander et al. (1998) states that the near constant ratio of organic carbon to presolar nanodiamonds is indicative of the accretion of a common organic progenitor by all carbonaceous chondrites. Furthermore, it was suggested that the current day variation observed between the IOM of different carbonaceous chondrites relates to the oxidation and/or thermal alteration of a common organic progenitor (Alexander et al., 2007).

Although the Raman response of the organic matter in Murchison and Mighei appears to be relatively homogeneous, organic heterogeneity below the µm scale has been suggested by a previous statistically based study (Carter and Sephton, 2013). Importantly the response from the D and G bands reported here overlap and do not deviate very much from each other in their spatial distribution. This observation would seem to contradict the findings of El Amri et al. (2005), who report variation in the R_1 ratio across their maps. The 2D maps reported here seem to show a variation in overall Raman intensity rather than the intensity of any specific band, as indicated by the near identical spatial distributions of the D and G peak responses shown in Fig. 3. This may be reflected in the use of peak centres for assigning Raman bands to maps for the current study versus the use of frequency ranges in El Amri et al. (2005). The ranges used by El Amri et al. (2005) are large, spanning the range of the bands found across a variety of distinct carbonaceous organic matter types, including organic matter which shows a Raman response similar to crystalline graphite (G peak centre $\sim$1580 cm^{-1}) and between nano-graphitic and amorphous carbon (G peak 1540 cm^{-1}) (Ferrari and Robertson, 2000). The current study has assigned D and G bands for each sample from the more intense areas of our spectrum and has used these to assess variation in those bands throughout our maps. Therefore, the results of the current study are more specific to the samples analysed and less likely to include other spectroscopic features or bands.

The homogeneity of the ROM fraction between chemically degraded and undegraded fractions reported here, supports the notion that aqueous alteration has had little effect on the ROM component of meteoritic organic matter. Previous studies indicate that IOM/MOM is converted to soluble components (FOM/SOM) during aqueous alteration and that in the case of Murchison this conversion has not reached completion (Sephton et al., 2003, 1998). The effects of the chemical degradation reported here simulate to some extent the process of aqueous alteration. Furthermore, the lack of a difference in the Raman response, between chemically degraded and undegraded Murchison and Mighei, suggests that the ROM is unaffected by the degradation process and most likely aqueous alteration. Such an interpretation is consistent with studies that suggested ROM is a common refractory component relatively unaltered by parent body processing (Sephton et al., 2003).

5. Conclusions

The labile organic matter (LOM) fraction of Murchison and Mighei CM2 chondrites was removed through treatment with KOH and HI. The p-values calculated for the Raman spectral parameters reported here (the G and D peak centres and FWHM values) indicate that the Raman response for the samples from the current study are nearly all indistinguishable. Furthermore, all the calculated p-values for the R_1 and R_2 ratios indicate that the Raman responses of Murchison and Mighei (both before and after chemical degradation) are statistically indistinguishable. The statistically indistinguishable nature of the Raman parameters, obtained for the pre- and post-chemically degraded samples, indicate that the ROM fraction is the main contributor to the Raman response of these meteorites. As such, Raman studies which investigate MOM/IOM should acknowledge that the data generated primarily represent only one component of this organic matter fraction. Additionally, there is minimal heterogeneity in the refractory organic matter (ROM) component, both within and between Murchison and Mighei.

The indistinguishable nature of the Raman responses, for pre- and post-chemically degraded Murchison and Mighei, also indicates that aqueous alteration has had little effect on the ROM of these two meteorites. The liberation of LOM through chemical degradation simulates the effects of aqueous alteration and thus, if this process affected the ROM, it should alter the Raman response. Therefore, the lack of significant changes to the Raman parameters between the pre- and post-chemically degraded samples supports the notion that aqueous alteration does not significantly affect the ROM fraction. Consequently, Raman spectroscopy will ~~not~~ give information concerning the effects of aqueous alteration on MOM/IOM. More targeted studies of FOM and LOM would be more suitable for investigating the chemical effects of aqueous alteration.

The apparent similarity of the ROM fractions in Murchison and Mighei suggests that these CM2 chondrites sampled the same organic reservoir, at least for ROM. Such an observation may indicate that the meteorites originate from the same parent body and/or that at least these CM2 chondrites and possibly all CM2 carbonaceous chondrites accreted a chemically-similar or even a common ROM progenitor.

CRediT authorship contribution statement

Christian Potiszil: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Wren Montgomery:** Data curation, Methodology, Software, Supervision, Validation, Visualization, Writing – review & editing. **Mark A. Sephton:** Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Experimental design, carrying out the research, data analysis, and writing of the manuscript were undertaken by the primary author, aided by Wren Montgomery and Mark Sephton (listed in order of the level of contribution).

We acknowledge SOLEIL synchrotron for the allocation of synchrotron radiation facilities (Proposal ID “20160040”). We would like to thank Christophe Sandt for his assistance in using the SMIS beamline and afterwards. We would also like to thank the Science and Technology Facilities Council (STFC) for the funding of the PhD (Award: 1394578) that enabled the work published in this study to be carried out.

References

Alexander, C.M.O., 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. Geochim. Cosmochim. Acta 71, 4380–4403. https://doi.org/10.1016/j.gca.2007.06.052.

Alexander, C.M.O., Russell, S.S., Arden, J.W., Ash, R.D., Grady, M.M., Pillinger, C.T., 1998. The origin of chondritic macromolecular organic matter: a carbon and nitrogen isotope study. Meteorit. Planet. Sci. 33, 603–622. https://doi.org/10.1111/j.1945-5100.1998.tb01667.x.

Anders, E., Zinner, E., 1993. Interstellar grains in primitive meteorites: diamond, silicon carbide, and graphite. Meteoritics 28, 490–514. https://doi.org/10.1111/j.1945-5100.1993.tb00274.x.

Baratta, G.A., Arena, M.M., Strazzulla, G., Colangeli, L., Mennella, V., Bussoletti, E., 1996. Raman spectroscopy of ion irradiated amorphous carbons. Nucl. Instrum. Methods Phys. Res., Sect. B, Beam Interact. Mater. Atoms 116, 195–199. https://doi.org/10.1016/0168-583X(96)00124-3.

Beyssac, O., Goffé, B., Chopin, C., Rouzaud, J.N., 2002a. Raman spectra of carbonaceous material in metasediments: a new geothermometer. J. Metamorph. Geol. 20, 859–871. https://doi.org/10.1046/j.1525-1314.2002.00408.x.

Beyssac, O., Goffé, B., Petitet, J.-P., Froigneux, E., Moreau, M., Rouzaud, J.-N., 2003. On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy. Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc. 59, 2267–2276. https://doi.org/10.1016/S1386-1425(03)00070-2.

Beyssac, Olivier, Rouzaud, J.-N., Goffé, B., Brunet, F., Chopin, C., 2002b. Graphitization in a high-pressure, low-temperature metamorphic gradient: a Raman microspectroscopy and HRTEM study. Contrib. Mineral. Petrol. 143, 19–31. https://doi.org/10.1007/s00410-001-0324-7.

Bonal, L., Bourot-Denise, M., Quirico, E., Montagnac, G., Lewin, E., 2007. Organic matter and metamorphic history of CO chondrites. Geochim. Cosmochim. Acta 71, 1605–1623. https://doi.org/10.1016/j.gca.2006.12.014.

Bonal, L., Quirico, E., Bourot-Denise, M., Montagnac, G., 2006. Determination of the petrologic type of CV3 chondrites by Raman spectroscopy of included organic matter. Geochim. Cosmochim. Acta 70, 1849–1863. https://doi.org/10.1016/j.gca.2005.12.004.

Bouchard, M., Smith, D.C., 2003. Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc. 59, 2247–2266. https://doi.org/10.1016/S1386-1425(03)00069-6.

Busemann, H., Alexander, C.M.O., Nittler, L.R., 2007. Characterization of insoluble organic matter in primitive meteorites by microRaman spectroscopy. Meteorit. Planet. Sci. 42, 1387–1416. https://doi.org/10.1111/j.1945-5100.2007.tb00581.x.

Carter, J.N., Sephton, M.A., 2013. A Bayesian statistical assessment of representative samples for asteroidal or meteoritical material. Meteorit. Planet. Sci. 48, 976–996. https://doi.org/10.1111/maps.12118.

Changela, H.G., Le Guillou, C., Bernard, S., Brearley, A.J., 2018. Hydrothermal evolution of the morphology, molecular composition, and distribution of organic matter in CR (Renazzo-type) chondrites. Meteorit. Planet. Sci. 53, 1006–1029. https://doi.org/10.1111/maps.13045.

Cody, G.D., Alexander, C.M.O., Tera, F., 2002. Solid-state (1 H and 13 C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: a self-consistent quantitative analysis. Geochim. Cosmochim. Acta 66, 1851–1865. https://doi.org/10.1016/S0016-7037(01)00888-2.

Connelly, J.N., Bizzarro, M., Krot, A.N., Nordlund, A., Wielandt, D., Ivanova, M.A., 2012. The absolute chronology and thermal processing of solids in the solar protoplanetary disk. Science 80 (338), 651–655. https://doi.org/10.1126/science.1226919.

Danger, G., Vinogradoff, V., Matzka, M., Viennet, J.-C., Remusat, L., Bernard, S., Ruf, A., Le Sergeant d'Hendecourt, L., Schmitt-Kopplin, P., 2021. Exploring the link between molecular cloud ices and chondritic organic matter in laboratory. Nat. Commun. 12, 3538. https://doi.org/10.1038/s41467-021-23895-2.

de Faria, D.L.A., Venâncio Silva, S., de Oliveira, M.T., 1997. Raman microspectroscopy of some iron oxides and oxyhydroxides. J. Raman Spectrosc. 28, 873–878. https://doi.org/10.1002/(SICI)1097-4555(199711)28:11<873::AID-JRS177>3.0.CO;2-B.

El Amri, C., Maurel, M.-C., Sagon, G., Baron, M.-H., 2005. The micro-distribution of carbonaceous matter in the Murchison meteorite as investigated by Raman imaging. Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc. 61, 2049–2056. https://doi.org/10.1016/j.saa.2004.08.005.

Ferini, G., Baratta, G.A., Palumbo, M.E., 2004. A Raman study of ion irradiated icy mixtures. Astron. Astrophys. 414, 757–766. https://doi.org/10.1051/0004-6361:20031641.

Ferrari, A.C., Robertson, J., 2000. Interpretation of Raman spectra of disordered and amorphous carbon. Phys. Rev. B 61, 14095–14107.

Glavin, D.P., Conel, C.M.O., Aponte, J.C., Dworkin, J.P., Elsila, J.E., Yabuta, H., 2018. The origin and evolution of organic matter in carbonaceous chondrites and links to their parent bodies. In: Primitive Meteorites and Asteroids: Physical, Chemical, and Spectroscopic Observations Paving the Way to Exploration. Elsevier Inc.

Höld, I., Brussee, N., Schouten, S., Sinninghe Damsté, J., 1998. Changes in the molecular structure of a Type II-S kerogen (Monterey Formation, U.S.A.) during sequential chemical degradation. Org. Geochem. 29, 1403–1417. https://doi.org/10.1016/S0146-6380(98)00158-2.

Huss, G.R., Rubin, A.E., Grossman, J.N., 2006. Thermal metamorphism in chondrites. In: Lauretta, D., McSween, H.Y. (Eds.), Meteorites and the Early Solar System II. University of Arizona Press, Tuscon, pp. 567–586.

Kebukawa, Y., Chan, Q.H.S., Tachibana, S., Kobayashi, K., Zolensky, M.E., 2017. One-pot synthesis of amino acid precursors with insoluble organic matter in planetesimals with aqueous activity. Sci. Adv. 3, e1602093.

Kitajima, F., Nakamura, T., Takaoka, N., Murae, T., 2002. Evaluating the thermal metamorphism of CM chondrites by using the pyrolytic behavior of carbonaceous macromolecular matter. Geochim. Cosmochim. Acta 66, 163–172. https://doi.org/10.1016/S0016-7037(01)00758-X.

Le Guillou, C., Bernard, S., Brearley, A.J., Remusat, L., 2014. Evolution of organic matter in Orgueil, Murchison and Renazzo during parent body aqueous alteration: in situ investigations. Geochim. Cosmochim. Acta 131, 368–392. https://doi.org/10.1016/j.gca.2013.11.020.

Le Guillou, C., Rouzaud, J.N., Bonal, L., Quirico, E., Derenne, S., Remusat, L., 2012. High resolution TEM of chondritic carbonaceous matter: metamorphic evolution and heterogeneity. Meteorit. Planet. Sci. 47, 345–362. https://doi.org/10.1111/j.1945-5100.2012.01336.x.

Martins, Z., Sephton, M.A., 2009. Extraterrestrial amino acids. In: Hughes, A.B. (Ed.), Amino Acids, Peptides and Proteins in Organic Chemistry: Origins and Synthesis of Amino Acids. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 1–42.

Matrajt, G., Borg, J., Raynal, P.I., Djouadi, Z., d'Hendecourt, L., Flynn, G., Deboffle, D., 2004. FTIR and Raman analyses of the tagish lake meteorite: relationship with the aliphatic hydrocarbons observed in the diffuse interstellar medium. Astron. Astrophys. 416, 983–990. https://doi.org/10.1051/0004-6361:20034526.

Motulsky, H., 2017. Quick calcs: t-test calculator. [WWW Document]. Graph Pad. https://www.graphpad.com/quickcalcs/ttest1.cfm.

Oba, Y., Naraoka, H., 2006. Carbon isotopic composition of acetic acid generated by hydrous pyrolysis of macromolecular organic matter from the Murchison meteorite. Meteorit. Planet. Sci. 41, 1175–1181. https://doi.org/10.1111/j.1945-5100.2006.tb00514.x.

Pizzarello, S., Shock, E., 2010. The organic composition of carbonaceous meteorites: the evolutionary story ahead of biochemistry. Cold Spring Harb. Perspect. Biol. 2, 1–19. https://doi.org/10.1101/cshperspect.a002105.

Quirico, E., Bonal, L., Beck, P., Alexander, C.M.O.D., Yabuta, H., Nakamura, T., Nakato, A., Flandinet, L., Montagnac, G., Schmitt-Kopplin, P., Herd, C.D.K., 2018. Prevalence and nature of heating processes in CM and C2-ungrouped chondrites as revealed by insoluble organic matter. Geochim. Cosmochim. Acta 241, 17–37. https://doi.org/10.1016/j.gca.2018.08.029.

Quirico, E., Borg, J., Raynal, P.I., Montagnac, G., D'Hendecourt, L., 2005. A micro-Raman survey of 10 IDPs and 6 carbonaceous chondrites. Planet. Space Sci. 53, 1443–1448. https://doi.org/10.1016/j.pss.2005.07.009.

Quirico, E., Montagnac, G., Rouzaud, J.N., Bonal, L., Bourot-Denise, M., Duber, S., Reynard, B., 2009. Precursor and metamorphic condition effects on Raman spectra of poorly ordered carbonaceous matter in chondrites and coals. Earth Planet. Sci. Lett. 287, 185–193. https://doi.org/10.1016/j.epsl.2009.07.041.

Quirico, E., Orthous-Daunay, F.R., Beck, P., Bonal, L., Brunetto, R., Dartois, E., Pino, T., Montagnac, G., Rouzaud, J.N., Engrand, C., Duprat, J., 2014. Origin of insoluble organic matter in type 1 and 2 chondrites: new clues, new questions. Geochim. Cosmochim. Acta 136, 80–99. https://doi.org/10.1016/j.gca.2014.03.025.

Quirico, E., Raynal, P.-I., Bourot-Denise, M., 2003. Metamorphic grade of organic matter in six unequilibrated ordinary chondrites. Meteorit. Planet. Sci. 38, 795–811. https://doi.org/10.1111/j.1945-5100.2003.tb00043.x.

Schouten, S., Hoefs, M.J.L., Koopmans, M.P., Bosch, H.-J., Sinninghe Damsté, J.S., 1998. Structural characterization, occurrence and fate of archaeal ether-bound acyclic and cyclic biphytanes and corresponding diols in sediments. Org. Geochem. 29, 1305–1319. https://doi.org/10.1016/S0146-6380(98)00131-4.

Sephton, M.A., 2013. Organic geochemistry of meteorites. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry, second edition. Elsevier, Oxford, pp. 1–31.

Sephton, M.A., Pillinger, C.T., Gilmour, I., 2000. Aromatic moieties in meteoritic macromolecular materials: analyses by hydrous pyrolysis and δ13C of individual compounds. Geochim. Cosmochim. Acta 64, 321–328. https://doi.org/10.1016/S0016-7037(99)00282-3.

Sephton, M.A., Pillinger, C.T., Gilmour, I., 1999. Small-scale hydrous pyrolysis of macromolecular material in meteorites. Planet. Space Sci. 47, 181–187. https://doi.org/10.1016/S0032-0633(98)00086-5.

Sephton, M.A., Pillinger, C.T., Gilmour, I., 1998. δ13C of free and macromolecular aromatic structures in the murchison meteorite. Geochim. Cosmochim. Acta 62, 1821–1828. https://doi.org/10.1016/S0016-7037(98)00108-2.

Sephton, M.A., Verchovsky, A.B., Bland, P.A., Gilmour, I., Grady, M.M., Wright, I.P., 2003. Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. Geochim. Cosmochim. Acta 67, 2093–2108. https://doi.org/10.1016/S0016-7037(02)01320-0.

Starkey, N.A., Franchi, I.A., Alexander, C.M.O., 2013. A Raman spectroscopic study of organic matter in interplanetary dust particles and meteorites using multiple wavelength laser excitation. Meteorit. Planet. Sci. 48, 1800–1822. https://doi.org/10.1111/maps.12196.

Strazzulla, G., Baratta, G., Palumbo, M., 2001. Vibrational spectroscopy of ion-irradiated ices. Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc. 57, 825–842. https://doi.org/10.1016/S1386-1425(00)00447-9.

Tuinstra, F., Koenig, J.L., 1970. Raman spectrum of graphite. J. Chem. Phys. 53, 1126–1130. https://doi.org/10.1063/1.1674108.

Vinogradoff, V., Bernard, S., Le Guillou, C., Remusat, L., 2018. Evolution of interstellar organic compounds under asteroidal hydrothermal conditions. Icarus 305, 358–370. https://doi.org/10.1016/j.icarus.2017.12.019.

Vollmer, C., Kepaptsoglou, D., Leitner, J., Busemann, H., Spring, N.H., Ramasse, Q.M., Hoppe, P., Nittler, L.R., 2014. Fluid-induced organic synthesis in the solar nebula recorded in extraterrestrial dust from meteorites. Proc. Natl. Acad. Sci. 111, 15338–15343. https://doi.org/10.1073/pnas.1408206111.

Watson, J.S., Sephton, M.A., Gilmour, I., 2010. Thermochemolysis of the Murchison meteorite: identification of oxygen bound and occluded units in the organic macromolecule. Int. J. Astrobiol. 9, 201–208. https://doi.org/10.1017/S1473550410000194.

Wojdyr, M., 2010. Fityk: a general-purpose peak fitting program. J. Appl. Crystallogr. 43, 1126–1128. https://doi.org/10.1107/S0021889810030499.

Q4

Sponsor names

Do not correct this page. Please mark corrections to sponsor names and grant numbers in the main text.

Science and Technology Facilities Council, *country*=United Kingdom, *grants*=`1394578`

Highlights

- The refractory organic matter Raman response is indistinct from bulk meteorite.
- Meteorite refractory organic matter is not affected by aqueous alteration.
- Raman spectroscopy does not record aqueous alteration in meteoritic organic matter.
- CM2 chondrites have Raman responses indistinguishable from each other.
- Refractory organic matter in CM2 chondrites is likely from the same reservoir.