Comparison of FTIR spectra of bulk and acid insoluble organic matter in chondritic meteorites: An implication for missing carbon during demineralization

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Abstract

Past studies of the various separable carbonaceous fractions have been unable to account for all of C in primitive chondrites. In particular, up to 20-50% of the C is lost during acid leaching of bulk samples even after the C in carbonates and soluble organic matter is accounted for. To try to better characterize the nature of this “missing C”, we have compared the bulk infrared (IR) absorption spectra of a number of primitive chondrites with those of their previously reported insoluble organic matter (IOM). The aliphatic C-H stretching bands, in particular, allows us to compare the molecular structures of bulk C with that of IOM. The spectral differences between bulk C and IOM reflect “missing C” phases that were lost during acid leaching, although we cannot completely exclude the possibility that the OM was modified after demineralization. Comparing IR spectra of bulk meteorite powder and IOM suggests that the missing C varies in its molecular structure, and that mildly thermally metamorphosed type 3 chondrites tend to be richer in an aliphatic fraction with lower CH₂/CH₃ ratios, relative to IOM, compared to aqueously altered carbonaceous chondrites

(CI/CM/CR). The missing C is most likely released from acid-labile functional groups, such as esters, acetals and amides, during demineralization, although, it cannot be ruled out that some fraction of the missing C is in small grains that are difficult to recover from suspension, or in water-soluble compounds trapped in phyllosilicates.

INTRODUCTION

Traditionally the organic matter in meteorites, particularly in primitive carbonaceous chondrites and some unequilibrated ordinary chondrites, is divided into two groups based on extraction properties; solvent/acid insoluble organic matter (IOM) and solvent soluble organic matter (SOM). There are also inorganic C-bearing components, e.g., carbonate and other minor components (nanodiamond, graphite, silicon carbide, etc.). Typically, ~50% of the bulk C can be isolated as IOM (Alexander et al. 2015). Up to ~50 % of the bulk C is unaccounted for after the demineralization process, excluding the loss of SOM and carbonate (Alexander et al. 2012, 2015; Smith and Kaplan 1970). Most of the “missing C” appears to be insoluble in typical solvents and is released by treatment with $\geq 1\text{M}$ HCl (Alexander et al. 2012). To date, the “missing C” has remained an uncharacterized major component that might be a unique organic phase that is distinct from IOM and SOM. Alexander et al. (2012) concluded that the “missing C” must have a composition that is similar to the IOM, and it seems likely that the acid soluble material is bonded to the IOM by acid hydrolysable functional groups, but it cannot be ruled out that some is trapped in phyllosilicates or as alkali and alkaline earth salts. Alternatively, as Alexander et al. (2015) suggest that very small grains of IOM may remain suspended in the solutions and be lost during bulk IOM recovery. None of these possibilities require that the missing C represents a unique organic phase.

Infrared (IR) spectroscopy is a suitable and well-established method for analyzing isolated IOM as well as bulk meteorites (e.g., Kebukawa et al. 2011; Kebukawa et al. 2010; Matrajt et al. 2004; Orthous-Daunay et al. 2013; Quirico et al. 2014). We have obtained bulk meteorite IR absorption spectra for a number of primitive chondrites and compared them to the spectra from their isolated

IOM to try to identify any spectral differences that might help constrain the molecular structure of the missing C.

SAMPLES AND METHODS

Two CMs, one CI, two CRs, one CV and one ordinary chondrite were selected for this study (Table 1). The IR spectra of their IOM (Fig. 1) were published previously (Kebukawa et al. 2011). The H, C and N elemental and isotopic compositions of the bulk meteorites and their IOM have also been previously determined (Alexander et al. 2012; Alexander et al. 2007; Alexander et al. 2010), as have their carbonate contents (Alexander et al. 2015). For the purposes of this study, the key features of the CsF-HF technique that was used to isolate the IOM is that everything was done at room temperature and that the CsF-HF step was conducted at relatively neutral pH (pH 5-7), but that prior to the CsF-HF step the samples were leached with 2M HCl (Alexander et al. 2007; Cody and Alexander 2005; Cody et al. 2002).

Prior to the measurement of their IR spectra, the bulk chondrite powders (crushed to <100-150 μm) were mixed with KBr powder that was freshly prepared from a KBr cubic crystal, and a KBr pellet was prepared using a standard press for each sample. A KBr pellet was typically made with ~0.005 g of meteorite powder and ~0.2 g KBr powder. The weights and thicknesses of the pellets were recorded for quantification of their IR spectrum. The KBr pellets were dried overnight at 50 °C under N_2 flow before analysis to reduce any contribution to the IR spectra by absorbed water.

The IR absorption spectra were obtained with a Fourier transform infrared (FTIR) spectrometer (Jasco FT/IR-6300), that employs a ceramic IR light source, a Ge coated KBr beam splitter, and a Triglycine sulfate (TGS) detector. The FTIR was continuously purged with dry N_2 . For the IR spectra of each sample, 128 scans were accumulated with a wavenumber resolution of 4 cm^{-1} , in the wavenumber range of 7800–400 cm^{-1} . Background spectra were acquired with blank KBr pellets.

RESULTS

According to the Lambert–Beer law, the IR absorbance (A_λ) at a given inverse wavelength λ (cm^{-1}) is a function of the absorption coefficient (ϵ_λ), the molar concentration (c), and the thickness of the sample (l);

$$A_\lambda = \epsilon_\lambda c l. \quad (1)$$

For the purpose of this study and in the absence of detailed absorption coefficients for all phases present in the samples, we normalize the spectra by the weight fractions of the samples in the KBr pellets (w) rather than the molar concentrations and the thicknesses of the KBr pellets (d). Thus, the spectral y-axis of the IR absorption spectra of the bulk meteorites are written as A_λ/wd instead of A_λ (Fig. 2). This approach makes it possible to compare the bulk meteorite spectra quantitatively.

All the IR spectra of the chondrites reveal strong absorption bands at around 1000 cm^{-1} that are assigned to the primary Si-O stretching modes of silicates. Some of the chondrites also exhibit absorption bands (1) at 3685 cm^{-1} that are assigned to OH in hydrous silicates, (2) at around 3400 cm^{-1} and 1640 cm^{-1} due to structural and/or absorbed H_2O of hydrous silicates, and (3) at about 1435 cm^{-1} from CO_3 of carbonates. The only uniquely organic bands observed in the IR spectra of the bulk chondrite powders were the aliphatic CH stretching modes at 2960 , 2930 and 2860 cm^{-1} . Thus, we compared the aliphatic CH stretching band structure with that present in the IR spectra of isolated IOM obtained in a previous study (Kebukawa et al. 2011).

When conducting quantitative analysis of aliphatic CH stretching bands, the possibility that there are overlapping peaks from carbonate sub-bands needs to be considered. IR spectra of carbonates have a main absorption band at around 1450 cm^{-1} , and weaker overtones in the 3050 – 2850 cm^{-1} region with peaks centered at 3015 – 3000 cm^{-1} and 2895 – 2875 cm^{-1} , as well as peaks at $\sim 2550 \text{ cm}^{-1}$ and $\sim 1800 \text{ cm}^{-1}$ (Salisbury et al. 1991). Some of the bulk meteorite IR spectra (Fig. 2) do show the main carbonate band at 1435 cm^{-1} , but none of these shows peaks at $\sim 2550 \text{ cm}^{-1}$ and $\sim 1800 \text{ cm}^{-1}$ that are usually much smaller than the main band ($\sim 1450 \text{ cm}^{-1}$) but larger than the bands at 3050 – 2850 cm^{-1} (Salisbury et al. 1991). Thus, we conclude that there are no significant overlapping peaks from carbonates to the aliphatic CH bands in the bulk meteorite spectra. Peak shifts of the

band at around 2860 cm^{-1} were observed in some chondrites, particularly Kaba (CV3.1), compared to other chondrites. The 2860 cm^{-1} band contains both CH_3 and CH_2 symmetric stretching. While these two bands are not well separated, the CH_3 symmetric stretching band appears at higher wavenumbers than CH_2 symmetric stretching band. Thus, the shifts of the $\sim 2860\text{ cm}^{-1}$ peak to lower wavenumbers are consistent with the increasingly CH_2 -rich nature of the OM.

To quantify the variation in the relative abundances in CH_2 and CH_3 functional groups, we obtain the peak heights F_{CH_x} ($x = 2, 3$) of the aliphatic CH_3 asymmetric stretching (2960 cm^{-1}) and CH_2 asymmetric stretching (2930 cm^{-1}) bands after a polynomial baseline correction (Fig. 3), and these values are shown in Fig. Fig. 4 and Table 1. It should be noted that the peak height F_{CH_3} is a function of the aliphatic CH_3 fraction in the bulk meteorite sample and absorption coefficient (ϵ_{2960}), and the same is true for the 2930 cm^{-1} peak for CH_2 , i.e., they are proportional to the relative amounts of CH_3 or CH_2 groups in the bulk meteorite samples. The aliphatic peak heights for Murchison (CM2) and Ivuna (CI1) were higher than those for the other chondrites, and no significant correlations with degree of alteration or chondrite group were observed.

We then calculate the relative aliphatic fractions in the bulk C by dividing the whole-rock aliphatic CH_x intensity obtained from the bulk IR spectra ($F_{\text{CH}_3} + F_{\text{CH}_2}$) by the bulk C abundance C_{bulk} (wt.%) using the values reported in Alexander et al. (2012) (Fig. 5a, Table 1). The order of the relative aliphatic fractions in bulk C is; Murchison (CM2) $\approx$ Elephant Moraine (EET) 92042 (CR2) $\approx$ Semarkona (LL3.00) $\geq$ Kaba (CV3.1) $\geq$ Grosvenor Mountains (GRO) 95577 (CR1) $>$ Ivuna (CI1) $>$ Bells (CM2 anomalous). We also compare these values with the estimated relative aliphatic fractions in their corresponding IOM using the aliphatic/aromatic IR peak intensity ratios $[(I_{\text{CH}_3} + I_{\text{CH}_2})/I_{\text{AroCC}}]$ that were recalculated from Kebukawa et al. (2011) (Fig. 5b). The order of the estimated relative aliphatic fractions in IOM is; Ivuna $\approx$ Murchison $\geq$ GRO 95577 $>$ Bells $\approx$ EET 92042 $>$ Kaba $\approx$ Semarkona. The order of the H/C ratios (at.) of their IOM is; GRO 95577 (0.786) $\geq$ EET 92042 (0.757 ± 0.02) $\geq$ Ivuna (0.723) $\geq$ Bells (0.685 ± 0.008) $>$ Murchison (0.588 ± 0.016) $>$ Semarkona (0.476) $>$ Kaba (0.313) (Alexander et al. 2007). The orders of the relative aliphatic fractions and H/C

in IOM are broadly consistent in the sense that the aliphatic fractions in type 1 and 2 chondrites are higher than those in type 3 chondrites. However, they are inconsistent with the detailed variations among meteorites, which is not entirely surprising since the aliphatic groups (CH₂ and CH₃) do not represent all the H in IOM. However, nuclear magnetic resonance (NMR) studies of IOM show that the aliphatic/aromatic ratio of EET 92042 is higher than that of Murchison (Cody and Alexander 2005), which is the opposite of the peak intensity ratio $[(I_{\text{CH}_3} + I_{\text{CH}_2})/I_{\text{AroCC}}]$ obtained from the IR spectra. This conflict could be explained by the fact that the IR is only sensitive to CH₂ and CH₃ but not CH₁ - the CH₁ peak at 2890-2880 cm⁻¹ cannot be clearly distinguished from the symmetric stretching bands of CH₂ at 2870-2840 cm⁻¹ and CH₃ at 2885-2865 cm⁻¹ (Socrates 2004), i.e., there is only one peak at ~2860 in the bulk meteorite spectra (Figs. 2 and 3). Thus, the inconsistency in the aliphatic fractions determined by IR and NMR might indicate that EET 92042 IOM contains larger amounts of CH₁, relative to CH₂ and CH₃, compared to Murchison IOM. Note that the peak tops of CH₃ and CH₂ asymmetric stretching bands at 2960 cm⁻¹ and 2930 cm⁻¹, respectively, are clearly distinguished to obtain the CH₂/CH₃ ratios.

By comparing the spectral characteristics of a bulk meteorite and its IOM, one can potentially evaluate the molecular structures of the missing C + SOM. Considering that the SOM fraction is relatively small compared to the missing C fraction (e.g., $C_{\text{SOM}}/C_{\text{bulk}} = 0.02$ vs. the fraction of missing C $[1-(C_{\text{IOM}}+C_{\text{SOM}}+C_{\text{carb}})/C_{\text{bulk}}] = 0.26$ for Ivuna, and $C_{\text{SOM}}/C_{\text{bulk}} = 0.04$ vs. the fraction of missing C = 0.33 for Murchison), the spectroscopic signatures of the [missing C + SOM] fractions largely reflect those of the missing C fractions. Thus, in the following discussion, we use the term “missing C” as shorthand for the “missing C + SOM fraction” while recognizing that the SOM will have contributed to the “missing C” IR signature.

Figure 6 plots the estimated relative aliphatic fractions in C_{bulk} vs. the aliphatic fractions in IOM. The aliphatic fractions are relative values and should only be quantitatively compared between either bulk samples or IOM. However, the relative ratios (Ali CH_x in bulk C)/(Ali CH_x in IOM) for each meteorite indicate the relative abundances of aliphatic groups in the missing C compared to IOM.

157 The ratios of the relative aliphatic fractions in the missing C compared to IOM vary in the order;
158 Kaba (CV3) $\approx$ Semarkona (LL3) > EET 92042 (CR2) > Murchison (CM2) > GRO 95577 (CR1) $\approx$
159 Bells (CM2 anom.) > Ivuna (CI1). The most obvious feature of this result is that the aliphatic
160 fractions in the missing C in type 3 chondrites are higher than in the type 1 and 2 chondrites, but that
161 there is no clear pattern amongst the type 1s and 2s.

162 Figure 7 compares the CH_2/CH_3 peak intensity ratios of the bulk C with the CH_2/CH_3 peak
163 intensity ratios in the IOM (Kebukawa et al. 2011). The IOM of type 3 chondrites show higher
164 CH_2/CH_3 ratios (Kebukawa et al. 2011). The CH_2/CH_3 ratios in bulk C show some variations, but no
165 clear systematic correlation with chondrite group or petrologic type. When comparing the CH_2/CH_3
166 ratios in bulk C and in IOM, data that plot on the slope=1 line have the same CH_2/CH_3 ratios in the
167 bulk C and IOM, and thus the CH_2/CH_3 ratios in the missing C and IOM are also the same. If data
168 plot above the slope=1 line, this indicates that they have higher CH_2 contents in the missing C than in
169 IOM, and conversely if they plot below the slope=1 they have higher CH_3 contents in the missing C
170 than in IOM. The missing C in Bells would seem to have a higher CH_2/CH_3 ratio than in the Bells
171 IOM. The CH_2/CH_3 ratios of the missing C in Ivuna, EET 92042 and Kaba appear to be very similar
172 to those in their IOM. The missing C in Murchison, GRO 95577, and Semarkona would seem to
173 have lower or similar CH_2/CH_3 than IOM, despite the larger uncertainties in the CH_2/CH_3 ratios of
174 their bulk C.

175

176 **DISCUSSION**

177 **Effects of demineralization**

178 The application of HF and HCl to demineralize rocks and liberate organic matter was developed
179 about 100 years ago by petroleum chemists studying the kerogens isolated from oil shales through
180 demineralization. It is routinely used to this day by organic geochemists and soil scientists. Low rank
181 coal is a good model for IOM at the functional group level, i.e., both low rank coals and IOM contain
182 small O-substituted aromatics, carboxyl and ketone moieties, and aliphatic moieties. Larsen et al.

(1989) explicitly studied whether HCl and HF demineralization affected the molecular structure of low rank coal and concluded that there was no effect. Kerridge et al. (1988) showed that there was little (~3-5 %) H isotopic exchange during the isolation of IOM even when using relatively harsh conditions, which also indicates that there is little modification of IOM during demineralization.

That demineralization with HF and HCl does not significantly modify IOM is consistent with what is known about the general reactivity of these acids in organic chemistry. While HF is able to destroy SiO₂, it is in fact a very weak acid. In addition, since HF and HCl are neither oxidants nor reductants, their ability to affect organic chemistry is very limited, i.e., neither can break C-C or C-H bonds. They can only break some acid-hydrolysable bonds such as amides and esters (e.g., Smith and March 2007). There is the potential of fluoride or chloride anion addition to double bonds, e.g., the conversion of ethylene to fluoro- or chloro ethane. Cody et al. (2002) analyzed IOM for fluorine (using energy dispersive X-ray Analysis) and detected none, indicating that if any fluoride addition did take place it did so at very low yields; more over HF addition to double bonds is typically performed in aprotic organic solvents, e.g., pyridine or tetrahydrofuran (Smith and March 2007), where the solvent catalyzes the reaction through strong H-bonding with HF. This does not happen in aqueous solutions.

The IOM IR spectra used here (Kebukawa et al. 2011) were obtained on IOM samples that were isolated from their host meteorites using the room temperature CsF-HF dissolution/extraction technique (Cody et al. 2002). The CsF method of demineralization should be even more benign than most HF-HCl protocols that generally involve a step in which the sample is treated with 6M HCl at 60-80°C to remove insoluble fluorides. The CsF method has been tested on various organic substrates, including low rank coal, and no evidence of any chemical reaction (e.g., fluorine addition or base catalyzed oxidation) was detected (Cody et al. 2002).

Since the missing C is almost certainly not the result of reaction with fluoride ions, the most likely causes of C loss are: (i) acid hydrolysis of susceptible functional groups, probably during leaching with 2M HCl prior to CsF-HF treatment, and/or (ii) very small grains remaining suspended

in the solutions even after centrifugation (Alexander et al. 2015). The missing C could be water soluble compounds trapped in phyllosilicates, but it seems unlikely as the missing C is present in CRs that have little phyllosilicate development (Alexander et al. 2012).

Molecular structure of the missing C phase?

Flynn et al. (2010) and Yabuta et al. (2010) reported direct comparisons of organic matter (OM) measured in-situ in Murchison and Murchison IOM prepared by the “classical” HF-HCl method. Flynn et al. (2010) reported that the C *K*-edge X-ray absorption near-edge structure (C-XANES) and IR spectra of non-extracted OM from Murchison showed lower C=O relative to aromatic C (by C-XANES) and a higher CH₂/CH₃ ratio (by IR) in non-extracted OM from Murchison than those in Murchison IOM. However, it should be noted that the C-XANES spectra varied significantly from spot to spot in the bulk Murchison sample. Yabuta et al. (2010) also reported that the C-XANES of non-extracted OM from Murchison has lower intensities of aliphatic C and C=O relative to aromatic C compared to IOM. However, the amount of carbonaceous material analyzed in situ will have been much smaller than in the IOM samples, so that it is unclear how significant these differences are.

Le Guillou et al. (2014) also reported in-situ measurements of Murchison, Orgueil (CI) and Renazzo (CR2) by C-XANES. There are nanometer scale heterogeneities in molecular structures and sub-micrometric individual grains showed lower aliphatic C and C=O relative to aromatic C compared to the diffuse organic matter that is finely interspersed within phyllosilicates. If the missing C is very small grains remaining suspended in the solutions even after centrifugation, the diffuse organic matter may contribute more to the missing C, although the diffuse organic matter may be dominated by SOM.

We could not observe the IR absorption bands at ~1700 cm⁻¹ due to C=O bonds in the bulk meteorite IR spectra because of the small amount of organic matter in the mineral matrix and the overlap with the water band centered at 1635 cm⁻¹. For the Murchison meteorite, the CH₂/CH₃ ratio in the missing C appears to be lower than in its IOM, which is inconsistent with the results of Flynn

et al. (2010). This could be due to the sample heterogeneity since Flynn et al. used microscopic FTIR and microtomed samples, while we used macroscopic FTIR of fine powder in KBr pellets that allowed us to obtain average spectra of several mg of samples.

What kind of compounds can be released from acid hydrolysis?

If the missing C is a component that is released from macromolecular OM during acid treatment, the following explanation for its nature would be most plausible. Not many acid-labile bonds are likely to exist in macromolecular organic matter (e.g., Smith and March 2007). Typical acid-labile bonds are esters, acetals and amides. An ester bond produces a carboxylic acid and an alcohol via acid hydrolysis. An amide bond produces a carboxylic acid and an amine (or occasionally an amino acid) via acid hydrolysis. Consequently, the missing C may be in low molecular weight water-soluble compounds (e.g., methanol, formate, acetate, etc.) that were produced by acid hydrolysis of ester, acetal and amide bridges during IOM isolation. Another possibility is that the missing C is released from alkali and alkaline earth salts, such as carboxylate salts. However, at present one cannot rule out that the missing C also includes IOM-like small (<100 nm) grains that are difficult to recover from suspension, and/or water-soluble compounds that are physically trapped in the meteorites.

Variations of missing C among chondrite groups

Our results suggest that the missing organic C material could be composed of a variety of molecular structures. The relative abundances of the aliphatic fractions in the missing C compared to IOM are in order of decreasing amount; Kaba (CV3) $\approx$ Semarkona (LL3) > EET 92042 (CR2) > Murchison (CM2) > Bells (CM2 anom.) $\approx$ GRO 95577 (CR1) > Ivuna (CI1) (Fig. 6). The order of the relative aliphatic fractions in the missing C compared to IOM is broadly consistent with the order of petrologic type. The CH₂/CH₃ ratios of missing C compared to IOM are in order of decreasing ratio; Bells (CM2 anom.) > Ivuna (CI1) $\approx$ EET 92042 (CR2) $\approx$ Kaba $\gtrsim$ Murchison (CM2) $\approx$ GRO

95577 (CR1) $\approx$ Semarkona (LL3) (Fig. 7). There is no clear pattern amongst the petrologic types, and there is no significant difference of the CH_2/CH_3 ratios between the missing C and IOM – type 3 chondrites have higher CH_2/CH_3 ratios than type 1 and 2 chondrites for both the missing C and IOM. Higher CH_2/CH_3 ratios indicate longer aliphatic chains and/or higher contents of cyclic aliphatic structures, and lower CH_2/CH_3 ratios indicate shorter chain lengths and/or higher branching levels. The observed higher CH_2/CH_3 ratios in thermally metamorphosed chondrites are consistent with previous work showing that the CH_2/CH_3 ratios were higher in IOM from thermally metamorphosed chondrites and heated CMs (e.g., Kebukawa et al. 2011; Orthous-Daunay et al. 2013; Quirico et al. 2018). Considering that the IOM from these thermally metamorphosed chondrites has lower H/C ratios (Alexander et al. 2007), the increase in CH_2/CH_3 ratios is likely due to terminations of CH_3 , rather than due to increasing of chain length.

The missing C in type 3 chondrites (that are slightly thermally metamorphosed) tend to be richer in aliphatic material with relatively low CH_2/CH_3 ratios compared to IOM. On the other hand, the missing C in Ivuna (CI) and Bells (CM2 anom.) tends to have less aliphatic material but CH_2/CH_3 ratios that are slightly higher than their IOM. Murchison and CRs have relatively high contents of aliphatic C in both bulk and IOM (and thus in the missing C) compared to other meteorites, and the CH_2/CH_3 ratios in the missing C are slightly lower than those in IOM. Considering that IOM in thermally metamorphosed (type 3) chondrites is dominated by aromatic C, unlike aqueously altered (type 1&2 CI/CM/CR) chondrites, type 3s have comparable amounts of aliphatic material in their bulk C relative to type 1&2s. It would suggest that the missing C in type 3 chondrites has similar aliphatic/aromatic ratios or even higher than those in type 1&2 chondrites. In addition, it should be remembered that Bells is an anomalous CM2 with a saponite- and magnetite-rich matrix that is somewhat similar to the mineralogies of CIs (Brearley 1995). Thus, conditions of parent body alteration could have influenced the organic compositions. Matrix mineralogy may also have had some influence on the release of the missing C, e.g., selective adsorption and catalytic bond-breaking reactions, during HCl treatment. Alternatively, if the missing C was water-soluble compounds

trapped in phyllosilicates, the characteristics of the missing C would reflect the interlayer spacings, cations or surface electric charges of the phyllosilicates, e.g., CM are dominated by serpentines, while CIs (and Bells) are dominated by serpentines interlayered with saponite (Brearley 2006). It is well known that cations and electric charges on mineral surfaces play important roles in catalytic activity (e.g., Weitkamp 2000).

CONCLUSIONS

We have obtained IR absorption spectra of various bulk chondrites and compared these with IR spectra of isolated IOM to see whether we were able to gain any insight to the molecular structure of the “missing” organic phase that is lost during demineralization procedures. The IR spectra indicates that the molecular structures of the missing C are somewhat different from the IOM from the same meteorites, and that they vary among the chondrite groups. The characteristics of aliphatic C-H stretching bands indicated the aliphatic fractions, relative to IOM, in “missing C” are ranked in order; Kaba (CV3) $\approx$ Semarkona (LL3) > EET 92042 (CR2) > Murchison (CM2) > GRO 95577 (CR1) $\approx$ Bells (CM2 anom.) > Ivuna (CI1), and the CH₂/CH₃ ratios of missing C are; Bells > Ivuna $\approx$ EET 92042 $\approx$ Kaba $\approx$ Murchison $\approx$ GRO 95577 $\approx$ Semarkona. Given the relatively mild procedures used for demineralization, the missing C is probably released from acid-labile bonds, e.g., ester, acetal and amide bonds, in macromolecular C. However, one cannot rule out other possibilities, such as that the missing C phases are IOM-like small (<100 nm) grains that are difficult to recover from suspension, or that it is in water-soluble compounds that are trapped in phyllosilicates, or as alkali and alkaline earth salts.

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References

- Alexander C. M. O'D., Bowden R., Fogel M. L., and Howard K. T. 2015. Carbonate abundances and isotopic compositions in chondrites. *Meteoritics & Planetary Science* 50:810-833.
- Alexander C. M. O'D., Bowden R., Fogel M. L., Howard K. T., Herd C. D. K., and Nittler L. R. 2012. The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets. *Science* 337:721-723.
- Alexander C. M. O'D., Fogel M., Yabuta H., and 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., Newsome S. D., Fogel M. L., Nittler L. R., Busemann H., and Cody G. D. 2010. Deuterium enrichments in chondritic macromolecular material—Implications for the origin and evolution of organics, water and asteroids. *Geochimica et Cosmochimica Acta* 74:4417-4437.
- Alexander C. M. O'D., Russell S. S., Arden J. W., Ash R. D., Grady M. M., and Pillinger C. T. 1998. The origin of chondritic macromolecular organic matter: A carbon and nitrogen isotope study. *Meteoritics & Planetary Science* 33:603-622.
- Becker R. H. and Epstein S. 1982. Carbon, hydrogen and nitrogen isotopes in solvent-extractable organic matter from carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 46:97-103.
- Brearley A. J. 1995. Aqueous alteration and brecciation in Bells, an unusual, saponite-bearing, CM chondrite. *Geochimica et Cosmochimica Acta* 59:2291-2317.
- Brearley A. J. 2006. The action of water. In *Meteorites and the Early Solar System II* (eds. D. S. Lauretta and J. H. Y. McSween), pp. 587-624. University of Arizona Press, Tucson.
- Cody G. D. and Alexander C. M. O'D. 2005. NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochimica et Cosmochimica Acta* 69:1085-1097.
- Cody G. D., Alexander C. M. O'D., and Tera F. 2002. Solid-state (H-1 and C-13) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: A self-consistent quantitative analysis. *Geochimica et Cosmochimica Acta* 66:1851-1865.
- Flynn G., Wirick S., Keller L., and Jacobsen C. (2010) Modification of the Murchison insoluble organic matter (IOM) by acid extraction. In *Astrobiology Science Conference*, pp. 5162.
- Kebukawa Y., Alexander C. M. O'D., and Cody G. D. 2011. Compositional diversity in insoluble organic matter in type 1, 2 and 3 chondrites as detected by infrared spectroscopy. *Geochimica et Cosmochimica Acta* 75:3530-3541.

- Kebukawa Y., Nakashima S., and Zolensky M. E. 2010. Kinetics of organic matter degradation in the Murchison meteorite for the evaluation of parent-body temperature history. *Meteoritics & Planetary Science* 45:99-113.
- Kerridge J. F., Chang S., and Shipp R. 1988. Deuterium exchange during acid-demineralisation. *Geochimica et Cosmochimica Acta* 52:2251-2255.
- Larsen J. W., Pan C. S., and Shawver S. 1989. Effect of demineralization on the macromolecular structure of coals. *Energy & Fuels* 3:557-561.
- Le Guillou C., Bernard S., Brearley A. J., and Remusat L. 2014. Evolution of organic matter in Orgueil, Murchison and Renazzo during parent body aqueous alteration: In situ investigations. *Geochimica et Cosmochimica Acta* 131:368-392.
- Matrajt G., Borg J., Raynal P. I., Djouadi Z., d'Hendecourt L., Flynn G., and Deboffle D. 2004. FTIR and Raman analyses of the Tagish Lake meteorite: Relationship with the aliphatic hydrocarbons observed in the Diffuse Interstellar Medium. *Astronomy & Astrophysics* 416:983-990.
- Orthous-Daunay F. R., Quirico E., Beck P., Brissaud O., Dartois E., Pino T., and Schmitt B. 2013. Mid-infrared study of the molecular structure variability of insoluble organic matter from primitive chondrites. *Icarus* 223:534-543.
- Quirico E., Orthous-Daunay F.-R., Beck P., Bonal L., Brunetto R., Dartois E., Pino T., Montagnac G., Rouzaud J.-N., Engrand C., and Duprat J. 2014. Origin of insoluble organic matter in type 1 and 2 chondrites: New clues, new questions. *Geochimica et Cosmochimica Acta* 136:80-99.
- Salisbury J. W., Walter L. S., Vergo N., and D'Aria D. M. 1991. *Infrared (2.1–25 micrometers) spectra of minerals*. John Hopkins University Press, Baltimore.
- Smith J. and Kaplan I. 1970. Endogenous carbon in carbonaceous meteorites. *Science* 167:1367-1370.
- Smith M. B. and March J. 2007. *March's advanced organic chemistry: reactions, mechanisms, and structure*. John Wiley & Sons.
- Socrates G. 2004. *Infrared and Raman characteristic group frequencies: tables and charts*. John Wiley & Sons.
- Weitkamp J. 2000. Zeolites and catalysis. *Solid State Ionics* 131:175-188.
- Yabuta H., Mita H., Kobayashi K., Hasegawa N., and Kilcoyne A. (2010) Direct Analysis of Organic Molecules in Carbonaceous Chondrite Through X-Ray Absorption Near Edge Spectroscopy Using Scanning Transmission X-Ray Microscope. In *Astrobiology Science Conference*, pp. 5317.

384 **Figure captions**

385 Fig. 1. FTIR spectra of the IOM from chondrites. The spectra were re-drawn using the data shown in
386 Kebukawa et al. (2011).

387
388 Fig. 2. Fourier transform infrared (FTIR) spectra of the chondrites. The Y-axis is the absorbance
389 divided by sample thickness and bulk meteorite concentration in the KBr pellet (wt.%), and the
390 spectra were offset from one another for clarity.

391
392 Fig. 3. (a) An illustration of the baseline correction for the aliphatic C-H stretching bands region
393 using a polynomial ($a_0 + a_1x + a_2x^2 + a_3x^3$) fit to the Murchison IR spectrum. (b) Aliphatic C-H
394 stretching bands region for the bulk chondrites after the baseline corrections.

395
396 Fig. 4. Aliphatic CH_3 (2960 cm^{-1}) and CH_2 (2930 cm^{-1}) peak intensities divided by the thicknesses of
397 the KBr pellets and the bulk meteorite concentrations (wt.%). Error bars are based on the
398 uncertainties in KBr pellet thicknesses.

399
400 Fig. 5. Relative aliphatic CH fractions in the carbon in the bulk samples. (A) The total aliphatic CH_x
401 intensities ($F_{\text{CH}_3} + F_{\text{CH}_2}$) divided by C contents (C_{bulk}) in the bulk meteorites (Alexander et al. 2012).
402 The error bars are based on the uncertainties in the KBr pellet thicknesses. (B) Aliphatic/aromatic
403 peak intensity ratios for IOM in these chondrites obtained from their IR spectra (Kebukawa et al.
404 2011).

405
406 Fig. 6. Relative aliphatic fractions in the bulk C (Missing C + IOM) and in the IOM. Each slope of
407 the line between a data point and (0, 0) indicates the relative aliphatic fraction of bulk C/IOM. It
408 should be noted that “Ali. CH in bulk C” is aliphatic CH_x intensity normalized by bulk C and “Ali.
409 CH in IOM” is aliphatic/aromatic peak intensity ratios $[(I_{\text{CH}_3} + I_{\text{CH}_2})/I_{\text{AroCC}}]$. Thus, one cannot
410 compare the absolute aliphatic fractions between missing carbon and IOM, but rather this diagram
411 indicates the relative aliphatic fractions in missing C among the chondrites.

412
413 Fig. 7. Relative aliphatic CH_2/CH_3 ratios in the bulk C (Missing C + IOM) and IOM. The slopes
414 indicate the relative aliphatic CH_2/CH_3 ratios of the bulk C and in IOM.

415

416

Table 1. Meteorite samples used in this study and their IR characteristics.

		C_{bulk}	C_{IOM}	C_{SOM}	C_{carb}	Missing	KBr pellet thickness, d / cm			Concentration of						
		(wt.%) ¹	(wt.%) ²	(wt.%) ³	(wt.%) ⁴	C ⁵				meteorite	F_{CH_2} ⁶		F_{CH_3} ⁶			
												powder, w				
												(wt.%)				
Ivuna	CI1	3.50	2.25	0.07	0.33	0.24	0.063	±	0.002	1.85	0.100	±	0.004	0.080	±	0.003
Bells	CM2	1.74	0.96		0.11	0.39	0.067	±	0.003	2.29	0.035	±	0.002	0.024	±	0.001
Murchison	CM2	2.08	1.06	0.09	0.09	0.40	0.053	±	0.013	1.81	0.116	±	0.030	0.109	±	0.028
GRO 95577	CR1	1.18	0.78		0.16	0.20	0.063	±	0.004	1.99	0.039	±	0.002	0.035	±	0.002
EET 92042	CR2	1.18	0.46		0.09	0.53	0.058	±	0.002	2.02	0.056	±	0.002	0.050	±	0.002
Kaba	CV3.1	1.13	0.68		0.01	0.39	0.050	±	0.008	1.88	0.050	±	0.008	0.033	±	0.005
Semarkona	LL3.00	0.59	0.36		0.02	0.36	0.040	±	0.008	2.03	0.031	±	0.006	0.024	±	0.005

		Ali CH _x in bulk C ⁷			CH ₂ /CH ₃ in bulk C ⁸		Ali CH _x in IOM ⁹			CH ₂ /CH ₃ in IOM ⁹			
Ivuna	CI1	0.051	±	0.001	1.26	±	0.07	1.77	±	0.18	1.22	±	0.12
Bells	CM2	0.034	±	0.001	1.44	±	0.10	0.85	±	0.08	1.13	±	0.11
Murchison	CM2	0.109	±	0.020	1.07	±	0.39	1.60	±	0.16	1.41	±	0.14
GRO 95577	CR1	0.063	±	0.002	1.10	±	0.08	1.32	±	0.13	1.42	±	0.14
EET 92042	CR2	0.090	±	0.002	1.10	±	0.06	0.86	±	0.09	1.16	±	0.12
Kaba	CV3.0/3.1	0.074	±	0.008	1.52	±	0.33	0.41	±	0.04	1.58	±	0.16
Semarkona	LL3.00	0.093	±	0.013	1.26	±	0.36	0.40	±	0.04	1.72	±	0.17

GRO: Grosvenor Mountains, and EET: Elephant Moraine

1: Alexander et al. (2012)

2: Alexander et al. (2007), the uncertainty is 10-15%.

3: Smith & Kaplan (1970), Becker & Epstein (1982)

4: Alexander et al. (2015), the uncertainty is 2-5%.

5: $1-(\text{IOM}+\text{SOM}+\text{Carb})/\text{BulkC}$

6: Peak height of CHx/*Cd*

7: $(F_{\text{CH}_2}+F_{\text{CH}_3})/C_{\text{bulk}}$

8: $F_{\text{CH}_2}/F_{\text{CH}_3}$

9: Recalculated from Kebukawa et al. (2011)

(A) Ali CH_x in bulk C (B) Ali CH_x in IOM