



## Mid-infrared study of the molecular structure variability of insoluble organic matter from primitive chondrites

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### ABSTRACT

Insoluble Organic Matter (IOM) found in primitive meteorites was formed in the Early Solar System and subsequently processed on the parent asteroids. The location, temporal sequence and processes of formation of this IOM are still a matter of debate. In particular, there is no consensus on the actual effect of post-accretionary aqueous alteration processes on the chemical composition and structure of IOM. In the most primitive chondrites (types 1 and 2), these alterations have so far been either neglected or generically assigned to oxidation processes induced by fluid circulation.

A series of IOM samples extracted from 14 chondrites with extensively documented post-accretionary histories have been studied by infrared spectroscopy. Aqueous alteration shows no detectable effect on the chemical composition and structure of IOM within or across chondrite classes. Indeed, the most effective post-accretionary process appears to be a high-temperature short-duration heating event and concerns essentially type 2 chondrites. In any case, post-accretionary processes cannot account for all the chemical and structural variations of IOM. Chondrites from the CI, CR and CM classes accreted IOM precursors with moderately variable compositions, suggesting a chemical heterogeneity of the protosolar disk. The 3.4  $\mu\text{m}$  band, and possibly its overtones and combinations in the near-infrared range, appear to be tracer(s) of the chemical class and possibly of surface heating processes triggered by impacts.

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### 1. Introduction

Among carbonaceous meteorites, those from the CI, CR and CM groups exhibit the highest content of a primitive organic matter (up to 4 wt%), mainly in the form of an insoluble macromolecular solid (Alexander et al., 2007; Robert and Epstein, 1982). This insoluble organic matter was inherited from the protosolar disk and is characterized by a polysubstituted aromatic structure in which a large diversity of functional groups coexist. Both  $\text{sp}^3$  and  $\text{sp}^2$  carbons are present together with heteroatoms such as O, N and S (Alexander et al., 2007; Cronin et al., 1987; Derenne and Robert, 2010).

Several competing hypotheses have been proposed concerning the location and chemical processes of the synthesis of the IOM. In the 1970s, Fischer–Tropsch Type (FTT) reactions in the solar nebula were proposed, but this type of process could not account for the polyaromatic nature of IOM nor its isotopic composition (Alexander et al., 1998; Hayatsu and Anders, 1981). In the 1980s,

high measured D/H ratios suggested formation in the interstellar medium through low temperature chemistry in a gas phase (Robert and Epstein, 1982). This formation mechanism was later supported by a good spectral match between mid-infrared signatures of carbon to hydrogen bonds (the so-called 3.4  $\mu\text{m}$  band) observed in Diffuse Interstellar Medium (DISM) and those measured in the laboratory for IOM from the CI1 chondrite Orgueil (Ehrenfreund et al., 1991) and Murchison (Sandford et al., 1995) chondrites.

Mid-infrared observations of the ISM have since shown differences with IOM spectra, and the 3.4  $\mu\text{m}$  band in diffuse ISM has been re-assigned to amorphous hydrogenated carbons. The spectral features expected for the IOM candidate have never been detected in dense molecular clouds (Dartois et al., 2004, 2007). This ruled out the hypothesis of single-step formation of IOM in the ISM followed by direct incorporation in solar nebula bodies and led to investigation of more complex scenarios. For instance, the observation of a correlation between the D/H ratio and the binding energy of the C–H bond has been interpreted as evidence of IOM formation in warm regions of the protosolar disk, followed by a deuteration process in the upper disk layer (Gourier et al., 2008; Remusat et al., 2006, 2009, 2010). Alternatively, Cody et al. (2011) have proposed formation on the parent asteroid through

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polymerization of an interstellar precursor (mostly H<sub>2</sub>CO) triggered by fluid circulation and followed by multiple dehydrations (Cody et al., 2011).

Most primitive meteorites bear mineralogical evidence of post-accretional processes that occurred on the parent asteroid. Identification of asteroidal organic reactions is a first step towards understanding how IOM chemical variability observed among chondrite groups relates to parent body processes. There is to date no clear consensus on the interpretation of these variations. While the effect of thermal metamorphism has been clearly demonstrated (Bonal et al., 2006, 2007; Busemann et al., 2007; Quirico et al., 2011; Yabuta et al., 2010), the role of aqueous alteration on the post-accretional evolution of IOM remains unclear. Aqueous alteration has been proposed as the dominant factor responsible for modifying the sp<sup>2</sup>/sp<sup>3</sup> ratio and the abundance of oxygenated functional groups in chondrites of petrologic types 1 and 2 (Cody and Alexander, 2005; Herd et al., 2011). The proposed molecular mechanism describes an oxidation process that accelerates with the extent and intensity of fluid circulation. Such a chemolytic mechanism has also been invoked to support the hypothesis of an asteroidal origin for the soluble molecules (Callahan et al., 2011). Nevertheless, the deduction that aqueous alteration produced the final structure of the IOM relies on the assumption that the initial precursors were homogeneous and common to every parent body before any hydrothermal episode. This common precursor assumption is important, since it implies that the overall diversity observed in meteorite IOM has to be related to parent body processes.

Here, in order to understand the balance between nebular and asteroidal processes on the origin and evolution of IOM, we have studied a series of IOM samples extracted from meteorites for which the parent body history is well known. We report the chemical composition of IOMs extracted from 14 chondrites: 3 CRs, 3 CIs, 6 CMs, Semarkona (LL/3.0) and C2 ungrouped Tagish Lake. This series of chondrites spans a large extent of aqueous alteration and also makes it possible to investigate the effect of parent body thermal processing. A lossless extraction procedure provided access to IOMs of chondrites available in minute amounts (Orthous-Daunay et al., 2010b). Among all techniques available, we employed infrared micro-spectroscopy because of its extended structural investigation capability and the small quantity of raw chondritic material required. In addition to providing the crosslinking level through the CH<sub>2</sub> and CH<sub>3</sub> relative quantities, this technique can be used to determine the alkyl and carbonyl abundances.

## 2. Materials and methods

### 2.1. Sample set

We selected 14 meteorites from several institutes that underwent post-accretional processes of different types and extents (see Table 1). Three CI1s (Ivuna, Orgueil and Alais) were chosen as chondrites that experienced the most intense aqueous alteration episodes, with the internal hierarchy of aqueous alteration intensity increasing from Alais to Orgueil (Endress and Bischoff, 1996; Morlok et al., 2006). The CM class spans a large range of different aqueous alteration degrees extensively described by Rubin et al. (2007). This class is the key to checking the aqueous alteration dependent hypothesis thanks to the accurately measured mineralogical and petrological marks of progressive alteration from type 2.0 to 2.5. Cold Bokkeveld (CM2) is thought to be a breccia combining different lithologies from different types and classes (Rubin et al., 2007). The CR class is the most petrologically pristine and is represented by three chondrites: Renazzo, QUE99177 and EET92042 (Weisberg et al., 1993). The ungrouped C2 Tagish Lake

**Table 1**

Name and origins of whole rock samples. MNHN stands for Muséum National d'Histoire Naturelle (Paris, France) and MWG-JSC stands for Meteorite Working Group at Johnson Space Center (Houston, USA).

| Name           | Type         | Provider |
|----------------|--------------|----------|
| Orgueil        | CI1          | MNHN     |
| Alais          | CI1          | MNHN     |
| Ivuna          | CI1          | MNHN     |
| Murray         | CM2          | MNHN     |
| PCA91008       | CM2          | MWG-JSC  |
| Cold Bokkeveld | CM2          | MNHN     |
| Murchison      | CM2          | MNHN     |
| Nogoya         | CM2          | MWG-JSC  |
| QUE93005       | CM2          | MWG-JSC  |
| Semarkona      | Ordinary LL3 | MWG-JSC  |
| Tagish Lake    | Ungrouped C2 | Private  |
| Renazzo        | CR2          | MNHN     |
| QUE99177       | CR2          | MWG-JSC  |
| EET92042       | CR2          | MWG-JSC  |

chondrite has distinct chemical and petrological characteristics (Herd et al., 2011). Its organic matter has been independently investigated in IR studies and found to be different than that of many type 1 and 2 chondrites (Kebukawa et al., 2011; Matrajt et al., 2004). PCA91008 is a heated CM2 (Alexander et al., 2007; Yabuta et al., 2010) that experienced a quick and intense heating event (Wang and Lipschutz, 1998). This type of thermal metamorphism is different from the common radiogenic heat induced metamorphism that can be found in type 3 to 6 ordinary chondrites. As a comparison sample, we included the ordinary chondrite Semarkona (LL/3.0) which is used as the metamorphism onset of radiogenic heated meteorites and which did not undergo extreme aqueous alteration (Alexander et al., 1989; Quirico et al., 2003).

### 2.2. IOM extraction

Every IOM was extracted by demineralization with HF/HCl acid attacks (Amari et al., 1994; Gardinier et al., 2000) to remove sulfates, carbonates, silicates and neo-formed fluorides. The chemical protocol was adapted for use in a continuous flux method described by Orthous-Daunay et al. (2010a). This method makes it possible to work with lesser than 0.1 mg of each chondrite for most of the sample set. The demineralization process takes less than 36 h. For this study, no IOM was measured more than 48 h after its extraction and the whole sample set was investigated in two 3-week campaigns. In this way, we limited storage contamination and oxidation (Kebukawa et al., 2009) as well as external reproducibility issues. Our procedure includes extensive steps of continuous washing before and after the acid attacks. We expect that no mobile molecule, from the sample and from possible contamination, can be found in a noticeable amount compared to the extraterrestrial IOM. Long term insoluble contamination cannot be ruled out but we consider reasonable to assume it would pollute every sample in a comparable way and thus not invalidate the differences measured, if any.

### 2.3. Sample preparation

Fragments of IOM were crushed between two diamond windows (3.5 mm by 0.5 mm). This produced thin patches of IOM with parallel edges. Their thickness was estimated to be around 1 μm. This procedure reduced volume heterogeneity and scattering artifacts. The typical probed surface was 50 μm by 50 μm. One window was removed to avoid interference during measurements in transmission mode. The FTIR instrument was a Bruker Hyperion3000 equipped with a globar black body source (400 °C). The

beam was modulated in a Michelson interferometer and intensity collected by a liquid N<sub>2</sub> cooled MCT detector. The spectral range was 4000–700 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup>. No sample required more than 200 scans (5 min) to get a satisfying signal-to-noise ratio.

All measurements were performed using an environmental cell (Beck et al., 2010). The cell consisted of a heated vacuum chamber with an optical path through two ZnS windows (2 times 2.5 mm) that cause a 10% loss in intensity. The loaded diamond window was put in a 10<sup>-7</sup> mbar vacuum and heated at 50 °C to desorb water and remaining solvents. The mounting and environment conditioning took less than 3 h. Blanks from a spot next to the sample patch were analyzed to monitor window cleanliness and reference backgrounds were acquired immediately before each IOM measurements.

#### 2.4. Data reduction

Infrared scattering and electronic absorption generated a spectral continuum (Fig. 1) corrected by subtraction of the following empirical sum of sinusoids and polynomials commonly used in

IR studies (Bassan et al., 2009; Kohler et al., 2008; Mohlenhoff et al., 2005; Romeo et al., 2006) (Fig. 2).  $K_{0-6}$  are free parameters and  $\bar{\nu}_{max}$  and  $\bar{\nu}_{min}$  limit the spectral range for polynomial validity.

$$B(\bar{\nu}) = K_0 - 4 \underbrace{\left( \frac{\sin(K_1 \bar{\nu})}{K_1 \bar{\nu}} + \frac{1 - \cos(K_1 \bar{\nu})}{(K_1 \bar{\nu})^2} \right)}_{\text{Light scattering approximation}} + \underbrace{\sum_{j=2}^6 K_j \times \cos \left( j \times \cos^{-1} \left( \frac{2\bar{\nu} - (\bar{\nu}_{max} + \bar{\nu}_{min})}{\bar{\nu}_{max} - \bar{\nu}_{min}} \right) \right)}_{\text{Complementary polynomials}}$$

This critical baseline correction step was facilitated by the intrinsic quality of our data and the use of fitted Tchebychev polynomials instead of cubic splines.

Each absorption feature identified in the spectra was fitted by Gaussian band models to extract the integrated absorption  $A$  and spectral position before normalization to tabulated integrated cross-sections  $A$  allowing relative quantification (Figs. 3 and 4 and Table 2). Thus the optical depth  $\tau(\bar{\nu})$ , and integrated cross-section  $A$  are defined as:

$$\tau(\bar{\nu}) = -\ln \left( \frac{I}{I_0} \right) = \sigma \ell N = \sigma \times \frac{n}{S}$$

$$A = \int \sigma d\bar{\nu} = \int \frac{\tau(\bar{\nu}) \times S}{n} d\bar{\nu} \equiv \text{cm/group}$$

where  $n$  is the number of molecular oscillators,  $\sigma$  the absorption cross-section (m<sup>2</sup>),  $\ell$  the probed optical length (m),  $N$  the oscillator density (cm<sup>-3</sup>) and  $S$  the probed cross-section (cm<sup>2</sup>).

The integrated absorbance can therefore be expressed as:

$$A = \frac{1}{\ln(10)} \int \tau(\bar{\nu}) d\bar{\nu} \equiv \text{cm}^{-1}$$

and the relative quantities as:

$$\frac{n_\chi}{S} = \ln(10) \times \frac{A_\chi}{A_\chi}$$

where  $n_\chi$ ,  $A_\chi$  and  $A_\chi$  are respectively the number, integrated cross-section and integrated absorbance of an oscillator named  $\chi$ . For each sample, the probed area was constant so that  $S$  is a parameter. The expression of ratios like  $\frac{n_{co} + n_{cc}}{n_c} = 0.7$  did not depend on the  $S$  parameter and was therefore used as the main comparison tool from one sample to another.

Values for  $A_\chi$  were selected from Dartois et al. (2007) and Risten et al. (1998) for the  $\chi$  of interest. The tertiary CH mode is probably overlapped by a Fermi resonance of CH<sub>2</sub> modes (Dartois et al., 2004) and relative quantities of this peculiar group are presented here as upper limit values. The integrated cross-section of the C=C mode varies greatly from one standard to another with respect to the direct chemical neighborhood of the sp<sup>2</sup> bond. Measured and calculated values for several PAHs (Hudgins and Sandford, 1998) are too low to be compatible with common H/C ratios of the IOM and laboratory analogues (Dartois et al., 2007).

Given the lack of appropriate integrated absorbances for C=C and C=O, an external calibration suitable for the IOM material was required.  $A_{C=C}$  and  $A_{C=O}$  were scaled to the other with respect to the following chemical parameter of the Murchison IOM in the NMR study (Cody et al., 2011). Assumptions were that, for Murchison, the carbonyl group is six times less abundant than the aromatic carbons:  $\frac{n_{co}}{n_c} = \frac{1}{6} \approx 0.166$  and that the aromatic carbon represents 70% of the NMR probed carbon:  $\frac{n_{co} + n_{cc}}{n_c} = 0.7$ . Therefore we obtain:

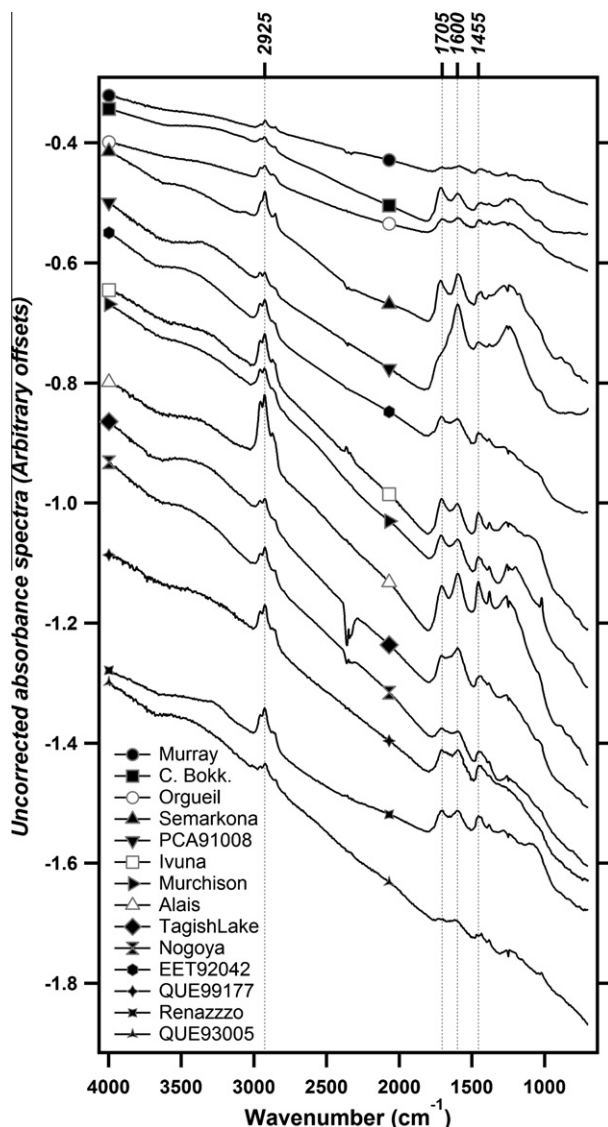


Fig. 1. Raw IR absorbance spectra used in this study. An arbitrary offset is applied for the sake of clarity.

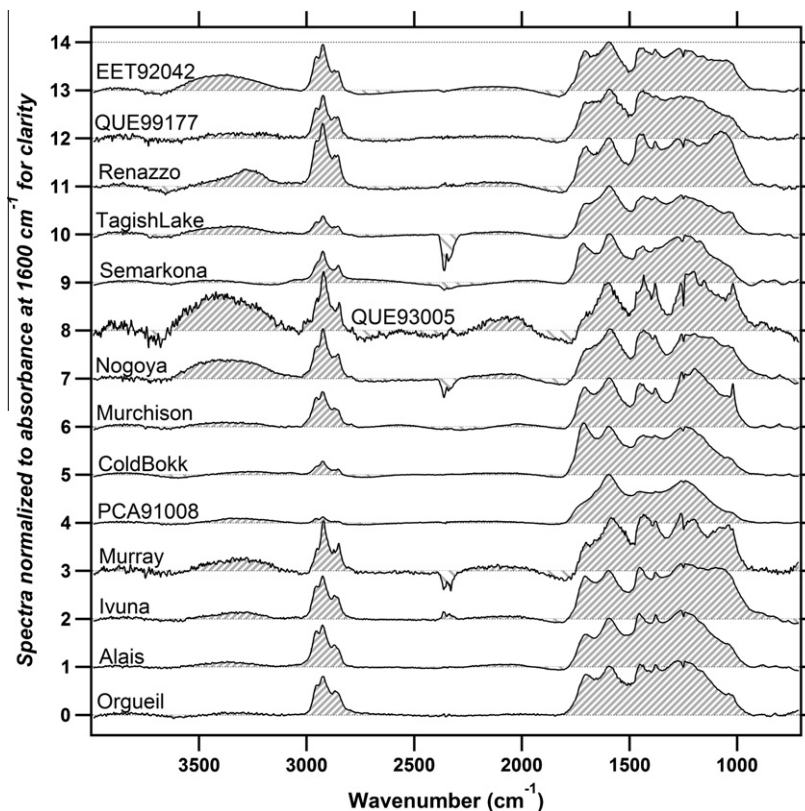


Fig. 2. Corrected and normalized absorbance spectra used for this study prior to Gaussian fitting.

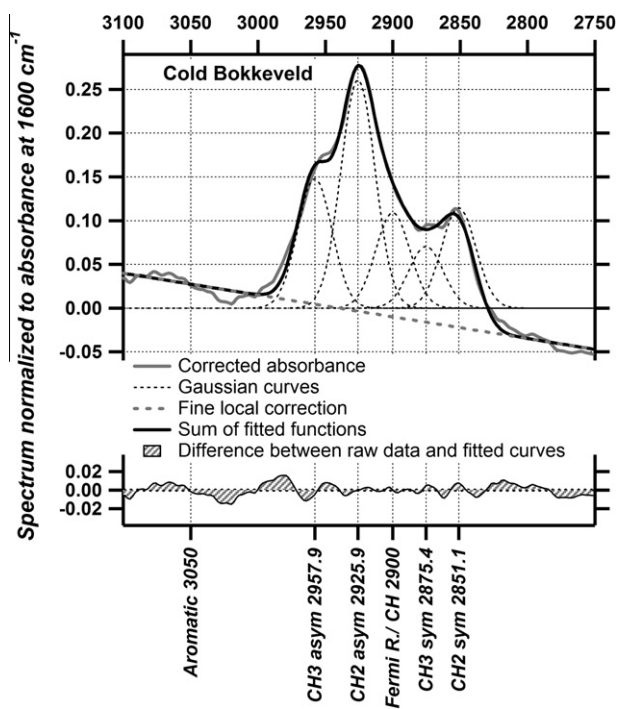


Fig. 3. Illustration of the fitting procedure to extract CH<sub>3</sub> and CH<sub>2</sub> integrated absorbance.

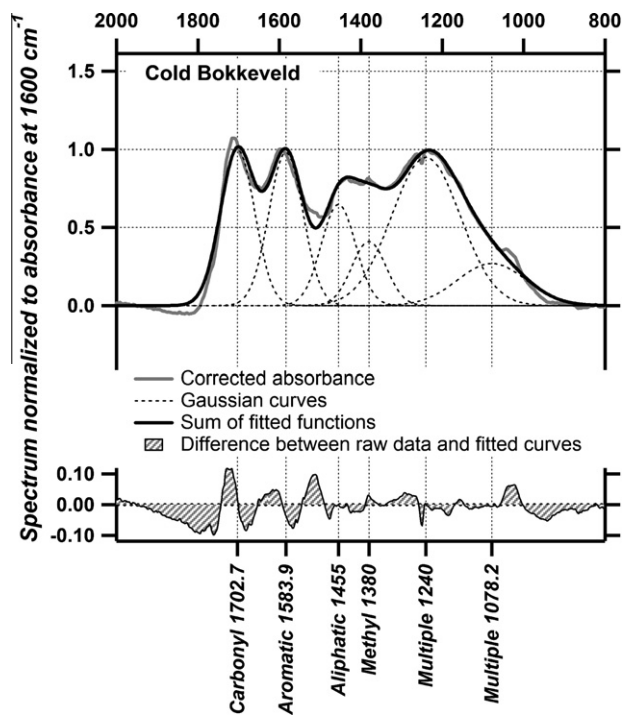


Fig. 4. Illustration of the fitting procedure to extract C=O and C=C integrated absorbance.

**Table 2**

Bandlist with absorption cross-sections in cm<sup>2</sup>/group (*A*) and typical values for the quantified absorption feature. The full width at half maximum (FWHM) of the Gaussian curves used to model the absorption bands is set to values consistent with previous studies and are the same for each functional group to allow estimation of the uncertainties due to varying spectra quality.

| Mode                 | Wavenumber (cm <sup>-1</sup> ) | FWHM (cm <sup>-1</sup> ) | <i>A</i> value (cm <sup>2</sup> /group) |
|----------------------|--------------------------------|--------------------------|---|
| CH <sub>3</sub> asym | 2960                           | 18                       | (1 ± 0.3) × 10 <sup>-17</sup>           |
| CH <sub>2</sub> asym | 2925                           | 18                       | (8 ± 0.6) × 10 <sup>-18</sup>           |
| C=O                  | 1690                           | 50                       | Calib. NMR 6 × 10 <sup>-17</sup>        |
| C=C                  | 1585                           | 60                       | Calib. NMR 1 × 10 <sup>-17</sup>        |

$$\begin{aligned} \left(\frac{n_{CO} + n_{CC}}{n_C}\right)^{Murchison} &= 0.7 = \frac{1.166 \times \ln 10 \times \frac{(A_{CC})^{Murchison}}{A_{CC}}}{(n_{CC} + n_{CO} + n_{CH_3} + n_{CH_2})^{Murchison}} \\ &= \frac{1.166 \times \ln 10 \times \frac{(A_{CC})^{Murchison}}{A_{CC}}}{(1.166 \times \ln 10 \times \frac{(A_{CH_3})^{Murchison}}{A_{CC}}) + (n_{CH_3} + n_{CH_2})^{Murchison}} \\ &\Leftrightarrow \frac{(A_{CC})^{Murchison}}{A_{CC}} = \frac{0.7 \times (n_{CH_3} + n_{CH_2})^{Murchison}}{0.3 \times \ln 10 \times 1.166} \\ &\Leftrightarrow A_{CC} = \frac{0.3 \times \ln 10 \times 1.166}{0.7 \times (n_{CH_3} + n_{CH_2})^{Murchison}} \times (A_{CC})^{Murchison} \end{aligned}$$

Since only  $\frac{n_C}{S}$  can be determined and the actual probed cross-section *S* might vary slightly from one preparation to another, inter-meteorite comparison is achieved by considering ratios between different  $n_C$ . The ternary diagram provides a convenient way to compare the relative abundance between more than two groups (Dartois et al., 2007).

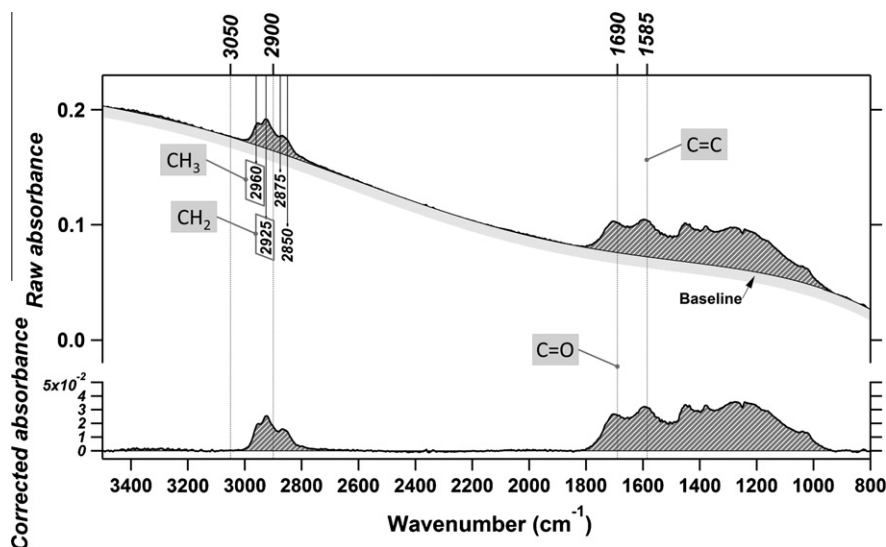
### 3. Results

#### 3.1. Variations of the abundance of functional groups in IOM

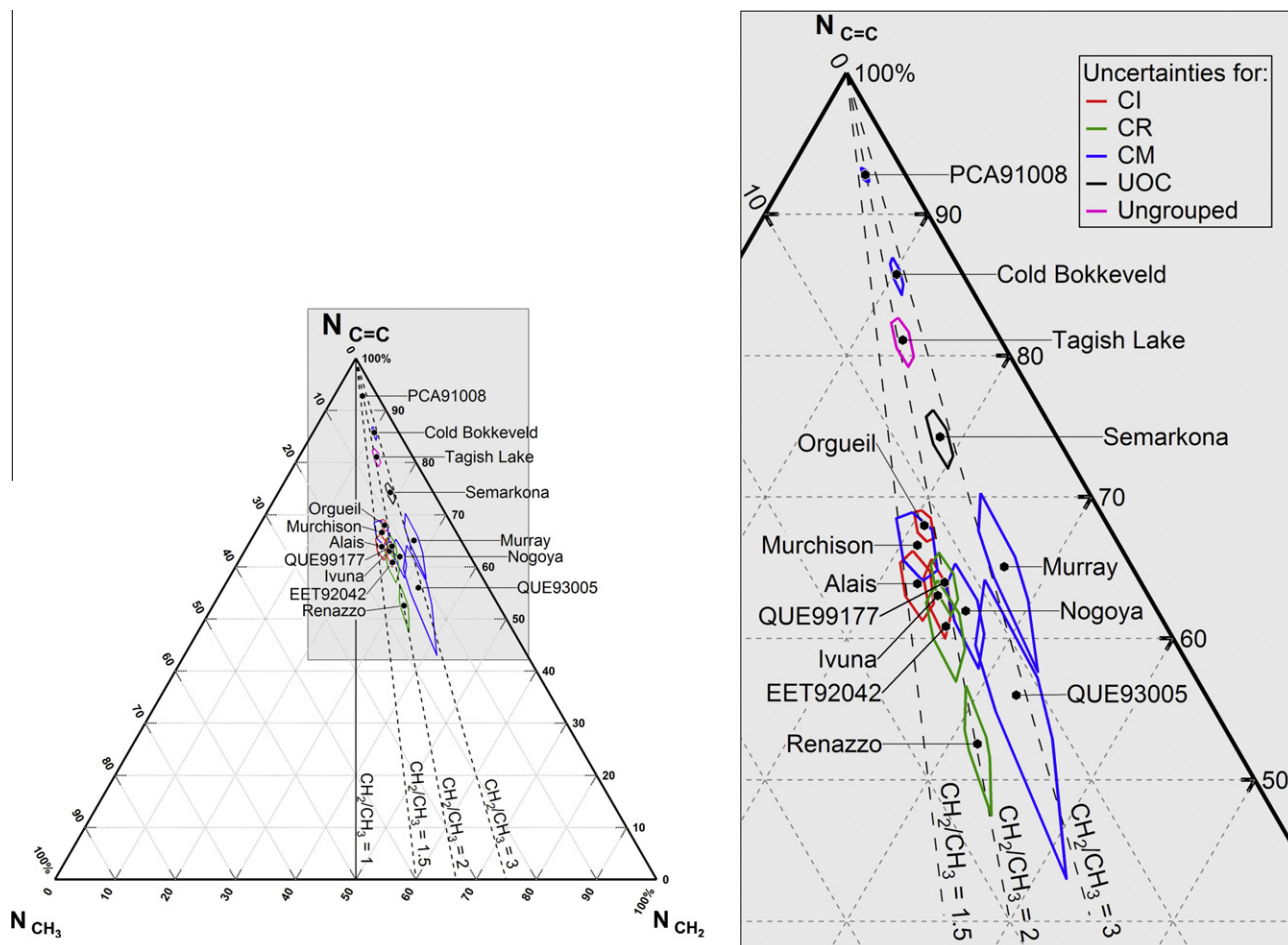
Given the molecular weight and complexity of IOM, the variations of its chemical composition from one chondrite to another are more easily quantified by the relative abundance of smaller functional groups than a molecular graph *stricto sensu*. Infrared spectroscopy provides a direct link with astronomical observations (Sandford et al., 1995). The 4000–800 cm<sup>-1</sup> spectral range is optimal to probe vibrational absorption due to the alkyl (CH<sub>2</sub> and CH<sub>3</sub>), carbonyl (C=O) and aromatic (C=C) functional groups (Fig. 5) (Ehrenfreund et al., 1991; Kebukawa et al., 2010; Painter

et al., 1981; Wdowiak et al., 1988). The two major sp<sup>2</sup> carbon absorption features are those of the carbon to carbon bond stretching mode found in aromatic rings (C=C, around 1590 cm<sup>-1</sup>) and those of carbon to oxygen bonds (C=O). The average position of the C=O band throughout the dataset lies around 1700 cm<sup>-1</sup>, consistent with a contribution dominated by carbonyls in moderately conjugated ketone functional groups. Protonated aromatics (sp<sup>2</sup> C–H, stretching around 3050 cm<sup>-1</sup> and out-of-plane bending around 800 cm<sup>-1</sup>) are almost undetectable in our spectra, which is consistent with high cross-linking and substitution of aromatics rings (Cody et al., 2002; Gardinier et al., 2000). The low intensity of the hydroxyl groups (O–H, stretching around 3600 cm<sup>-1</sup>) suggests that carboxylic acid is a minor species in our IOM. This result contrasts with earlier infrared studies which were not performed in a controlled atmosphere and thus biased by the contribution of atmospheric water (Gardinier et al., 2000; Kebukawa et al., 2011). Hydrogenated sp<sup>3</sup> carbon (C–H<sub>n</sub>) is identified in all IOM from the anti-symmetric and symmetric stretching modes of methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>) functional groups. The contribution of possible tertiary CH is much less constrained due to the possible presence of a Fermi resonance and contributions from combinations and overtones of the bending mode region (Dartois et al., 2005).

The relative abundances of the different chemical groups depict a large chemical heterogeneity across the chondrites and three groups termed I, II, III can be distinguished (Figs. 6 and 7). Group I contains the three CIs, the CM Murchison and the three CRs. The IOM from these chondrites has high alkyl abundance and a low CH<sub>2</sub>/CH<sub>3</sub> ratio (i.e. N<sub>CH<sub>2</sub></sub>/N<sub>CH<sub>3</sub></sub>). The three CRs have a slightly higher CH<sub>2</sub>/CH<sub>3</sub> ratio than the others and Renazzo has the highest alkyl abundance among all. Group II contains 4 individual objects (PCA 91008; Semarkona; Tagish Lake and Cold Bokkeveld) that have low alkyl abundance. Group III contains the CM chondrites (Murray, Nogoya and QUE93005). They have a high alkyl content but a higher CH<sub>2</sub>/CH<sub>3</sub> ratio than objects from Group I. Across the three groups, the CM chondrites are very heterogeneous. Murchison plots close to the CI group, but Nogoya, Murray and QUE93005 plot apart, with a higher N<sub>CH<sub>2</sub></sub>/N<sub>CH<sub>3</sub></sub>. QUE93005 may have the highest aliphatic abundance. As reported above, Cold Bokkeveld is very different from other CMs with a lower aliphatic abundance. The C=O/C=C content is lowest for PCA91008 and QUE93005, and highest for Cold Bokkeveld.



**Fig. 5.** Uncorrected (top) and baseline stripped (bottom) infrared spectra. Reported wavenumbers are those of the modes used in the fitting procedure. Highlighted attributions (CH<sub>3</sub> and CH<sub>2</sub> anti-symmetric modes and C=O and C=C stretching modes) are those used for quantitative study.



**Fig. 6.** Ternary diagram representing the relative abundance of carbon atoms engaged in  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{C}=\text{C}$  groups. The shaded area highlights the range of variability observed among the sample set. In addition, three oblique dashed lines mark theoretical compounds with three different  $\text{CH}_2/\text{CH}_3$  ratios and  $\text{C}=\text{C}$  content varying from 100% (top corner) to 40% (bottom of the shaded area).

The lower aliphatic content of Tagish Lake and Semarkona with regard to Murchison is in qualitative agreement with previously reported IR studies from Matrajt et al. (2004) and Keller et al. (2004). The alkyl abundance of Tagish Lake, Orgueil, and EET 92042 relative to Murchison are in a remarkable agreement with the NMR measurements of Cody and Alexander (2005). The  $\text{CH}_2/\text{CH}_3$  ratio is plotted against the H/C ratio in Fig. 8, revealing the 3 groups described above. The alkyl abundance correlates with the H/C ratio (Fig. 8), demonstrating that H/C is controlled mainly by the alkyl abundance. However, the correlation is degraded for objects from group II, indicating that other chemical groups might also influence this ratio.

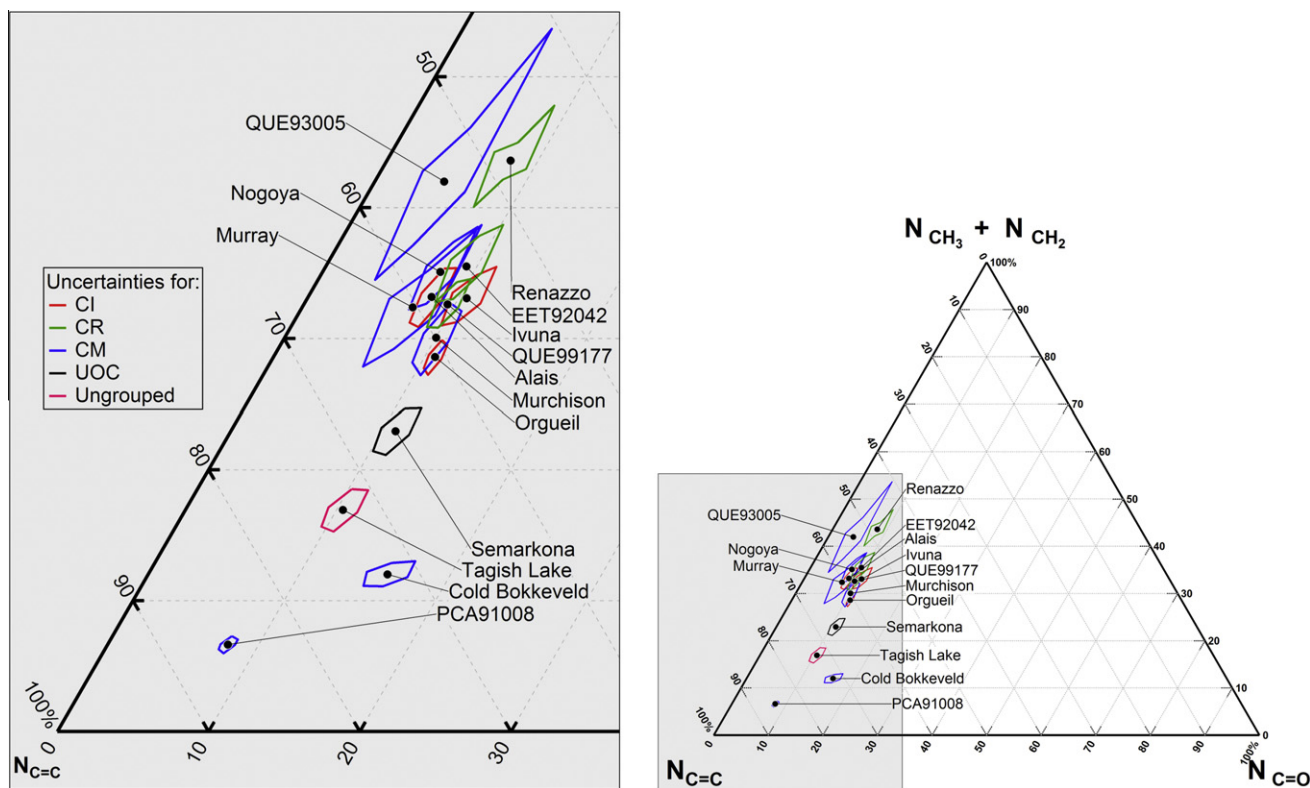
#### 4. Discussion

##### 4.1. The absence of aqueous alteration effects on the IOM

The chemical variations we observe possibly took place in the IOM precursors accreted on the parent asteroids and/or were the result of the action of post-accretion processes. Group I (Fig. 6) contains chondrites with low  $\text{CH}_2/\text{CH}_3$  ratios, implying abundant and highly crosslinked alkyls. The three CI chondrites (Orgueil, Ivuna and Alais) belong to this group and have experienced the most intense aqueous alteration among all chondrites (petrologic type 1). Their mineralogical composition consists mostly (~99 wt%) of hydrated silicates (serpentine and saponite), oxides and oxyhydroxides (magnetite, ferrihydrite), carbonates and sulfates (Morlok

et al., 2006). The CM chondrite Murchison is a member of group I and is one of the least aqueously altered meteorites from the CM class (petrologic type 2.5). Its matrix mineralogy points to a much lower degree of processing than in CIs. CR class chondrites are described as bearing the least processed components and all belong to group I. A detailed study of petrological and mineralogical characteristics reveals the following scale of increasing aqueous alteration intensity: QUE 99177 < EET92042 < Renazzo.

In our results, alkyl abundance does not correlate with the extent of aqueous alteration. Tracks of progressive combustion (conversion to  $\text{CO}_2$ ), organics and condensation by dehydration that have been reported in the literature (Cody and Alexander, 2005; Cody et al., 2011) are not correlated with petrological classification. The alkyl abundance of the IOM of the CIs is close to that of Murchison as well as to that of the very primitive CR QUE99177 (Fig. 7). Within the CR subset, the most aqueously altered CR (Renazzo) has the highest alkyl abundance. Subtle differences in IOM sulfur speciation were recently detected between chondrite groups (Orthous-Daunay et al., 2010b). Sulfur speciation can be a sensitive tracer of maturation conditions (Kelemen et al., 2007; Sarret et al., 1999). Oxidized organic sulfur has been detected in the three CIs mentioned above but not in CMs, Renazzo or Tagish Lake. As the composition of the IOM of chondrites from the CI class and of Murchison are fairly similar (Cody and Alexander, 2005; Gardinier et al., 2000), in agreement with our systematic IR observations, fluid circulation must have had a limited impact on the structural modification of the IOM.



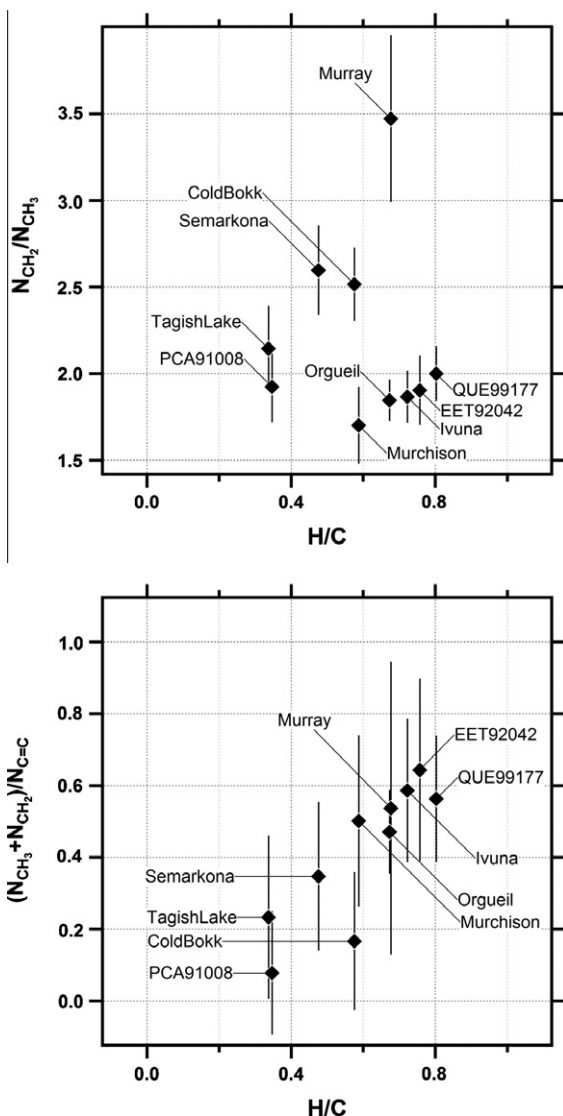
**Fig. 7.** Ternary diagram showing the relative abundance of C=C and C=O and the sum of CH<sub>2</sub> and CH<sub>3</sub> groups. The shaded area highlights the variability of the sample set. The main variation concerns the C=C/(CH<sub>2</sub> + CH<sub>3</sub>) ratio that ranges from ~90% to ~50% whereas the C=O/C=C ratio lies between ~20% and ~5%.

#### 4.2. The importance of thermal processes on the parent body

Group II contains chondrites with IOM that has a lower H/C than group I and a low alkyl content. The composition of the IOM from PCA 91008 can be accounted for by thermal processing on the parent body. PCA 91008 is classified as a metamorphosed CM chondrite and therefore has experienced a high-temperature and short-duration thermal event, demonstrated by a dehydrated matrix and peculiar mineralogical features (Wang and Lipschutz, 1998; Yabuta et al., 2010). Semarkona (LL/3.0) has been defined as the onset of thermal metamorphism in the standard petrologic classification of chondrites. There is however clear evidence that this chondrite experienced a mild thermal metamorphism of radiogenic origin, as shown by the composition and structure of IOM (Bonal et al., 2006; Quirico et al., 2003), the Cr composition of olivine phenocrysts in oxidized chondrules (Grossman and Brearley, 2005) and the abundance of the P3 noble gas component trapped in nanodiamonds (Huss and Lewis, 1994). The low alkyl abundance or the high CH<sub>2</sub>/CH<sub>3</sub> ratios of the IOM of these two chondrites are most likely the result of parent body thermal processing. The high and low C=O abundance in Semarkona and PCA 91008, respectively, suggests a thermal event of greater magnitude for PCA 91008, since similar depletion amounts are observed in metamorphosed type 3 chondrites (Kebukawa et al., 2011). However, the different nature of the thermal events – short versus long duration – leads to a kinetic control that renders comparison difficult (Yabuta et al., 2010). Our data support a different organic evolution for the two kinds of thermal metamorphism: a long-duration low-temperature event (~250 °C; Alexander et al., 1989) that preferentially expels CH<sub>3</sub> groups in Semarkona and a short-duration high-temperature event that expels equally CH<sub>2</sub> and CH<sub>3</sub> groups in PCA 91008. Continuing with group II, Tagish Lake is an ungrouped C2 chondrite, described as a complex breccia with different lithol-

ogies and a low porosity (Nakamura et al., 2003). Chemical variations of IOM for different lithologies have been reported recently and interpreted as the effect of varying degrees of aqueous alteration (Herd et al., 2011). Indeed, the polyaromatic content of Tagish Lake IOM is clearly dissimilar to that of CI or CM chondrites and evidence of structural variations has also been found at a micro-metric spatial scale (Matrajt et al., 2004; Quirico et al., 2011). These structural properties, also reported in the heated CM PCA 91008, as well as the nitrogen speciation (Herd et al., 2011), are consistent with a short-duration thermal event. The alkyl and C=O abundances of Tagish Lake IOM appear to be larger than for PCA 91008 (Fig. 7), suggesting that the intensity of the thermal event for the Tagish Lake IOM must have been lower than for the PCA 91008 IOM. Finally, Cold Bokkeveld is certainly the most intriguing chondrite of group II. Its low alkyl abundance and high CH<sub>2</sub>/CH<sub>3</sub> ratio suggests a thermally processed chondrite, in apparent contradiction with its petrologic assignment as an unmetamorphosed 2.1 CM chondrite (Rubin et al., 2007). Indeed, this CM chondrite is an anomaly in the CM class: the mineralogical composition of its matrix is dominated by Mg-rich serpentines (Howard et al., 2009), it contains abundant sulfates and its IOM contains abundant aromatic sulfur while those of other CMs do not (Orthous-Daunay et al., 2010b). Clumped carbonate thermometry on different splits of Cold Bokkeveld revealed that this chondrite contains clasts that experienced a higher temperature (71 °C) than others (28 °C) (Guo and Eiler, 2007). Murchison and Murray typically experienced a ~30 °C temperature. These results clearly suggest that Cold Bokkeveld is a breccia with unmetamorphosed and metamorphosed clasts.

Group III contains the three CM chondrites, i.e. Murray (2.4/2.5), QUE 93005 (2.1) and Nogoya (2.2) (petrologic subtypes from Rubin et al. (2007)). We observe no correlation of the extent of aqueous alteration with any of the compositional parameters of the IOM: al-



**Fig. 8.** Crosslinking ( $CH_2/CH_3$ , top) and  $sp^3/sp^2$  ( $(CH_2 + CH_3)/C=C$ , bottom) estimators plotted versus H/C data from Alexander et al. (2007). While  $sp^3/sp^2$  shows general trends related to the H/C ratio, the chain crosslinking highlights the existence of groups of meteorites as described in text.

kyl abundance,  $CH_2/CH_3$  ratio or  $C=O$  abundance, reinforcing the view that aqueous alteration has no effect on IOM composition. This heterogeneity may rather reflect variations in the IOMs accreted, but parent body thermal processing cannot be excluded. Indeed, the structure of the IOM in QUE93005 suggests thermal processing (Quirico et al., 2011). Short-duration heating of low intensity, possibly induced by shocks, could have occurred in Murray or Nogoya. Such process in these chondrites would be of low intensity, implying no significant loss of hydrogen (the H/C ratio is similar to those of CIs and Murchison) and with no detectable shock deformation features in minerals.

#### 4.3. Heterogeneities of solar nebula organic matter present and preserved in chondritic IOM

Evidence of the heterogeneity of the chemical composition of the accreted IOM precursors has been found in type 3 chondrites (Quirico et al., 2009): the precursors exhibit chemical variations that are reflected in the thermally processed IOM by the H/C ratio. The data presented here provide new clues in the case of type 1

and 2 chondrites. With respect to the other type 2 chondrites we studied, CR chondrites have higher H/C ratios than CIs (Alexander et al., 2007), higher alkyl contents in the case of EET92042 and Renazzo and slightly higher  $CH_2/CH_3$  ratios (Fig. 6). Note that the latter trend can also be observed in the intensity of the symmetric modes of  $CH_2$  and  $CH_3$  (Fig. 2). A parent body process that would transform a CR into a CI IOM would have to remove alkyl functional groups to decrease the H/C ratio and at the same time decrease the  $CH_2/CH_3$  ratio. These three constraints rule out the possibility of a simple organic rearrangement, since most mechanisms that decrease the  $CH_2/CH_3$  ratio (the non-opening of  $sp^3$  substituted rings for instance) would increase the H/C ratio. Therefore, our data suggest that CI and CR class chondrites have accreted distinct organic precursors.

Finally, our chondritic sample set sheds new light on the organic content of stratospheric Interplanetary Dust Particles (IDPs). These particles sampled either asteroid or comets, presumably at higher heliocentric distances. The presence of a polyaromatic compound in IDPs that has chemical, structural and isotopic similarities with chondritic IOM suggests that radial mixing within the protosolar disk was effective for organic grains (Busemann et al., 2006). Such a statement may not be strictly valid, given the significant chemical and structural differences between IOM in chondrites and IDPs, as suggested by XANES spectroscopy at the K-edge and by Raman and IR microscopy (Busemann et al., 2009; Dobrica et al., 2011; Flynn et al., 2003; Keller et al., 2004; Quirico et al., 2005). In our sample data set, infrared spectra exhibit large variations in the spectral region of the stretching modes of the functional groups  $CH_2$  and  $CH_3$ , indicating a large range of  $CH_2/CH_3$  ratios (Figs. 6 and 8).

Two possible interpretations could account for these variations. First, high  $CH_2/CH_3$  values could be interpreted as the result of thermal processing, assuming a  $CH_3$ -rich primitive starting material as observed in CI and CR chondrites. This thermal processing could be due to parent body shock metamorphism, to heating within the solar cavity during transport of the grain or induced by slowing in the atmosphere (Dobrica et al., 2011). The other explanation simply considers that these variations are controlled by chemical heterogeneity in the protosolar disk prior to the accretion of chondritic parent bodies. If correct, this would imply that IOM precursors can differ by their crosslinking level and have different  $CH_2/CH_3$  ratios as well. Among preaccretional processes, two are consistent with the observed crosslinking variability. The carbonaceous skeleton of the organics before accretion could have been produced by structural rearrangement during a  $sp^2$  to  $sp^3$  carbon conversion comparable to energetic shock-wave impacts on carbonaceous matter (Marks et al., 2012; Stroud et al., 2011). Alternatively, thermal or irradiation processes within the protosolar disk can change the crosslinking level. Experiments on irradiation by UV photons or energetic particles show that an initial  $CH_3$ -rich organic solid preferentially loses  $CH_3$  groups and that the carbon skeleton is modified (Munoz-Caro et al., 2006).

## 5. Conclusion

The IOM extracted from types 1 and 2 chondrites exhibits large chemical and structural variations from one chondrite to another. In this paper, we have presented evidence that these variations are not controlled as previously thought by the extent of aqueous alteration undergone by the parent body. Whereas the  $sp^3/sp^2$  variability among primitive chondrites favors a mechanism involving short-duration thermal processing on the parent body, the distribution of the carbonaceous chain crosslinking in the sample-set is likely due to the chemical heterogeneity of the precursors in the protosolar disk before accretion. The two sources of variability



are not mutually exclusive and some chondrites seem to have traces of both. The heterogeneity found in the organic molecular structure of the precursor compounds is closely related to the conditions of radial mixing in the protosolar disk. Our results encourage detailed investigation of organics in stratospheric IDPs and Antarctic micrometeorites that could provide us with material coming from the most outer regions of the protosolar disk. Our technique can be used to directly compare organics from these outer regions with those from the part of the disk that was already sampled by CI, CR and CM chondrites.

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