



## 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-accretional 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-accretional 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-accretional process appears to be a high-temperature short-duration heating event and concerns essentially type 2 chondrites. In any case, post-accretional 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

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