

PRE-ACCRETION HETEROGENEITY OF ORGANIC MATTER IN TYPES 1 AND 2 CHONDRITES E.

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Introduction: Insoluble polyaromatic organic matters (IOM) accreted by type 3 chondrites have been found chemically and structurally fairly, but not strictly, similar [1]. On the other hand, IOMs in types 1 and 2 chondrites exhibit some slight variations in their elemental, chemical, isotopic, and structural compositions [2]. A pending question lies in the origin of these variations: did chondrites accrete similar organic precursors, which subsequently evolved through parent-body processes or were the organic precursors heterogeneous prior to the accretion ?

To distinguish the effects of post-accretion processes from pre-accretion heterogeneities of IOMs, we have performed a survey of the structural and chemical variations of the IOMs from a series of chondrites including CI1 (Orgueil, Ivuna, Alais), CM2 (Murchison, Murray, QUE93005, QUE93355, QUE97990, Cold Bokkeveld, Nogoya), CR2 (Renazzo), ungrouped C2 chondrites (PCA91008, WIS91600, Tagish Lake), and the OC Semarkona (LL3.0) and Bishunpur (L/LL3.1). The structure of the polyaromatic skeleton was characterized by Multiple Wavelength Raman Spectroscopy (MWRS), using the 244, 514 and 785 nm excitation wavelengths, following the procedure defined by [3]. This structural information was then confronted to (1) the relative abundances of the CH₂/CH₃/C=O chemical groups, derived from micro-IR spectroscopy ([4] and new measurements) and to (2) the sulfur speciation in the IOM determined by XANES micro-spectroscopy at the K-edge [5].

Experimental: 514 nm Raman measurements were performed with a LabRam HR800 (Horiba Jobin-Yvon), implemented with a single dispersive grating. Olympus x80 objective was used providing spot size diameters of 1–2 μm. Unpolarized UV Raman spectra were excited by the 244 nm wavelength of a frequency doubled argon-ion laser (Spectra Physics) and collected with a LabRam HR800 (Horiba Jobin-Yvon) designed for UV radiation. An OFR X40 objective lens was used providing a spot size of 4–5 μm across. 785 nm Raman measurements were performed with a Renishaw In Via, equipped with a single 1200 l/mm grating and a Leica microscope (x50 objective was used). Note that measurements were performed on both raw matrix extracts and IOM extracted by acid demineralization, to ensure the lack of any artifacts.

Results and discussion: 514 nm Raman spectra all exhibit the first-order carbon bands G and D, peaking

around 1600 and 1350 cm⁻¹, respectively. They were fitted using a two-component model with a Lorentzian (D peak) and a Breit-Wigner-Fano (G peak) profiles, after subtraction of the fluorescence background. The fluorescence background in 785 nm Raman spectra is not monotonic and difficult to subtract. At the present time, only a preliminary analysis with the naked eye has been performed. 244 nm Raman spectra were found poorly sensitive to structural variations, so we did not perform a detailed analysis.

The spectral parameters the most sensitive to the structure of very disordered polyaromatic carbon materials are the width and the peak position of the G-band, and the peak intensity ratio of the D and G band I_D/I_G [6]. Within the 514 nm Raman data set (Fig. 1), we can observe one main group which contains Renazzo, the CIs, and all unmetamorphosed CMs but QUE93005. Within this group, there is no obvious correlation between the Raman spectral parameters and the extent of aqueous alteration as rated by sub-petrologic types [7].

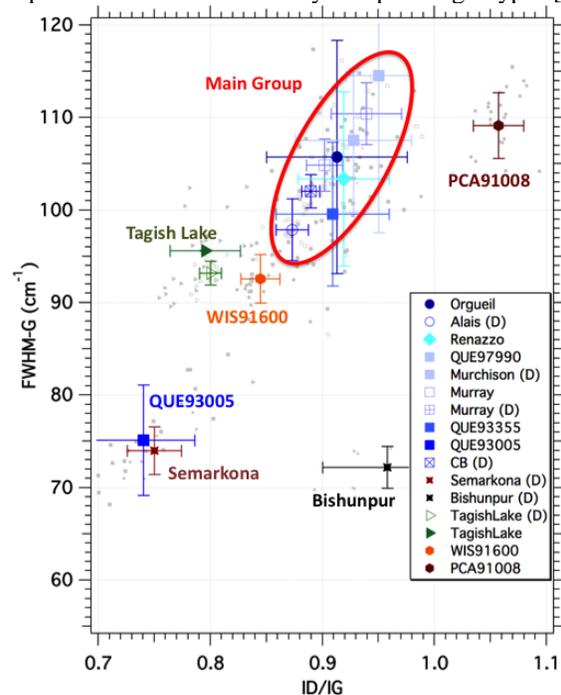


Fig. 1: FWHM-G vs ID/IG diagram (514 nm excitation; 2 sessions of measurements with slightly different conditions).

The metamorphosed CM PCA91008, and to a lesser extent WIS91600, plot apart from this group. This is also the case of the ungrouped C2 Tagish Lake. Surprisingly, QUE93005 plots along with the slightly meta-

morphosed OC Semarkona. Bishunpur (L/LL 3.1) plots apart all objects. This figure clearly evidences the peculiar nature of the short duration metamorphism experienced by PCA91008 and WIS91600, and appear perfectly consistent with the recent measurements by Nuclear Magnetic Resonance performed by [8].

785 nm Raman spectra probe a different fraction of the polyaromatic skeleton, thanks to the resonant process [3]. While QUE93005 plots along with Semarkona in the 514 nm data set, they are distinguished using the 785 nm excitation (Fig. 2). Based on the structural data of IOMs, QUE93005 appears more similar to, but distinct from the unmetamorphosed CMs. The very different structures of the metamorphosed chondrites WIS91600, PCA91008, Semarkona and Bishunpur IOMs are confirmed. In contrast, Tagish Lake appears more similar to unmetamorphosed CMs. Last, we note that the 244 nm Raman spectra appear less informative than the spectra acquired with a visible excitation.

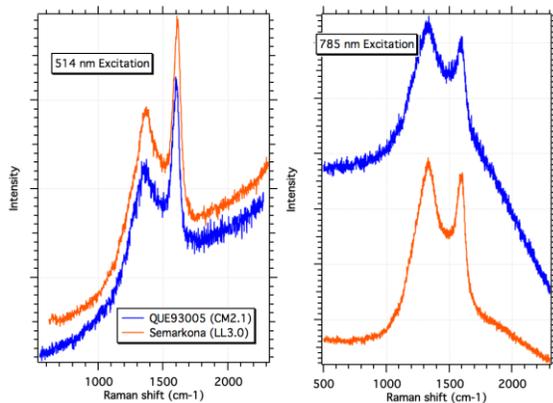


Fig. 2: Raman spectra of Semarkona and QUE93005 acquired with 514 nm (left) and 785 nm (right) excitation wavelengths. While 514 nm Raman spectra are similar, 785 nm Raman spectra reveal that the polyaromatic structure of the IOMs of these chondrites is different.

Sulfur speciation determined by K-edge XANES micro-spectroscopy has been determined recently [5]. Three groups have been distinguished as (1) CIs, with the notable presence of oxidized organic sulfur; (2) Renazzo, Tagish Lake, QUE99355, Murray, Murchison without oxidized organic sulfur, and (3) Cold Bokkeveld. CIs and Cold Bokkeveld are characterized by the presence of abundant heterocyclic sulfur. All of these objects plot within the same main group as defined on Fig. 1.

Micro-IR data show that the abundance of the CH_2/CH_3 functional groups follows the trend $\text{QUE93005} > \text{CIs} / \text{Murray} / \text{Nogoya} / \text{Murchison} > \text{Semarkona} > \text{Tagish Lake} > \text{Cold Bokkeveld} > \text{PCA91008}$ (Fig. 3). The abundance of the terminating group $\text{C}=\text{O}$ follows the trend: Cold Bokkeveld > Se-

markona / Murchison / Orgueil / Ivuna > Tagish Lake / Alais / Nogoya / Murray > PCA91008.

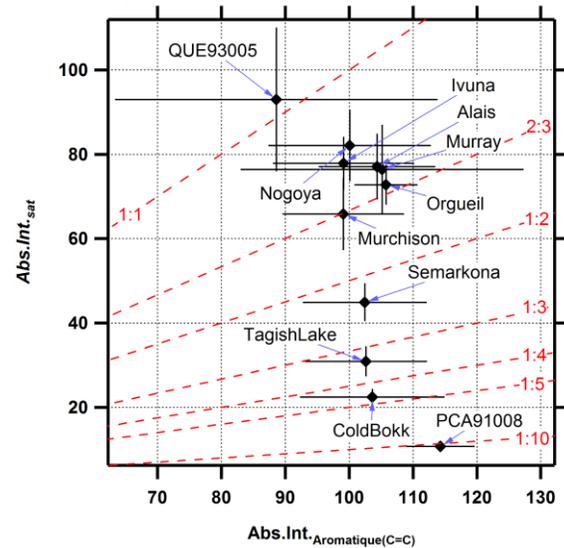


Fig. 3: Abundance of the CH_2+CH_3 functional groups in CI and CM chondrites (absorbance of the aliphatic stretch and anti-stretch bands vs absorbance of the 1600 cm^{-1} band).

The infrared and Raman data definitely evidence that the thermal event experienced by PCA91008 and WIS91600 was different from long duration metamorphism recorded by the IOMs of Semarkona and Bishunpur. In the case of unmetamorphosed objects, the post-accretion effects testified by sulfur speciation are not retrieved by the whole chemical composition of IOM. Except in QUE93005, IOMs in CIs and CMs appear fairly similar, and the slight observed differences do not correlate with the sub-petrologic types. Finally, all of these observations appear more consistent with a pre-accretion heterogeneity of the organic precursors than an effect of hydrothermalism.

The intriguing characteristics of QUE93005 compels us to consider a possible contribution of a post-accretion heating. Cold Bokkeveld and Tagish Lake, polymict breccia, have probably accreted organic precursors of different origins. The chemical characteristics of their IOMs are difficult to interpret in terms of a single process.

References:

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