

ORBITRAP-MS AND FT-ICR-MS OF FREE AND LABILE ORGANIC MATTER FROM CARBONACEOUS CHONDRITES. F.-R. Orthous-Daunay¹, R. Thissen¹, V. Vuitton¹, A. Somogyi², M. Mespouledé¹, P. Beck¹, J.-Y. Bonnet¹, O. Dutuit¹, B. Schmitt¹, E. Quirico¹. ¹Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), UJF-Grenoble-1 CNRS-INSU UMR 5274, Grenoble, F-38041, France. E-mail: forthous@ujf-grenoble.fr ²Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721 USA, E-mail: asomogyi@u.arizona.edu

Introduction: The study of organic-rich and aqueously altered carbonaceous chondrites (CI, CM and CR) is required to trace back the origin of prebiotic molecules as protosolar or hydrolysis products [1]. A minor fraction, the free organic matter (FOM) is easily extractable by common solvents and consists of small molecules [2], for 30wt.% of the total organic matter. The insoluble organic matter (IOM) is made of highly branched polyaromatic macromolecules. Harsh conditions like supercritical fluid (SF) extraction, pyrolysis or desorption techniques can release a labile organic matter (LOM) from the IOM [3]. The relationship between the free organic matter and the IOM remains unknown but may unravel clues about the history of the organics in the solar system.

Branched polyaromatic hydrocarbons have been detected by laser desorption TOF-MS in the bulk organic matter of altered chondrites, consistent with a similar carbonaceous structure and a water-induced degradation of IOM in FOM [4]. On the contrary, heteroatomic functions seem to be concentrated in the labile and water-soluble organic matter (e.g. sulfonic acids are present in SF extracts but not in the IOM), as results of an independent chemical history [5, 6]. In parallel, GC-MS after thermochemolysis of the IOM highlighted nitrogen-depleted hydrolysis product, suggesting a presolar origin of the amino acids [7]. The heavy isotopes enrichment for C, H, O, N and S in the labile and free molecular functions is seen as a signature of interstellar organochemistry [8].

A recent FT-ICR (Fourier Transform Ion Cyclotron Resonance) MS study took advantage of electro-spray ionization (ESI) to reveal directly the huge molecular diversity of the FOM in Murchison [9]. We present similar ESI-FT-MS of the soluble organic matter from six carbonaceous chondrites. We also perform Laser Desorption Ionization (LDI) FT-ICR-MS of bulk chondrites to investigate the molecular relationship between LOM and FOM.

Methods: For the solvent extraction experiment, 6 samples were selected to span a large range of aqueous alteration index: 2 CI1 (Orgueil, Ivuna), 3 CM2 (Cold Bokkeveld, Nogoya, Murchison) and 1 CR2 (Renazzo). For the LDI experiments, 1 CI1 bulk rock (Orgueil) was studied. 3 standard polymers (polyoxymethylene "POM", polyacrylonitrile "PAN" and polymethylmethacrylate "PMMA"), 2 terrestrial kerogens, 1

coal and 1 CI1 bulk rock (Orgueil) were selected as well to monitor the effects of laser impacts.

We performed two series of FT-MS:

ESI-FT-Orbitrap-MS at IPAG: Up to 4mg of each of the 6 samples was crushed in an agate mortar and put with 3mL of ultrapure Methanol in Teflon corked Duran glassware for 24h. After 5 minutes of 5000g centrifugation, the supernatant was injected in the ESI device at a flow rate of a few $\mu\text{L}/\text{min}$ for 30 minutes in positive and negative ionization modes. Mass spectra of the molecules ionized by the electro-spray were recorded with a Thermo LTQ Orbitrap XL in the 50-500 m/z range at resolving power $m/\Delta m=100000$ [10].

LDI-FT-ICR-MS at the UA dept. of Chemistry: Each of the 7 samples were powdered and flattened directly on a matrix-free steel stage. Repeated shots of a pulsed 266nm Nd-YAG laser desorb and ionize molecules driven to a Bruker ICR 7T trap.

Data treatment: FT-MS techniques provide the exact mass of ions at very high resolving power ($m/\Delta m=100000$ for the Orbitrap and 150000 for the ICR), revealing molecular diversity. Thanks to a $\pm 10^{-4}$ u accuracy, molecular formulas can be computed from each exact mass by a chemically constrained combination algorithm developed in-house. We developed statistical tools that take advantage of the mass defect versus mass (MDvM) representation. MDvM plots represent the raw data and do not require any assumptions on the elements present in the sample. As a consequence, they are useful tools for preliminary analysis of complex samples of unknown composition.

The magnesium sulfate contribution: In all CI and CM chondrites, the most intense peaks were attributed to Mg and Na sulfates adducts with methanol and water. These aggregates appear clearly on the MDvM plot with typical inorganic negative slope due to the highly negative mass defect of atoms like S, O, Mg and Na. The presence of Mg is undoubtedly comforted by its isotopic signature. The islets in black in Figure 1 exhibit regular spacing that correspond to the aggregation of SO_4 (95.951 u) and Mg (23.985 u). The positive slope of each islet is due to methanol (32.026 u) and water (18.011 u) solvation. These spacing can be reproduced with terrestrial standards of MgSO_4 in a methanol solution. Magnesium sulfate appears to be chondritic, its intensity increasing with its relative abundance in the bulk rock [11].

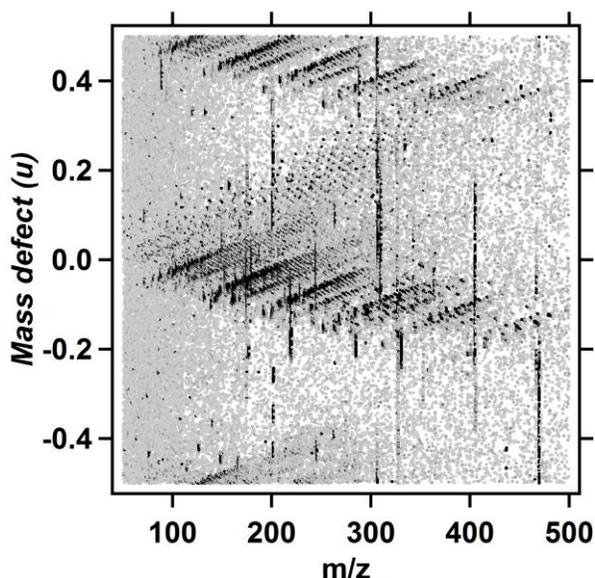


Figure 1: MDvM diagram of the methanol extract of Orgueil in positive ESI-FT-Orbitrap-MS. Grayscale is for intensity. Points alignments are due to the variable amount of a defined group. The global negative slope is due to adduction of several heavy atoms.

Identification of Organics in Renazzo: As sulfates are absent in CR, inorganic adducts are not observed in the methanol extract of Renazzo. Its MDvM plot main trend is a positive slope due to hydrogen rich compounds attributed to organics. These organics show heteroatomic features: micro-alignments along several strong slopes with a mass defect systematically lower than the alkanes (C_nH_{2n+2}) simulation (Figure 2).

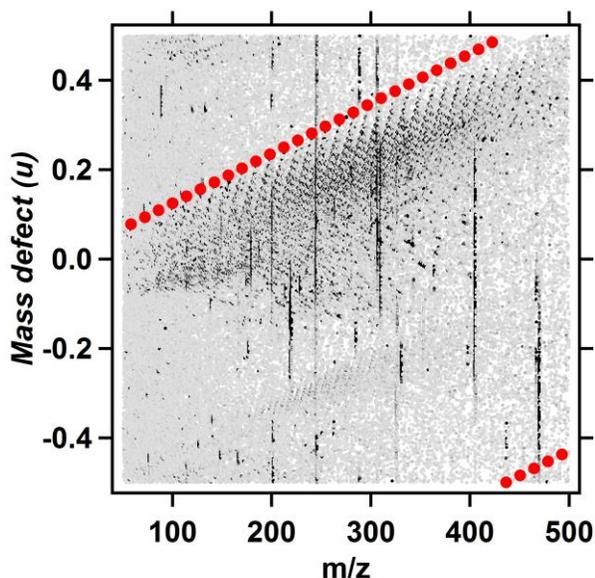


Figure 2: MDvM diagram of Renazzo methanol extract in positive ESI-FT-Orbitrap-MS. Red dots are for theoretical alkanes mass defects and masses.

Combinations of C, H, O, N and S were simulated to match the exact masses found in the Renazzo spectrum and 259 molecular formulas were confidently assigned. These represent 70% of the cumulative peaks intensity. Heteroatomic composition in molecules is heterogeneous and is associated with highly variable relative intensities (e.g. most common (37% of assignments) formulas bear only C, H and N whereas they represent only 6% of the cumulative assigned intensity). Otherwise, O bearing molecules seem to have systematically more intense peaks. Taking this distribution into account, we calculate a bulk formula for the methanol-soluble organic matter of Renazzo: $C_{100}H_{142}O_{23}N_6S_1$. This is close to the bulk formula found by [9] in Murchison and suggest H and N enrichment in the methanol extractable organic matter toward the IOM.

Laser desorbed organics of Orgueil: Organic molecules were found in the positive mode of LDI-FT-ICR-MS spectrum of Orgueil. Inorganic sulfur was absent of the MS with this technique. The organic molecules seem to be less abundant and much simpler than those in Renazzo ESI-FT-MS or organics released by LDI of coals or kerogens. LDI appears to release heteroatomic-poor molecules. This can be due to high sensitivity of aromatic moieties to the laser wavelength that may cause parts of the polyaromatic macromolecule to evaporate and ionize just like MALDI matrix. This is consistent with previous studies using laser desorption that report large amount of alkylated PAHs [4].

Our results tend to show that ESI and LDI techniques probe different parts of the chondritic organics. The methanol extraction is a good way to access the most functionalized molecules. Despite Renazzo is the unique fully organic sample, it exhibits significant difference toward the IOM such as a higher saturation and heteroatomic content. Current work on desalination and differential solubility could refine the molecular description of the FOM in an extended number of chondrites.

References:

- [1] Sephton, M.A., et al. (1998) *GCA*, 62, 1821-1828. [2] Botta, O. and J.L. Bada (2002) *Surveys in Geophysics*, 23, 411-467. [3] Sephton, M.A., et al. (2004) *GCA*, 68, 1385-1393. [4] Elsila, J.E., et al. (2005) *GCA*, 69, 1349-1357. [5] Cooper, G.W. and J.R. Cronin (1995) *GCA*, 59, 1003-1015. [6] Pizzarello, S., et al. (2001) *Science*, 293, 2236-2239. [7] Remusat, L., et al. (2005) *GCA*, 69, 3919-3932. [8] Cooper, G.W., et al. (1997) *Science*, 277, 1072-1074. [9] Schmitt-Kopplin, P., et al. (2010) *PNAS*, 107, 2763-2768. [10] Markarov, A., et al. (2006) *Analytical Chemistry*, 78, 2113-2120. [11] Burgess, R., et al. (1991) *Meteoritics*, 26, 55-64.