

MOLECULAR COMPLEXITY OF INTERSTELLAR ORIGIN IN LARGE POLYMERIC COMPOUNDS FROM MURCHISON. F. R. Orthous-Daunay¹, R. Thissen¹, V. Vuitton¹, L. Flandinet¹, F. Moynier², E. Zinner³.

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Introduction: The study of organic-rich and aqueously altered carbonaceous chondrites (CI, CM and CR) has led so far to the detection of several types of organic compounds characterized by their extraction methods [1]. A minor fraction, the so-called “free organic matter” (FOM), is easily extractable by common solvents and consists of small molecules [2], for up to 30wt.% of the total organic matter. The insoluble organic matter (IOM) is made up of highly branched polyaromatic macromolecules. Harsh treatment 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 a matter of debate as isotopic evidence favors interstellar/nebular molecular growth [4] whereas recent morphological and molecular investigations imply liquid phase polymerization on a parent body [5].

From a molecular point of view, some links have been drawn between FOM and IOM. Branched polyaromatic hydrocarbons have been isolated by laser desorption TOF-MS from the bulk of altered chondrites [6], revealing free compounds with IOM-like bond types. Recently, irradiation experiments have produced large polyaromatic molecules from benzene [7], highlighting a possible pathway from small to IOM-sized molecules under interstellar conditions. Heteroatomic functions seem to be concentrated in the FOM and depleted in the IOM (e.g., in Murchison, sulfonic acids are present in SF extracts but not in the IOM), as result of an independent chemical history [8-10].

A recent FT-ICR (Fourier Transform Ion Cyclotron Resonance) MS study revealed the dramatic molecular diversity of the FOM in Murchison [11]. In order to look for the missing link between the FOM and the IOM, we undertook a FT-MS study of the water-insoluble fraction of the FOM extracted from Murchison. We thoroughly investigated the molecular complexity of more than 2000 compounds at a time and could put some strong constraints on the processes required to produce such a mixture.

Materials: The phase we extracted will be referred to as WI-FOM (for Water-Insoluble Free Organic Matter). The goal is to focus on the products of extended molecular growth and to eliminate potential contamina-

tion. 65 g of Murchison were washed with distilled water during freeze-thaw disaggregation. The resulting powder is free of water-soluble magnesium sulfates, which jeopardized electrospray measurements carried out in a previous study [12]. The sample was macerated in a Fisher Optima Methanol and Toluene (1:2) mixture for 1 week in a dark clean room with no sonication. Glassware was washed several times in Ethanol with caustic soda and baked at 250°C for at least 12 hours before use. Extracts were recovered after centrifugation and stored in glass tubes.

Mass spectra were acquired with a Thermo LTQ Orbitrap XL coupled with an Electrospray ionization (ESI) source, in the 50-500 and the 150-1000 m/z range, both for cations and anions at resolving power $m/\Delta m=100000$ [13, 14].

Data treatment: FT-MS techniques yield the exact mass of ions at very high resolving power, revealing molecular diversity. We developed statistical tools that take advantage of the mass defect versus mass (MDvM) representation. The mass defect of a molecule is the difference between its exact mass and the closest integer. It is, in most cases, the sum of the nuclear mass defects of the atoms in this molecule. MDvM plots (Figure 1, top panel) represent raw data and do not require any assumption on the elements present in the sample. In such diagrams, a polymeric pattern sticks out because of the alignment it generates. If some molecules differ from one another by the addition or subtraction of a given number of atoms, the difference in mass and mass defect between those molecules will correlate. The description of chemical diversity relies here on the correct identification of the most frequent slopes along which data points are aligned.

In favorable cases, differential chemistry is described by few consistent “molecular patterns”. The complete understanding of a mixture is achieved by the identification of the invariant parts of the molecular population. These “seeds” are as many as required to explain each detected mass by addition or subtraction of one or several molecular pattern(s) to a seed. Thanks to a $\pm 10^{-4}$ u accuracy, molecular formulas can be computed from each exact mass by a combination algorithm that takes into account stoichiometric rules.

Results: We consider here only the cations. Most of the molecular content is restricted to the 150 to 500 m/z range. The resolving power is high enough to rule out any isobaric interference in this m/z range. More than 2000 singly charged cations have been identified. Figure 1 shows at the bottom the spectrum itself in the classic intensity vs mass-per-charge space and on top the MDvM diagram. Alignments are already visible at this scale.

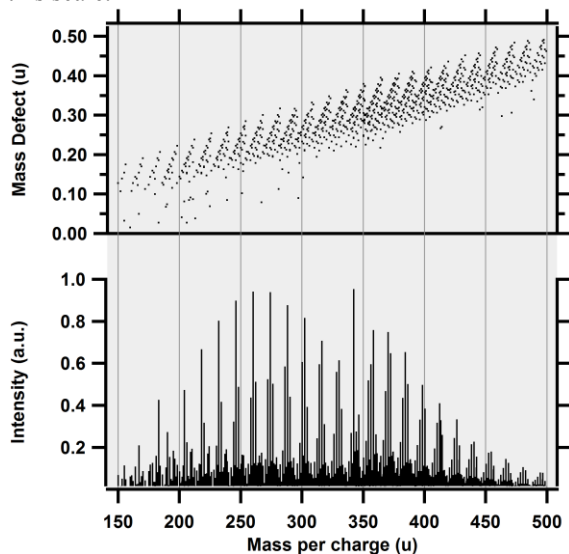


Figure 1

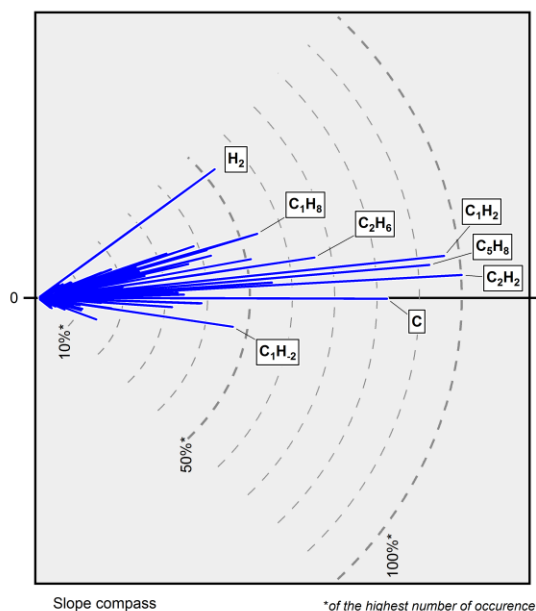


Figure 2

Figure 2 shows a representation of the most common sets of formulae that explain differences between detected masses. The so-called “slope compass” displays only C and H combinations as potential polymer-

ic patterns. For the sake of clarity, we do not label all but it appears that the compounds found in our extracts belong exclusively to polymeric series based on C_xH_y , which means that the spread in mass is due to a variability of the hydrocarbon skeleton of the molecules at first place. The lightest detected molecule in this WI-FOM phase has 10 carbon atoms while the heaviest considered here has 35 carbon atoms. We have identified 5 seeds which are N, N_2 , NO, NO_2 and N_2O_2 . Every detected ion belongs to the H_2 series, which relates to the variation of the degree of unsaturation with a constant number of C atoms. The saturation in this WI-FOM goes from 0 to 0.5 per carbon (unsaturation in the bulk IOM is close always to 0.7 per carbon). This confirms that the WI-FOM is more saturated than the IOM.

The variability of C and H depends on the number of carbon atoms. We demonstrate that the saturation decreases with mass at the rate of 1 saturation per 5 atoms of carbon added. This is consistent with a cyclization process that stabilizes molecules that form cycles of 6 sp^3 carbons at the expense of H_2 .

We will discuss in detail the observational biases of the ionization method. We will propose a comprehensive synthesis pathway relying on the addition of atomic hydrogen on unsaturated molecules. We will discuss the possibility of an interstellar origin of the molecular complexity observed in this organic phase of Murchison.

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