STUDY OF SOLUBLE ORGANIC COMPOUNDS FROM MARTIAN REGOLITH BRECCIA NWA 7533 BY ORBITRAP MASS SPECTROMETRY. F. R. Orthous-Daunay[1], R. Thissen[1], L. Flandinet[1], A. Néri[1], V. Vuitton[1], P. Beck[1]. frod@ujf-grenoble.fr. [1]Institut de Planétologie et d'Astrophysique de Grenoble, Univ. Grenoble Alpes/CNRS, F-38000 Grenoble, France.

Introduction: Exploration of Mars is partly motivated by the question of its habitability and the timing of a possible origin of life like on Earth. This lead to the study of the most blatant life markers that are organic molecules. Due to lack of meteoritic sample very little is known about Martian organic matter with respect to carbonaceous chondrites'. The most simple organic molecule, methane, has been detected in the Mars atmosphere at steady state [1]. This implies the existence of an organic carbon cycle given the quick destruction of methane in this planetary environment. UV photodegradation of exogenous chondritic-like organics delivered to Mars by impacts is thought to be a sustainable source of methane [2]–[4]. Recent measurements of the methane content variability in the Mars atmosphere [5] raised new interest upon the origin of this unstable organic molecule.

The comparison between chondritic and Martian organic matter at the molecular scale should provide insights on the processes occurring in the carbon cycle. Mass spectrometry is the technique of choice to track the evolution of small molecules that don't have isomers like H_2O and CH_4. The first study of soluble organic matter (SOM) from Murchison by ultra-high resolution MS has revealed outstanding molecular density [6]. It also highlighted a high hydrogen content relative to the insoluble fraction (IOM). The Orbitrap technique helped relate this molecular complexity to chemical processes [7]. A significant fraction of Murchison compounds are saturated chains bearing a few N and O atoms and showing complexity consistent with pristine interstellar grains surface polymerization.

NWA7533 is a Martian regolithic breccia wich multiple lithologies described in [8]. It bears clasts with Ir and Ni contents comparable to lunar soils, interpreted as exogenous CI-like material for up to 5wt%. This unique sample possibly carries residues of chondritic organics that underwent the processes related to the CH_4 cycle.

We applied our Orbitrap method to NWA7533 and Murchison. We propose to use the SOM diversity as a proxy of transformation processes occurring on Mars assuming these two samples are representative of their parent bodies history.

Method: *Organics extraction:* Twice 30 milligrams of NWA7533 were ground in agate mortar for specific surface maximization. The first batch was soaked in 6mL of Methanol/Toluene (1:2) solvents for maceration during 48h. This mixture is commonly used to optimize both polar and apolar compounds solubility. Methanol often solubilizes inorganic species like sulfates that impair conclusive measurements. In order to avoid salt contamination we prepared a second batch that was first macerated with water for 1 week then soaked in the same Methanol/Toluene (6mL) mixture. Special attention will be paid to the comparison of these two samples. Glassware was washed in ethanol with caustic soda and baked at 250°C for 12 hours.

Data treatment: Mass spectra were acquired with a Thermo LTQ Orbitrap XL at its highest resolving power (120000 at m/z = 400). Ions are produced with Electrospay ionization (ESI), both for cations and anions.

FT-MS techniques yield the exact mass of large numbers of ions, without isobars in our mass ranges. This enables a statistical analysis of the 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.

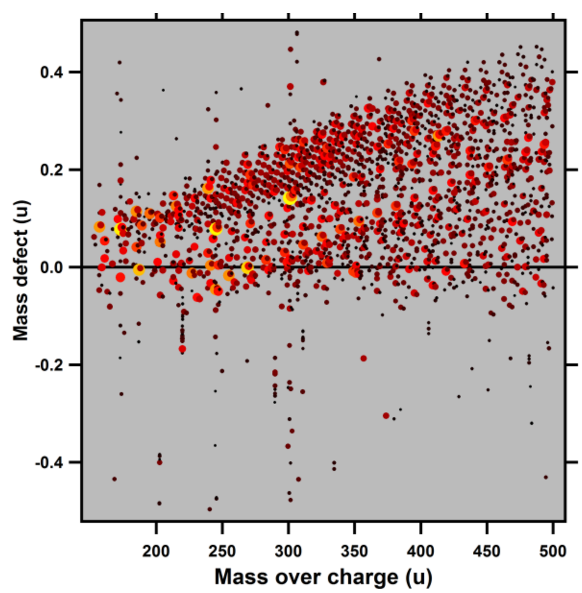

Figure 1: MDvM plot for the NWA7533 met./tolu. extract cations for m/z between 150 and 500 u. Zero mass defect ions along the whole mass range is remarkable.

Those diagrams plot (Fig.1) one point per exact mass measured. If more than two molecules differ from one another by the addition or subtraction of the same set of atoms, their corresponding points will align on a line of which slope is characteristic of the atoms set. 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 ± 10^{-4} u accuracy, molecular formulas can be computed from each exact mass by a combination algorithm that takes into account stoichiometric rules.

Results: Martian extracts are slightly simpler than the chondritic mixture. Considering only the cations, the molecular density is lower (~2000 compound for NWA7533 vs. ~2600 for Murchison in the 150-500 m/z range). The Martian extract cations have m/z up to 800 whereas chondritic cations are extremely rare above m/z = 650 with respect to the instrument dynamic range. Martian cations have systematically much lower mass defect than Murchison's. This is due to higher oxygen content, probably in the organic structure, and to the presence of Na adducts.

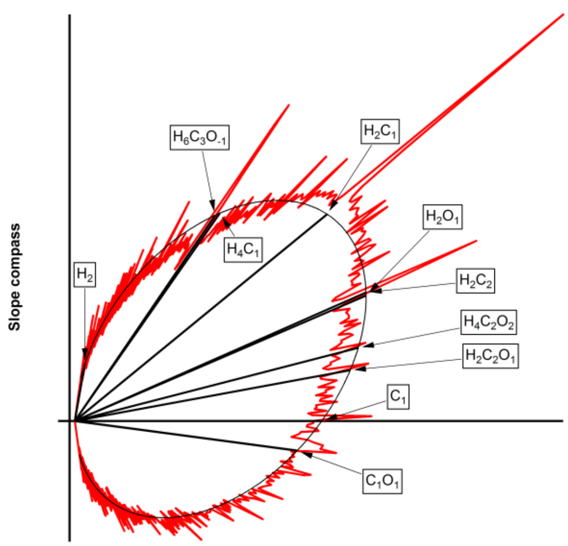

Figure 2: "Slope compass" (red line) counts the number of points couples that align in a given direction in MDvM diagram (Fig.1).

Repetitive patterns in the NWA7533 are combinations of C, H and O (Fig.2). The most frequent pattern in NWA7533 is CH_2. This group is also very frequent in the Murchison extract. The mass distribution in Murchison is consistent with polymeric molecular growth whereas it is absolutely not the case for NWA7533. The two other major patterns in NWA7533 are C_2H_2 and the $C_3H_6O_{-1}$ permutation. Where oxygen is part of several other patterns in the Martian extract, it does not appear in the chondritic mixture. Another major difference is the absence of nitrogen in any cations observed whereas it is a characteristic feature in Murchison mixture. This explains partly the presence of Na adducts in NWA7533: the presence of amine group in chondritic compounds favors protonation whereas lack of basic groups in Martian molecules favors sodium adduction.

The CH_4 pattern is noticed but is not a major one. The involvement of oxygen in the chemical diversity tends to rule out the hypothesis of a single process modifying chondritic organics.

References:

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