MARTIAN METHANE CYCLE AND ORGANIC COMPOUNDS FROM MARTIAN REGOLITH BRECCIA NWA 7533 BY ORBITRAP MASS SPECTROMETRY. F. R. Orthous-Daunay1, R. Thissen1, L. Flandinet1, L. Bonal1, V. Vuitton1, P. Beck1, M. Hashiguchi2 and H. Naraoka2. 1Institut de Planétologie et d’Astrophysique de Grenoble, Univ. Grenoble Alpes/CNRS, F-38000 Grenoble, France. 2Research Center for Planetary Trace Organic Compounds, Kyushu University.

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.

NWA7533 is a Martian regolithic breccia with multiple lithologies described in [6]. 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 CH₄ 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 samples are representative of their parent bodies history.

Method: The preparation requires direct physical access to the sample in open air at room pressure. Twice 30 milligrams of NWA7533 were ground and soaked in 6mL of Methanol/Toluene (1:2) solvents for maceration during. Glassware was washed in ethanol with caustic soda and baked at 250°C for 12 hours to eliminate contamination. The sample amount needed depends directly on the organic content. For carbonaceous chondrites, down to 1mg is enough.

Mass spectra were acquired with a Thermo LTQ Orbitrap XL at its highest resolving power (12000 at m/z = 400). Ions are produced with Electrospay ionization (ESI), both for cations and anions.

Very high resolution mass spectrometry enables a statistical analysis of the molecular diversity. In favorable cases, differential chemistry is described by few consistent “molecular patterns”. The identification of a process is achieved by finding a signature distribution among the molecular families with a given pattern. 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 (~1000 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.

Repetitive patterns in the NWA7533 are combinations of C, H and O. The most frequent pattern in NWA7533 is CH₂. This group is also very frequent in the carbonaceous chondrites extracts. The mass distribution in carbonaceous chondrites is consistent with polymeric molecular growth whereas it is absolutely not the case for NWA7533. The two other major patterns in NWA7533 are C₂H₄ and the C₆H₄O₃ permutation. Where oxygen is part of several other patterns in the Martian extract, it does not appear in the chondritic mixture. The CH₂ pattern is noticed but is not a major one. The absence of signature polymeric distribution in the Martian sample is interpreted as a destruction of an existent mixture similar to the carbonaceous chondrites one. Recent experiment on the irradiation of Murchison organics indicate UV photons can destroy chains effectively [7]. We conclude that the organic matter in this Mars sample was not synthetized on place and is likely to be exogenic chondritic matter that underwent extreme UV irradiation and/or heating on the Mars surface.

Perspective: As the amount of returned sample is very limited, liquid extraction is not guaranteed. Desorption ionization at millimeter scale is currently developed to ionize molecules in dry conditions [8].