INTERSTELLAR ORIGIN OF SOLUBLE ORGANIC MATTER FROM THE MURCHISON METEORITE REVEALED BY ORBITRAP-MS. F. R. Orthous-Daunay[1], L. Flandinet[1], R. Thissen[1], V. Vuitton[1], F. Moynier[2], E. Zinner[3] frod@ujf-grenoble.fr. [1]IPAG, CNRS Univ. Grenoble Alpes, IPAG, F-38000 Grenoble, France, [2]Institut de Physique du Globe de Paris, [3]Physics Department of Washington University, St-Louis, MO

Introduction: Organic matter in Murchison splits into large insoluble and small soluble molecules. The latter is made of thousands of compounds varying in mass up to 2000 Da [1] with an unmatched continuity in diversity. These compounds size is in-between the molecules detected in space environments [2] (tens of atoms) and heavier macromolecules found only in meteorites [3]. They may have recorded signatures of molecular complexification during the transition from the diffuse interstellar medium to dense molecular clouds. They also may have undergone hydrothermal transformation on the meteorite parent body [4], [5]. We seek for mass spectrum signature univocally related to one stage of the meteoritic material evolution.

Method: 65 g of Murchison were washed with water and freeze-thaw disaggregated to eliminate magnesium sulfates, which jeopardize the use of electrospray. The sample was macerated in Methanol and Toluene (1:2) for 1 week in a dark room. Glassware was washed in Ethanol with caustic soda and baked at 250°C for 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 Electrospay ionization (ESI) source, in the 150-1000 m/z range, both for cations and anions at resolving power m/Δm=100000.

Results: Detected ions are in the 150-750 Da range. For the cations, the average mass is ~350 Da and the average diversity is 5.1 ions per Da. In this mass range, the Orbitrap nominal resolution is high enough not to compromise stoichiometry computation for each exact mass. Each mass detected bears at least NH, consistently with the ESI ionization bias for amines in positive polarity. The maximal number of heteroatoms is 2 for N and 3 for O. The average H/C is 1.6 regardless of the mass. There is no convergence toward macromolecular-like low saturation. We interpret the periodicity in mass as a repetition of stoichiometric patterns. CH_2, H_2 and C_5H_8 are the most frequent patterns. The latter corroborates a very slow loss of saturation and is consistent with full sp^3 cyclization. Molecules varying only by a given number of CH_2 all exhibit a lognormal distribution. This requires randomly distributed sp^3 chains cut events to be interpreted. We will show that the H_2 distribution is correlated to the chains cut mechanism. The chain rearrangements, cuts and cycling signatures along with the very limited loss of hydrogen are all together consistent with chemical processes detected in space. Randomized additions of CH_2 and H_2 are reported to occur on grain surface in dense molecular clouds [6]. Their boundaries can be highly UV-irradiated, providing an efficient C bonds cut mechanism [7] as seen here in Murchison.

References: [1]Schmitt-Kopplin P. et al. (2010) *PNAS*, *107*, 7 pp. 2763–8. [2]Caselli P. and Ceccarelli C. (2012) *Astron. Astrophys. Rev.*, *20*, 1 p. 56. [3]Sephton M. a (2002) *Nat. Prod. Rep.*, *19*, 3 pp. 292–311. [4]Le Guillou C. et al. (2014) *GCA*, *131* pp. 368–392. [5]Cody G. D. et al. (2011) *PNAS*, *108*, 48 pp. 19171–19176. [6]Belloche A. et al. (2014) *Science (80-.).*, *345*, 6204 p. 15841587. [7]Alata I. et al. (2015) *A&A*, *123* pp. 1–9.

EXTENSIVE ALKYLATED N-CONTAINING CYCLIC COMPOUNDS IN THE MURCHISON METEORITE. H. Naraoka[1] Y. Yamashita[1] and M. Yamaguchi[2], [1]Dept. Earth & Planet. Sci., Kyushu Univ. 744 Motooka, Nishi-ku, Fukuoka, 819-0395 Japan; naraoka@geo.kyushu-u.ac.jp, [2]Thermo Fisher Scientific, C-2F, 3-9 Moriya-cho, Kanagawa-ku, Yokohama 221-0022 Japan.

Various organic compounds are reported in solvent extracts of carbonaceous meteorites. Recent ultrahigh-resolution mass spectral analysis has detected tens of thousands of different mass peaks in the Murchison meteorite [1]. Considering the structural and optical isomers, hundreds of thousands organic compounds may be present. However, the compound distribution is largely unknown, which is critical to understand the origins and formation processes of meteoritic organic compounds. In this study, we examined detailed compound distributions in the methanol extract of Murchison by HPLC/ultrahigh resolution mass spectrometry to reveal organic reaction mechanisms on the parent body in the early solar system.

Significantly large numbers of positive ions were observed between m/z 80 and 1400, where strong ion peaks were dominated between 90 and 400 with the maximum at m/z ~300. Most peaks have CHN compositions with minor CHO and CHNO compositions, even though the CHN compositions were not reported by [1]. More than 600 ions were assigned to $C_nH_mN^+$ and $C_nH_mN_2^+$ in elemental compositions, in which saturate and unsaturate-alkylated pyridines ($C_nH_{2n-5}N$ and $C_nH_{2n-7}N$) and imidazoles ($C_nH_{2n-2}N_2$) were predominant peaks followed by alkylpyrroles ($C_nH_{2n-3}N$) and alkylpiperidines ($C_nH_{2n}N$). Both alkylpyridines and alkylimidazoles could be produced from aldehydes and ammonia through aldol condensation and imine formation under an alkaline condition. Futher redox reactions could have proceeded during water-rock interaction to give alkylpiperidines and pyridine carboxylic acids (e.g. nicotic acid) on the parent body (Fig. 1). These redox reactions could be associated with aqueous alteration of meteoritic olivine (i.e. serpentinization; $3(Mg,Fe)_2Si_2O_8 + 6H_2O= 2Mg_3Si_2O_5(OH)_4 + 2SiO_2 + 2Fe_3O_4 + 2H_2$) under an alkaline environment.

Simulation experiments were performed to produce the N-containing cyclic compounds using aldehydes and ammonia in water in the presence of olivine. Several alkylpyridines were produced to show the similar isomer distributions as observed in Murchison [2]. Aldehyde polymerization with ammonia is an important process to produce the high-molecular alkylated N-containing cyclic compounds on the meteorite parent body.

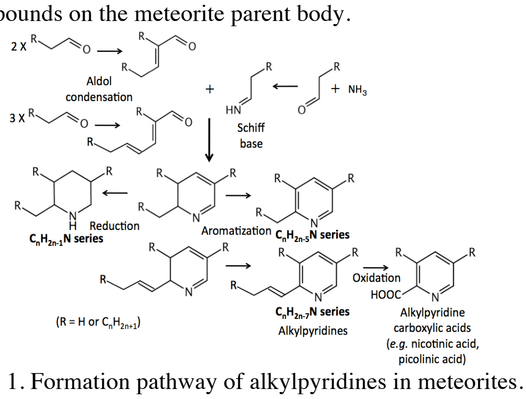

Fig. 1. Formation pathway of alkylpyridines in meteorites.

References: [1]Schmitt-Kopplin et al. (2010) *PNAS* **107**, 2763. [2]Yamashita & Naraoka (2014) *Geochem. J.* **48**, 519.