

High-resolution mass imaging for organic species in the Murchison meteorite using desorption electrospray ionization with an Orbitrap mass spectrometer

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[INTRODUCTION] Primitive meteorites contain a wide variety of organic molecules, which are identified using mass spectrometry (MS) with gas or liquid chromatography (GC or LC). Recent high-mass resolution chemical analyses for the solvent extracts revealed presence of various CHO, CHNO, CHNOS [1] and CHN species [2]. Furthermore, in-situ chemical analyses with MS have been performed on primitive meteorites using two-step laser desorption/ photoionization mass spectrometry [3] or matrix assisted laser desorption ionization [4]. Such investigations of spatial distribution of the organic species are necessary to understand evolution of organics in extraterrestrial materials.

Now, we are trying to apply the high mass resolution imaging using two dimensional (2D) desorption electrospray ionization (DESI) [5], which is a spray based ionization technique, with Orbitrap-MS to surface of carbonaceous chondrites [6].

[EXPERIMENTAL] The DESI-MS analysis was performed in a clean room at the Research Center for Planetary Trace Organic Compounds of Kyushu University. Fragments of Murchison (CM2) (~ a few mm) were obtained by chipping and a fragment with flat surface was embedded in Indium or alloy with low melting point. To comparison of analyzed area of sample surface and obtained DESI imaging data, a few points (~100 μm) on metal around the fragments were marked by rhodamine B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$). The imaging was performed ~10x10 mm area of the sample surface using a DESI ion source (Omni Spray Source 2-D, Prosolia) equipped with a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Scientific). Methanol (100%) was sprayed on the sample surface with 1 $\mu\text{l}/\text{min}$ flow rate. The nebulizer N_2 gas pressure was 100 psi. Electrospray voltage were set at 3 kV. The positive ions were obtained with mass resolution of 140,000 (m/z 200) from sample surface in full scan mode motorized x-y stage.

[RESULTS AND DISCUSSION] Numerous ion peaks with m/z 70-700 were detected from sample surface. The signal of rhodamine B ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3^+$) were clearly detected from marked region of the sample surface. Then, we carefully compared with DESI images and stereoscope image of the sample. Alkylated imidazole homologs ($\text{C}_n\text{H}_{2n-1}\text{N}_2$) ($n=4-10$) were detected from surface of Murchison distinguishing from surrounding metal. The identification of the alkylated imidazole homologs was consistent with bulk chemical analysis for the methanol extract of the Murchison sample using high-performance LC-MS [2]. Our results suggest usefulness of the DESI-MS analysis for understanding of spatial distribution of polar organic species in primitive meteorites. Further investigations (e.g. comparison of mineralogy) are needed and they will provide us important sights of the evolution of the extraterrestrial organic materials.

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Molecular Diversity of Soluble Organic Matter Synthesized through the Formose-like Reaction

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Introduction: Several formation pathways have been proposed for extraterrestrial organic matter (e.g., photochemical reaction in a cold molecular cloud or outer solar system environment [1] and hydrothermal reaction in planetesimals [2]). Cody *et al.* [2] and Kebukawa *et al.* [3] reported that chondritic insoluble organic matter could be produced by the formose-like reaction in planetesimals. The formose-like reaction also produces soluble organic molecules (SOMs). In this study, we applied the high mass resolution mass spectrometer (HRMS) to identify a series of SOMs formed by the formose-like reaction and their possible formation pathway.

Methods: Organic synthesis experiments were carried out as follow [3]. A mixture of paraformaldehyde, glycolaldehyde, $\text{Ca}(\text{OH})_2$, ammonium hydroxide and ultra-pure water was sealed in pyrex glass tubes and heated at 90°C for 72 hours. Experiments on the mixture without NH_3 were also performed for comparison. Supernatant liquids of run products were diluted with solvents and analyzed with a positive ion mode by HPLC-ESI-HRMS (EASY nLC-Orbitrap Elite, Thermo Fisher Scientific) at Hokkaido University. The obtained mass spectra were analyzed with the software ATTRIBUTOR [4] to identify molecular formulas.

Results and Discussion: Molecules synthesized with and without NH_3 had the same retention time in liquid chromatography, and similar peak abundance distributions from m/z -50 to ~600 on the mass spectra. Considering the presence of doubly-charged ions, molecules with masses up to ~1200 were synthesized irrespective of the presence of NH_3 . The most frequent mass difference between molecules synthesized either with and without NH_3 corresponds to the mass of $\text{C}_2\text{H}_2\text{O}$. More detailed analysis of molecular distribution indicates that addition of 2 CH_2O accompanied by dehydration of 1 H_2O occurred to synthesize the SOMs which resulted in the mass difference of $\text{C}_2\text{H}_2\text{O}$. A characteristic mass difference observed in molecules synthesized with NH_3 was the mass of CHN. However, the number of nitrogen in one molecule is limited, and the N-bearing molecules are expressed as $[\text{CHN}]_m[\text{C}_x\text{H}_y\text{O}_z]$ ($m = 1, 2$) which were possibly formed by a reaction between NH_3 and products of the formose-like reaction.-

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