**ORGANIC COMPOUND IMAGING ON THE SURFACE OF CM2 CARBONACEOUS CHONDRITES USING DESORPTION ELECTRSPRAY IONIZATION (DESI) WITH HIGH-RESOLUTION MASS SPECTROMETER.** M. Hashiguchi[1] and H. Naraoka[1,2], 1Research Center for Planetary Trace Organic Compounds, Kyushu University. (hashigchi.minako.123@m.kyushu-u.ac.jp). [2]Department of Earth and Planetary Sciences, Kyushu University.

**Introduction:** Primitive meteorites contain a wide variety of organic molecules, which have been generally identified using mass spectrometry (MS) with gas or liquid chromatography (GC or LC). Recently, high-mass resolution chemical analyses on the solvent extracts from Murchison meteorite found various CHO, CHNO, CHNOS [1] and CHN compounds [2].

In-situ chemical analyses with MS have currently been performed on primitive meteorites using two-step laser desorption/photoionization mass spectrometry ($L^2MS$) [3, 4] or matrix assisted laser desorption ionization (MALDI) [5]. The in-situ investigations of spatial distribution of the organic species are necessary to understand evolution of organics in extraterrestrial materials because the extraterrestrial organic species should have evolved by complex interaction with minerals and water through interstellar medium to early solar system [6, 7].

Desorption electrospray ionization (DESI) is a spray based ionization technique [8, 9]. The ionization is carried out by directing electrosprayed charged droplets and the impact of the charged particles on the surface produces gaseous ions of material on the surface. By motorization of sample stage, in-situ two (2D) dimensional chemical analysis can be achieved using the DESI [e.g. 9]. In this study, the 2D DESI with high-resolution MS analysis on carbonaceous chondrites were performed to reveal spatial distribution of the organic compounds on surface of the meteorites.

**Experimental:** Murray (CM2) and Murchison (CM2) meteorites were used in this study. A few mm sized fragments of these meteorites were obtained by chipping. For only Murchison sample, surface of the fragment was polished with alumina polishing film without water and any solvent. Then a fragment with flat surface of each meteorite were embedded in indium or alloy with low melting point. For Murchison sample, a few points (~100 µm) on metal around the fragments were marked using rhodamine B ($C_{28}H_{31}ClN_2O_3$) to comparison of analyzed area of sample surface and obtained DESI images. The in-situ chemical analysis was performed using a 2D DESI ion source (Omni Spray Source 2D, Prosolia) equipped with a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Scientific). Electrospray voltage were set at 3 kV. A spray solvent is methanol (100%) and flow rate is 1 µl/min flow rate. The nebulizer $N_2$ gas pressure was 100 psi. DESI images were acquired by continuously moving the surface beneath the spray at a constant velocity. The positive ions were collected in a full scan mode ($m/z$=100-500 for Murray or 70-700 for Murchison) with mass resolution of 70,000 or 140,000 ($m/\Delta m$ at $m/z$ 200) on ~1 x 1 mm for Murray and ~ 10 x 10 mm for Murchison by motorized x-y stage.

In these experiments, mass spectral data files are converted into the cube format using the FireFly™ (Prosolia Inc.) software then DESI MS spectra images were reconstructed using BioMap (free software, www.maldi-msi.org).

**Results and Discussion:** Numerous ion peaks were detected from both Murray and Murchison. Figure 1a shows high-resolution spectra obtained from surface of Murchison. Among these numerous peaks, alkylated imidazole homologues and alkylated piperidine homologues detected from Murchison (Figures 1b and 1c). Figure 2 indicates stereomicroscope image and spatial distribution of Rhodamine B, alkylated imidazole and alkylated piperidine detected from Murchison, respectively. The signal of rhodamine B positive ion ($C_{28}H_{31}N_2O_3^+$) were clearly detected from marked region on Al around Murchison embedded alloy (Figure 2b). The marked region was very useful to compare the DESI images using stereomicroscope image. Alkylated imidazole homologues ($C_nH_{2n-1}N_2^+$) and alkylated piperidine homologues ($C_nH_{2n+2}N^+$) were clearly detected from the surface of Murchison (Figures 2c and 2d). Similarly, the alkylated imidazole homologues and alkylated piperidine homologues were also identified from the Murray meteorite. Furthermore, alkylated pyridines ($C_nH_{2n-4}N^+$) was also found but they were not detected from Murchison. The identification of such CHN compounds was consistent with compound analysis for the methanol extract of the Murchison sample using high-performance LC-MS [2, 10]. Lack of detection of alkylated pyridine homologues from Murchison sample in this study possibly be result from loss of the species by dry polishing of the surface. Intriguingly, spatial distribution of alkylated pyridine homologues in Murray were very similar to that of alkylated piperidine homologues but different with alkylated imidazole homologues. In Murchison, no clear difference of spatial distribution between alkylated imidazole and alkylated piperidine was found in this study, although intensity of signals of those CHN compounds were variable. Although the difference of spatial resolution is possibly attributed to water activity on parent body, further investigations are needed for more detailed discussions.

This study suggests usefulness of the DESI-MS analysis for understanding of spatial distribution of polar organic compounds in primitive meteorites. Particularly, CHN compounds such as alkylated pyridine found in this study may have escaped chemical oxidation during parent-body aqueous alteration and may be primitive compounds [e.g. 2]. We plan further investigation, such as comparison of spatial distribution of the organic compounds with mineralogy using SEM observations. It should provide us important insight of the evolution of the extraterrestrial organic materials.

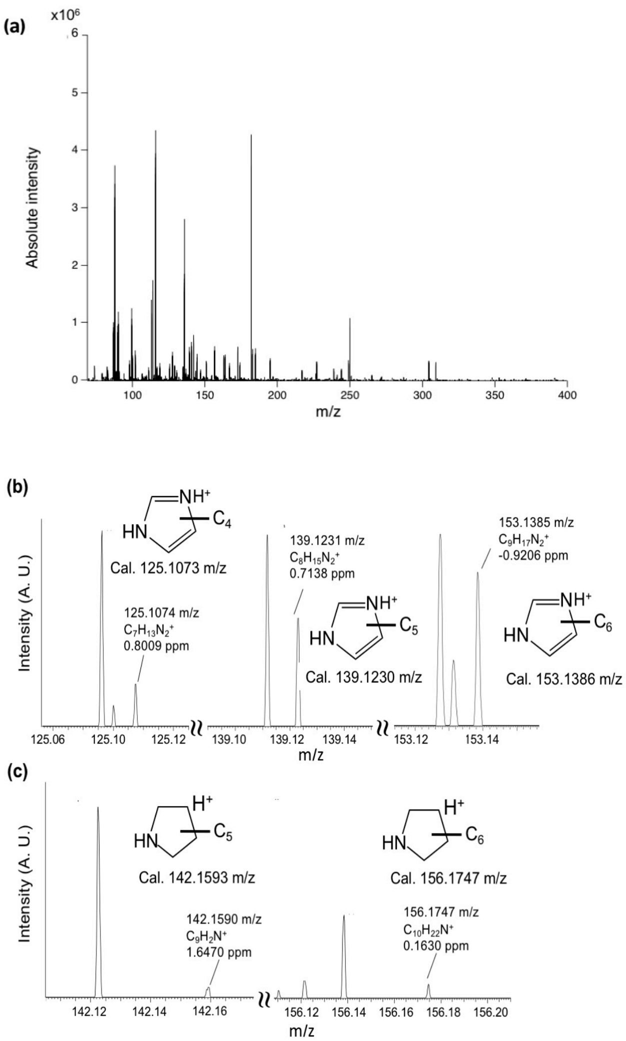


**Figure 1.** High-resolution spectra obtained from surface region of Murchison meteorite. (a) Mass spectra of *m/z* 70–400. Example of spectra of (b) alkylated imidazole homologues ($C_nH_{2n-1}N_2^+$; n=7–9) and (c) alkylated piperidine homologues ($C_nH_{2n+2}N^+$; n=9, 10). Note that these alkylated imidazoles and alkylated piperidines were protonated as $[M+H]^+$. The observed exact mass matched with the corresponding calculated mass value within ~2 ppm in mass precision.

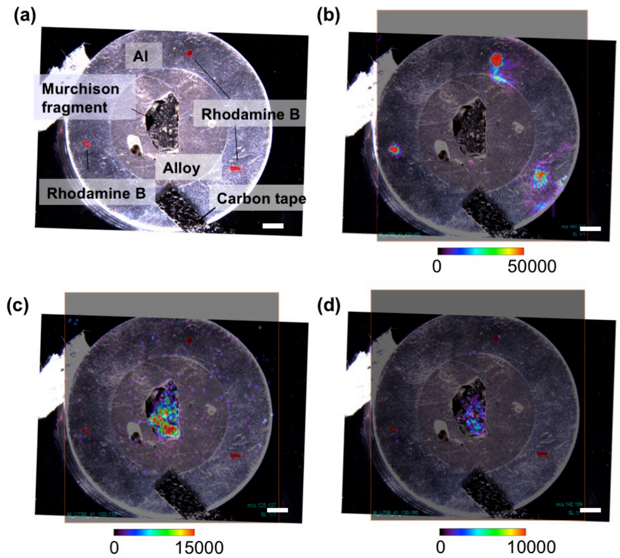


**Figure 2.** (a) Stereomicroscope image of the Murchison meteorite embedded in alloy surrounding by aluminum ring. (b-d) combined DESI-MS spectra images of (b) Rhodamine B positive ion **(**$C_{28}H_{31}N_2O_3^+$; 443.233 m/z) (c) Alkylated imidazole (n=7) ($C_7H_{13}N_2^+$; 125.107 m/z) and (d) Alkylated piperidine (n=9) ($C_9H_{20}N^+$; 142.159 m/z). Note that the mass resolution of these DESI images are within *m/z* ~ 0.001. All white scale bars indicate 1 mm. Color bars correspond intensity of these signals.

**References:** [1] Schmitt-Kopplin P. *et al.* (2010) *PNAS,* 107: 2763-2768. [2] Yamashita Y. and Naraoka H. (2014) *Geochem. J*, 48: 519-525. [3] Clemett S. J. *et al.* (2012) *43rd LPSC* Abstract *#2889*. [4] Clemett S. J. *et al.* (2014) *45th LPSC* Abstract *#2896*. [5] Ito M. *et al*. (2016) *Goldschmidt Conference*, *2016*. Abstract #1297. [6] Pearson V. K. *et al.* (2002) *MAPS*, 37: 1829–1833. [7] Le Guillou C. and Brearley A. (2014) GCA 131: 344-367. [8] Takáts Z. *et al.* (2004) *Science*, 306: 471-473. [9] Wiseman *et al.* (2008) *PNAS,* 105: 18120-18125. [10] Naraoka H. *et al. in prep.*

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