

**FINDING OF NITROGEN-RICH ORGANIC MATERIAL IN ANTARCTIC ULTRACARBONACEOUS MICROMETEORITE.** H. Yabuta<sup>1</sup>, S. Itoh<sup>2</sup>, T. Noguchi<sup>3</sup>, N. Sakamoto<sup>2</sup>, M. Hashiguchi<sup>2</sup>, K. Abe<sup>2</sup>, S. Tsujimoto<sup>3</sup>, A. L. D. Kilcoyne<sup>4</sup>, A. Okubo<sup>5</sup>, R. Okazaki<sup>6</sup>, S. Tachibana<sup>5</sup>, K. Terada<sup>7</sup>, T. Nakamura<sup>8</sup> and H. Nagahara<sup>5</sup>. <sup>1</sup>Dept. Earth and Space Science, Osaka University, Osaka, Japan. <sup>2</sup>Dept. Natural History Sciences, Hokkaido University, Hokkaido, Japan. <sup>3</sup>The College of Science, Ibaraki University, Ibaraki, Japan. <sup>4</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, CA 94720, USA. <sup>5</sup>Dept. Earth and Planetary Science, University of Tokyo, Tokyo, Japan. <sup>6</sup>Dept. Earth and Planetary Sciences, Kyushu University, Fukuoka, Japan. <sup>7</sup>Dept. Earth and Planetary Systems Science, Hiroshima University, Hiroshima, Japan. <sup>8</sup>Dept. Earth and Planetary Materials Science, Tohoku University, Miyagi, Japan. E-mail: hyabuta@ess.sci.osaka-u.ac.jp

**Introduction:** Ultracarbonaceous micrometeorites (UCMMs) are unique extraterrestrial materials that represent large sizes of high carbon contents [1]. The mineralogical and isotopic investigations of UCMMs by [1] have revealed the association of extreme D-rich organic matter with both crystalline and amorphous silicates, which appears to be compatible to cometary origin. However, there have been only two UCMMs reported so far, and little has been known about the nature of UCMMs. In this study, for an UCMM, which was found in ~200 MMs collected in 250 kg of the surface snow near the Dome Fuji Station, Antarctica, we have carried out the systematic studies applying isotope microscopy, focused ion beam (FIB) extraction, scanning transmission X-ray microscopy (STXM) and transmission electron microscopy (TEM) observation to investigate the origin and formation of UCMMs.

**Experimental:** A polished thick section of an ultracarbonaceous micrometeorite (UCMM-DO5IB80) was used in this study.

Isotope imaging of UCMM-DO5IB80 was performed by a Hokudai isotope microscope system (Cameca ims-1270 SIMS equipped with SCAPS) [2]. A ~100 - ~200 pA Cs<sup>+</sup> primary beam in an aperture illumination mode was used to achieve uniform secondary ion emission from a sample area of ~30 × 40 μm<sup>2</sup>. The normal incident electron gun was used to compensate for sample charging. The isotopographs of <sup>1</sup>H-, <sup>2</sup>D-, <sup>12</sup>C-, <sup>13</sup>C-, <sup>12</sup>C<sup>14</sup>N-, <sup>12</sup>C<sup>15</sup>N-, <sup>32</sup>S- and <sup>16</sup>O- were obtained. Hydrogen, carbon and nitrogen isotopic compositions of the UCMM were normalized to the SMOW scale regarding δD, δ<sup>13</sup>C and δ<sup>15</sup>N values of the epoxy used to embed the UCMM as the same as those of SMOW. The digital image processing using a moving average of 3 × 3 pixels (corresponding to 0.6 × 0.6 μm<sup>2</sup>) was applied to the isotope ratio image in order to reduce the statistical error.

A tungsten strap of 1.3 μm thickness was deposited on the surface of the UCMM for FIB extraction (Fig. 2a), and an FIB section with ~100 nm thickness was extracted from the UCMM by a JIB-4501 FIB-SEM microscope at Ibaraki University (Fig. 2b).

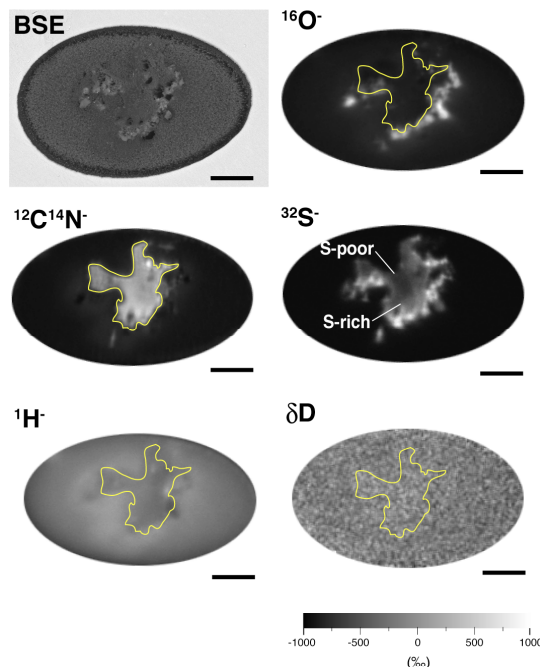


Fig. 1. Isotopographs of UCMM-DO5IB80. Scales are 10 μm. Yellow curves denote the boundary of N-rich carbonaceous matters. A color bar represents the variation of δD.

Carbon-, Nitrogen-, and Oxygen-X-ray absorption near edge structure (XANES) spectra of the FIB section were acquired using STXM at the beamline 5.3.2.2., Advanced Light Source, Lawrence Berkeley National Laboratory. The beamline employs a bending magnet providing the energy range of 270 - 700 eV. Energy calibration was conducted by measuring CO<sub>2</sub> and N<sub>2</sub> gas prior to the measurements. The absorption spectra (optical density, OD) were obtained as  $OD = -\ln(I/I_0)$ , where  $I$  is the X-ray intensity transmitted from the sample and  $I_0$  is that recorded without the sample.

**Results:** Figure 1 shows the <sup>12</sup>C<sup>14</sup>N-, <sup>32</sup>S-, <sup>16</sup>O-, δD images along with the BSE image of the sample. The <sup>12</sup>C<sup>14</sup>N and <sup>32</sup>S distributions in carbonaceous matters from the UCMM clearly show that the carbonaceous matter has the heterogeneously-distributed N-rich and S-rich signatures relative to the surrounding epoxy.

The size of N-rich and S-rich carbonaceous matter is  $\sim 10 \times 20 \mu\text{m}^2$ .  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  images were also taken for the FIB section, and the isotope-ratio images for hydrogen, carbon and nitrogen show that there is no significant difference in isotopic compositions of the UCMM from those of epoxy within analytical uncertainties ( $\delta\text{D} = \sim +100 \pm 300\%$ ,  $\delta^{13}\text{C} = \sim 0 \pm 70\%$ ,  $\delta^{15}\text{N} = \sim +100 \pm 110\%$ ).

A STXM Carbon map clearly shows that organic carbon is distributed all over the FIB section (Fig. 2c). Combining the C-map with a STXM Nitrogen map enabled the identification of organic N-rich and poor regions, respectively (Fig. 2d). N-XANES spectra of N-rich regions 1 and 2 (Fig. 2d) exhibit intense peaks of imine (E), nitrile (F), and amide (G), while that of N-poor region 3 shows a less characteristic spectrum (Fig. 2f). Moreover, the relative abundance of nitrile is varied between the regions 1 and 2. These nitrogen speciations help the characterization of carbon functional groups. Although peaks at  $\sim 286.6$  eV are detected from C-XANES spectra of the entire region, they can be assigned to different functional groups: nitrile (C) for the N-rich regions 1 and 2 and vinyl-keto (B) for the N-poor region 3, respectively (Fig. 2e). Likewise, the peak D is assigned to C=O of amide for the regions 1 and 2, while it is assigned to C=O of carboxyl/ester for the region 3. Aromatic C=C (A) are likely associated to nitrogen in the regions 1 and 2, e.g., pyridine, while that in the region 3 is rather similar to typical chondritic and/or IDP organics [3].

**Discussion:** The N-rich regions within a large range of the UCMM provided a quite sufficient signal-to-noise (S/N), which has not been generally observed in chondritic insoluble organic matter (IOM) and even IDPs, where S/N of their N-XANES spectra are much lower than those of C-XANES [4]. It is noted that the N-XANES spectral patterns of the N-rich regions are very similar to those observed from the three samples of Comet 81P/Wild 2 dust particles, one of which was an organic globule [5, 6]. Nitrogen isotopic composition of the Comet Wild 2 organic globule is indistinguishable from terrestrial values [5], which is consistent to that in this study. Referring to [5], the XANES spectral patterns might be partially reflected by an ion beam artifact, e.g., aromatic nitrogen. Nonetheless, the spectrum is very likely derived from a nitrile (CN)-rich organic matter of UCMM-origin, since we did *not* use any artificial organic nitrogen polymer, e.g., cyanoacrylate glue, for the sample preparation. In addition, that the N-rich and N-poor regions co-exist with a sharp boundary within the particle (Fig. 2d) is intriguing. This may indicate that there exists more than one precursor for extraterrestrial organic matter. Further

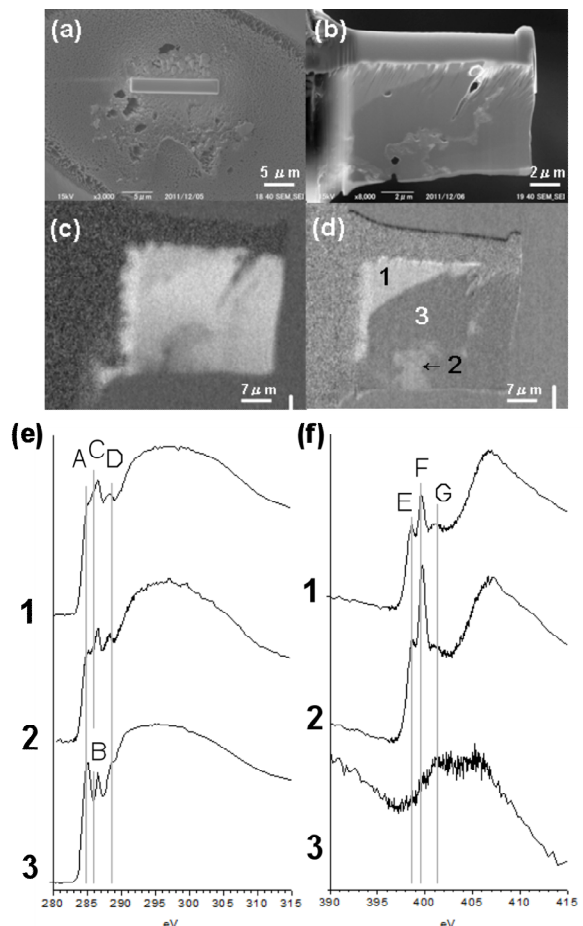


Fig. 2. (a) Tungsten strap of  $1.3 \mu\text{m}$  thickness deposited on the surface of UCMM for FIB extraction, (b) An SEM image of the FIB section, (c) Carbon- and (d) Nitrogen- distribution maps obtained by STXM, and (e) Carbon- and (f) Nitrogen-XANES spectra of the regions 1, 2, and 3 indicated in (d). Peak assignments are based on [4]; A (285.1 eV): C=C, B (286.6 eV): C=C-C\*=O, C (286.6 eV): C\* $\equiv$  N, D: NHx(C\*=O)C ( $\sim 288.3$  eV) or OR(C\*=O)C ( $\sim 288.6$  eV), E (398.8 eV): C=N\*, F (399.7 eV): C $\equiv$ N\*, G ( $\sim 401.5$  eV): N\*Hx(C=O)C.

studies on the possible relationships of the UCMM with IDPs, comets and meteorites from the comprehensive perspectives of mineralogy, isotope, and organic chemistry will be expected. Achievements by TEM observation will also be included at the meeting.

**References:** [1] Duprat J. et al. (2010) *Science*, 328, 742-745. [2] Yurimoto H. et al. (2003) *Appl. Surf. Sci.*, 203-204, 793-797. [3] Cody G. et al. (2011) *PNAS* doi : 10.1073/pnas.1015913108. [4] Cody G. et al. (2008) *Meteoritics & Planet. Sci.* 43, 353-365. [5] De Gregorio et al. (2010) *GCA*, 74, 4454-4470. [6] De Gregorio et al. (2011) *Meteoritics & Planet. Sci.* 46, 1376-1396.