

EVIDENCE OF MINIMUM AQUEOUS ALTERATION IN ROCK-ICE BODY: UPDATE OF ORGANIC CHEMISTRY AND MINERALOGY OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITE.

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Introduction: Ultracarbonaceous micrometeorites (UCMMs) are unique extraterrestrial materials that represent large sizes of high carbon contents [1]. In our recent study of an UCMM D05IB80 collected from near the Dome Fuji Station, Antarctica [2], it has been revealed that: (i) very large-sized organic material (~10 x 20 μm^2) accounted for most part of the sample, (ii) the organic material was extremely rich in nitrogen functional groups such as nitrile, imine, and amide, (iii) sulfur is identified within the organic material surrounded by pyrrhotite rim, and (iv) there was no difference in hydrogen, carbon and nitrogen isotopic compositions between D05IB80 and terrestrial values within analytical uncertainties. These features have not been observed from typical chondritic organic material, while they are partially similar to those from QUE 99177 CR3 [3] and some particles from Comet Wild 2 [4]. In order to enhance our understanding of the origin and formation of UCMMs, we have carried out TEM observation of the focused ion beam (FIB) section of D05IB80.

Sample and Methods: An UCMM D05IB80 was found from the surface snow collected in the 2005 period by the 46th and 47th Japan Antarctic Research Expedition (JARE) teams near the Dome Fuji Station, Antarctica. The collected snow was melted and filtered in a class 1000 clean room at Ibaraki University. The residual particles were manually picked up under a stereomicroscope. Micrometeorites (MMs) were identified by using JEOL JSM-5600LV scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS) at Ibaraki University. Bulk mineralogy of D05IB80 was investigated by using synchrotron radiation X-ray diffraction (SR-XRD) at the Photon Factory Institute of Materials Structure Science, High Energy Accelerator Research Organization.

Then, D05IB80 was embedded in epoxy resin and ultramicrotomed into 70-nm-thick sections. After ultramicrotomy, the potted butt of the micrometeorite was embedded again in epoxy resin to make a flat epoxy disk of 6 mm in diameter for the isotope imaging by a Hokudai isotope microscope system (Cameca ims-1270 SIMS equipped with SCAPS) [5] at Hokkaido

University. Based on the isotopic mapping analysis, a thin section was prepared by the dual beam FIB-SEM JEOL JIB-4501 at Ibaraki University. Because the FIB section of the UCMM was mainly composed of “soft” organic matter and embedding epoxy, the section has almost twice the thickness (200 nm) of the normal FIB section. Carbon-, Nitrogen-, and Oxygen-X-ray absorption near edge structure (XANES) spectra of the FIB section were acquired using a scanning transmission x-ray microscope (STXM) at the beamline 5.3.2.2., Advanced Light Source, Lawrence Berkeley National Laboratory. After STXM, the FIB section was observed by JEOL JEM-2100F field emission TEM at JEOL Corporation and by JEOL JEM-2100 at Ibaraki University.

Results: Approximately 200-nm-thick FIB section is translucent brown under a transmitted light (Fig. 1a). As we can expect from its tenuous external shape, both optical and HAADF-STEM images suggest that the boundary between embedding epoxy (light brown) and the UCMM is complicated.

HAADF-STEM image of the FIB section has parallel grooves that run from upper right to lower left. They are tracks formed by Cs^+ ion implantation during the SIMS mapping analysis (Fig. 1b). Squares are where elemental mapping analysis and high resolution observation of the boundaries between the UCMM and the epoxy were performed. There are two types of boundaries between them, one is smooth and another is globular. As can be seen at the lower left corner, these boundaries are continuous. Therefore, the surface of the UCMM has various surface morphologies.

Although morphologies are considerably different between these boundaries, high-resolution images revealed that there are very thin (< 5 nm) layers composed of less electron transparent material than carbonaceous material at the surfaces of both boundaries. The less electron transparent material is almost amorphous because no lattice fringes were observed. Elemental distribution mappings of these areas have a common feature. Both of the surface areas containing less electron transparent material are enriched in C, O, Si, S, and Fe (Fig. 2a, b). In addition, uniform enrich-

ment of Na and K were observed on the smooth surface (Fig. 2a). On the other hand, sporadic enrichment of Na and Cl were observed in the globular boundary (Fig. 2b).

Minor crystalline phases identified are olivine and Ni-bearing pyrrhotite. Olivine occurs as a polycrystalline aggregate. On the other hand, Ni-bearing pyrrhotite occurs as fine-grained (<50 nm) subhedral to rounded crystals embedded in amorphous silicate. The size and morphology of the amorphous silicate object containing Ni-bearing pyrrhotite are similar to GEMS (glass with embedded metal and sulfide) that are commonly observed in chondritic porous interplanetary dust particles (CP IDPs) (e.g., [6]). However, no Fe-Ni alloy was identified from these GEMS-like objects.

Discussion: Observation of Ni-bearing pyrrhotite and GEMS-like objects without Fe-Ni alloy implies that the UCMM are very slightly aqueously altered.

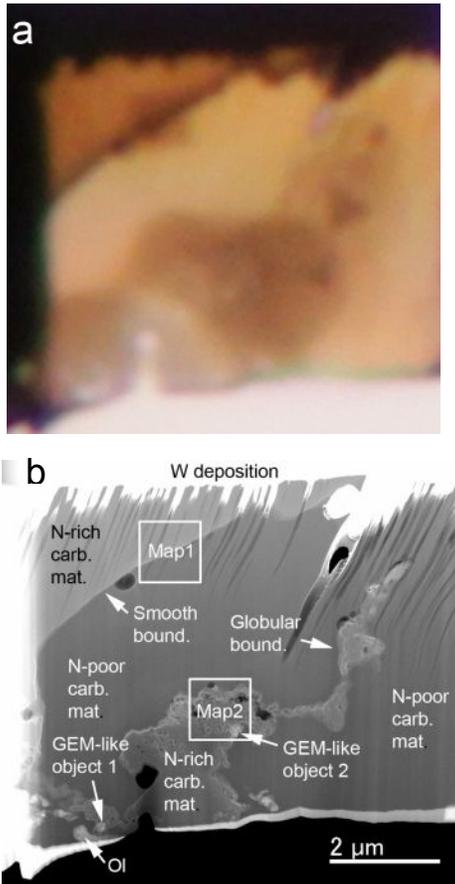


Fig. 1 (a) Transmitted optical image and (b) HAADF-STEM image of the FIB section of D05IB80. The surface of the boundary between the dark (nitrogen-rich) and light brown (epoxy, nitrogen-poor) areas shows two different morphologies: smooth and globular. Two GEMS-like objects and a polycrystalline olivine are also indicated.

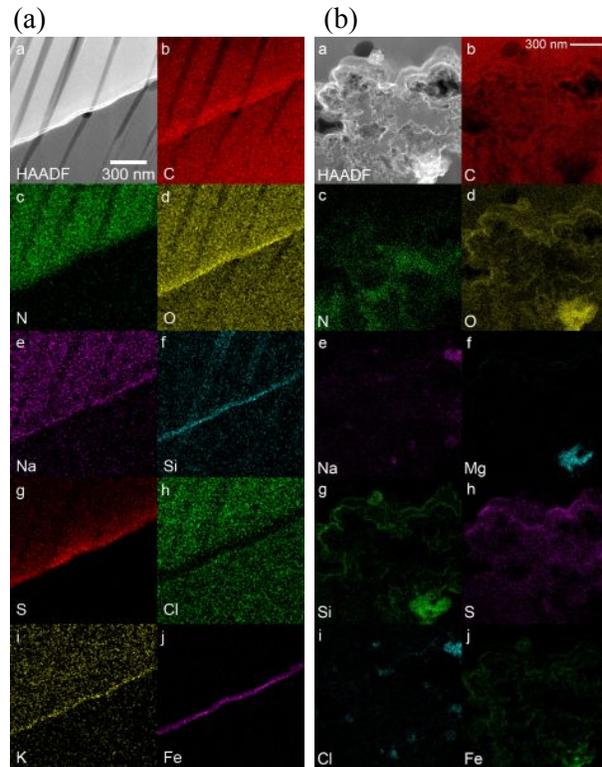


Fig. 2 Elemental distribution maps of (a) "Map1" and (b) "Map 2" in Fig. 2.

This condition could have been locally occurred at the early formation stage of the rock-ice bodies including comets and icy asteroids. The repetitive warming process of ice might have promoted the formation of ten micron-sized large, nitrogen-rich organic material observed from D05IB80, as demonstrated by a photochemical synthesis of complex organic molecules from simulated interstellar/precometary ices (e.g., $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{NH}_3-\text{CO}$) followed by a wetting-drying cycle [7]. According to [7], the experimental organic products are amphiphilic and can assemble into membranous vesicles in polar solvent. This nature seems consistent with the observed globular phases in D05IB80. Finally, association of organic material and sulfur supports the presence of fluid chemistry on the parent body. These features appear to be a very pristine signature of interaction of mineral, ice, and organics in the primitive small body.

References: [1] Nakamura T. et al. (2005) *Meteoritics & Planet. Sci.*, 40, A110. [2] Yabuta H. et al. (2012) *LPSXXXIII*, Abstract 2239. [3] Peeters Z. et al. (2012) *LPSXXXIII*, Abstract 2612. [4] De Gregorio et al. (2010) *GCA*, 74, 4454-4470. [5] Yurimoto H. et al. (2003) *Appl. Surf. Sci.*, 203-204, 793-797. [6] Bradley J. P. and Dai Z. R. (2004) *Ap. J.* 617, 650-655. [7] Dworkin J. P. et al. (2001) *PNAS* 98, 815-819.