

SPATIAL DISTRIBUTION OF SOLUBLE ORGANIC COMPOUNDS AND THEIR RELATIONSHIP WITH MINERALS IN A RYUGU'S GRAIN.

M. Hashiguchi¹, D. Aoki¹, K. Fukushima¹, H. Naraoka², H. Yurimoto³, T. Nakamura⁴, T. Noguchi⁵, R. Okazaki², H. Yabuta⁶, K. Sakamoto⁷, S. Tachibana^{7,8}, S. Watanabe¹, Y. Tsuda⁷, The Hayabusa2-initial-analysis SOM team. ¹Nagoya University (Furo-cho, Chikusa-ku, Nagoya, 464-8601, Japan, hashiguchi@eps.nagoya-u.ac.jp). ²Kyushu University, Fukuoka 819-0395, Japan, 739-8526, Japan, ³Hokkaido University, Sapporo 060-0810, Japan, ⁴Tohoku University, Sendai 980-8578, Japan, ⁵Kyoto University, Kyoto 606-8502, Japan, ⁶Hiroshima University, Higashi-Hiroshima, Hiroshima, ⁷Japan Aerospace Exploration Agency (JAXA), Sagami-hara 252-5210, Japan, ⁸The University of Tokyo, Bunkyo-ku, Tokyo, 113-0033, Japan,

Introduction: The Hayabusa2 spacecraft collected samples from two touchdown sites on asteroid 162173 Ryugu, which is a C-Type asteroid, and returned in December 2020. According to near-infrared spectra from the surface of Ryugu [1] and returned samples [2], Ryugu is expected to contain organic compounds. The carbonaceous chondrites (CCs) contain a variety of such compounds as components of their soluble organic matter (SOM) [e.g., 3], although most of the organic matter in CCs exists as insoluble organic matter (IOM). The properties and distribution of extraterrestrial organic matter are important to understanding the chemical evolution of the solar system and the origin of life; for this reason, understanding the interactions between organics, water, and minerals in samples of Ryugu's surface is necessary to reveal the chemical evolution of its organic compounds, and constitutes one of the prime goals of the Hayabusa2-initial analysis SOM team. In this study, we performed *in-situ* analysis on a Ryugu sample using the desorption electrospray ionization (DESI) technique [4, 5], time of flight-secondary ion mass spectrometry (ToF-SIMS), and mineralogical observation, in order to investigate the relationship of organic compounds to minerals.

Experimental Methods: A Ryugu's grain (A0080) was analyzed in this paper. The grain was embedded in a soft alloy, without any blazing or polishing, because of its fragile nature. Organic molecular imaging was performed on an area 2.8×2.8 mm of the sample surface, using a 2D-DESI ion source (Omni Spray Source 2D, Prosolia Inc.) equipped with a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Scientific) at Kyushu University. The spray solvent was 100% Methanol and the positive ions (m/z 50–500) were collected in full scan mode with a mass resolution of 140,000 ($m/\Delta m$ at $m/z = 200$). After the imaging, the ToF-SIMS measurement was performed using a TRIFT III spectrometer (ULVAC-PHI, Inc.) at Nagoya University. Positive and negative spectra were obtained using an Au⁺ gold beam. Finally, detailed observation for mineralogy was performed using FE-SEM-EDS at Nagoya University. We also analyzed an antigorite grain for the blank and Murchison meteorite (CM2) for comparison.

Results and Discussion: More than 200 positive ion mass spectral peaks were identified from the grain surface of A0080 by DESI imaging. The CHN, CHO, and CHON compounds were assigned m/z values within ± 3 ppm in mass precision. The CHO compounds were dominant among the identified species (~65% in relative intensity). In contrast to many carbonaceous chondrites including Murchison and Tagish Lake [6, 7], Mg-containing compounds were not identified from A0080. This result indicates that Ryugu experienced a lower intensity of metamorphism and/or alteration relative to Murchison and Tagish Lake [6, 7]. The positive ions were heterogeneously distributed in the sample surface, having a single concentrated region. The grain surface showed up to about 150 μm of roughness after DESI imaging, we infer because of the loss of tiny particles from the surface by the spray solvent and/or N₂ gas flow of the DESI system, and the identified positive ions were mainly distributed. However, DESI images of total ions of CHN, CHO, and CHON compounds showed different distributions among these compound classes across the analyzed region (Fig. 1). Fe-sulfide grains, mainly pyrrhotite, and magnetite often occur in the A0080 grain. They have various shapes (large hexagonal tabular, irregular shape, plaquette, and, only for magnetite, framboidal); in this respect, the grain is texturally similar to Orgueil (CI) [8], which is a highly hydrated meteorite. Carbonate grains and rarely anhydrous silicate grains (pyroxene) were also observed, and we detected no chondrule-like object. The region around where organic ions were detected contains two different lithologies: A) large ($>10 \mu\text{m}$) Fe-sulfide, magnetite, and carbonate-rich region and B) a region poorer in such minerals. The CHN compounds appear to be concentrated in the lithology-B, whereas CHO and CHON compounds were distributed across both lithologies (Fig. 2). The different distributions might suggest different synthesis pathways and/or evolution processes for CHN, CHO, and CHON compounds including loss by fluid reaction or migration during aqueous alteration [4, 9].

The identified CHN compounds have many CH₂ families (e.g., C_{*n*}H_{2*n*-8}N⁺), like the Murchison meteorite [3, 4]. Interestingly, each species showed a unique spatial distribution, different from other members of the same chemical family (Fig. 3) — an observation also

similar to a previous study of the Murchison meteorite [4]. The C number of SOM and their spatial distribution in the same CH₂ families in A0080 did not show a clear relationship, whereas CHN compounds in the same CH₂ families in Murchison meteorite tend to be distributed in a carbonate-rich sample as their C number increased. Our results possibly suggest a difference between A0080 and Murchison in the chemical evolution of SOM by the interaction between minerals during aqueous alteration.

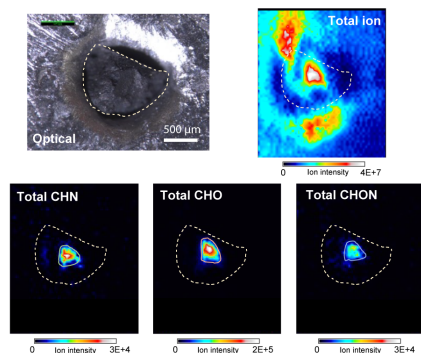


Fig. 1. An optical microscope image and DESI images of total ion, total CHN, CHO, and CHON compounds, respectively. A dotted line in the each image shows the boundary between the A0080 grain and the surrounding metal.

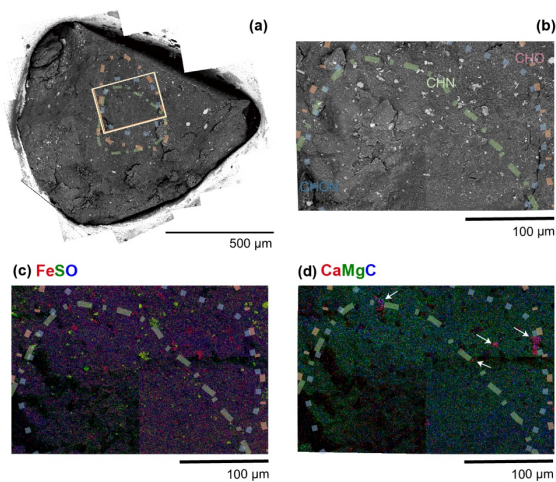


Fig. 2. A back-scattered image (BSE) of the A0080. (b) BSE image obtained from a rectangle in (a). (c) (d) Combined X-ray elemental maps obtained from the same area in (b). Light green grains red grains in (c) correspond to Fe-sulfide (almost pyrrhotite) and almost magnetite, respectively. White arrows in (d) indicate large Ca-carbonate. Dotted lines show the distribution of total CHN (green), CHO (pink), and CHON (blue) compounds. Note that the lower-left region in (c, d) shows low X-ray intensity due to the high roughness and

that the positioning of DESI images and BSE and X-ray map images contains the error of $\pm \sim 20 \mu\text{m}$.

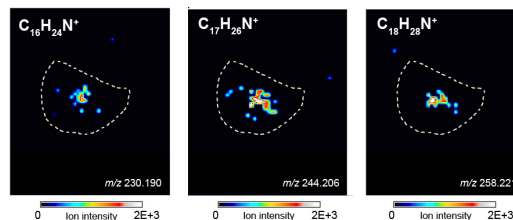


Fig. 3. Various spatial distributions of compounds in the $C_nH_{2n-8}N^+$ series in A0080.

Organic-related ions (e.g. CH_2^+ , CN^- , and CO_2^-) were identified by ToF-SIMS from several regions of the sample surface, however, the abundance of these ions was not consistent with the spatial distribution revealed by DESI imaging. This inconsistency suggests that ions measured by ToF-SIMS mostly come from methanol-insoluble organic compounds, perhaps IOM. Future investigation of the relationship between SOM and IOM in the Ryugu sample may provide us further understanding of the nature and history of the chemical evolution of its organic compounds.

References: [1] Kitazono K. *et al.* (2019) *Science*, 365, 272–275. [2] Pilorget C. *et al.* (2021) *Nat Astron.* <https://doi.org/10.1038/s41550-021-01549-z>. [3] Naraoka H. *et al.* (2017) *ACS Earth Space Chem.* 1, 540–550. [4] Naraoka H. and Hashiguchi M. (2018) *Rapid Comm. Mass Spec.* 32, 959. [5] Hashiguchi M. and Naraoka H. (2019) *MAPS* 54, 452–468. [6] Ruf A. *et al.* (2017) *PNAS* 114, 2819–2824. [7] Hashiguchi M. and Naraoka H. (2019) 50th *LPSC* Abstract #1499. [8] Gounelle M. and Zolensky M. (2014) *MAPS* 49, 1769–1794. [9] Muneishi K. and Naraoka H. (2021) *MAPS* 56, 195–205.

The Hayabusa2-initial-analysis SOM team:

Hiroshi Naraoka, Yoshinori Takano, Jason P. Dworkin, Kenji Hamase, Aogu Furusho, Minako Hashiguchi, Kazuhiko Fukushima, Dan Aoki, José C. Aponte, Eric T. Parker, Daniel P. Glavin, Hannah L. McLain, Jamie E. Elsila, Heather V. Graham, John M. Eiler, Philippe Schmitt-Kopplin, Norbert Hertkorn, Alexander Ruf, Francois-Regis Orthous-Daunay, Cédric Wolters, Junko Isa, Véronique Vuitton, Roland Thissen, Nanako O. Ogawa, Saburo Sakai, Toshihiro Yoshimura, Toshiki Koga, Haruna Sugahara, Naohiko Ohkouchi, Hajime Mita, Yoshihiro Furukawa, Yasuhiro Oba, Yoshito Chikaraishi.