

## The Dark Macromolecular Organic Matter in Asteroid Ryugu Samples Collected by the Hayabusa 2 Spacecraft

Organic matter is an important component in the evolution of the Solar System. On December 6, 2020, samples of the carbonaceous asteroid Ryugu were returned to Earth by the Hayabusa2 spacecraft. The macromolecular organic matter in Ryugu samples contains aromatic and aliphatic carbon, ketone and carboxyl groups. The chemical, isotopic and morphological features of the organic matter in Ryugu samples are consistent with those in primitive carbonaceous chondrite meteorites. Association of Ryugu's organic matter with phyllosilicate and carbonate is likely resulted from reaction with liquid water on the asteroid parent body. The diversity of the organic matter indicates variable levels of aqueous alteration on Ryugu's parent body.

Hayabusa2 is JAXA's asteroid sample return mission that collected samples from the surface of the carbonaceous asteroid Ryugu [1]. The mission's goal was to unveil the origin and evolution of organic compounds and water in the early Solar System as building blocks of planets and Earth-life. After the sample return on December 6, 2020 and the half-year-curatorial work at JAXA [2], the Hayabusa2 Initial Analysis Team conducted one-year mission to achieve the scientific objectives of the mission through high-precision analysis of the asteroid samples [3-8].

The Hayabusa2 Initial Analysis Organic Macromolecule team has investigated macromolecular organic matter from the Ryugu samples by coordinating various analytical techniques; micro-Fourier transform infrared (FTIR) spectroscopy, micro-Raman spectroscopy, scanning transmission X-ray microscopy (STXM), X-ray absorption near edge structure (XANES), scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS), atomic force microscope based IR spectroscopy, and nanometer-scale secondary ion mass spectrometry (NanoSIMS) [8]. Intact Ryugu grains and insoluble carbonaceous residues isolated by acid treatment of the Ryugu samples were examined, respectively. The insoluble residues recovered in high yield and in high purity was dark-colored organic solids.

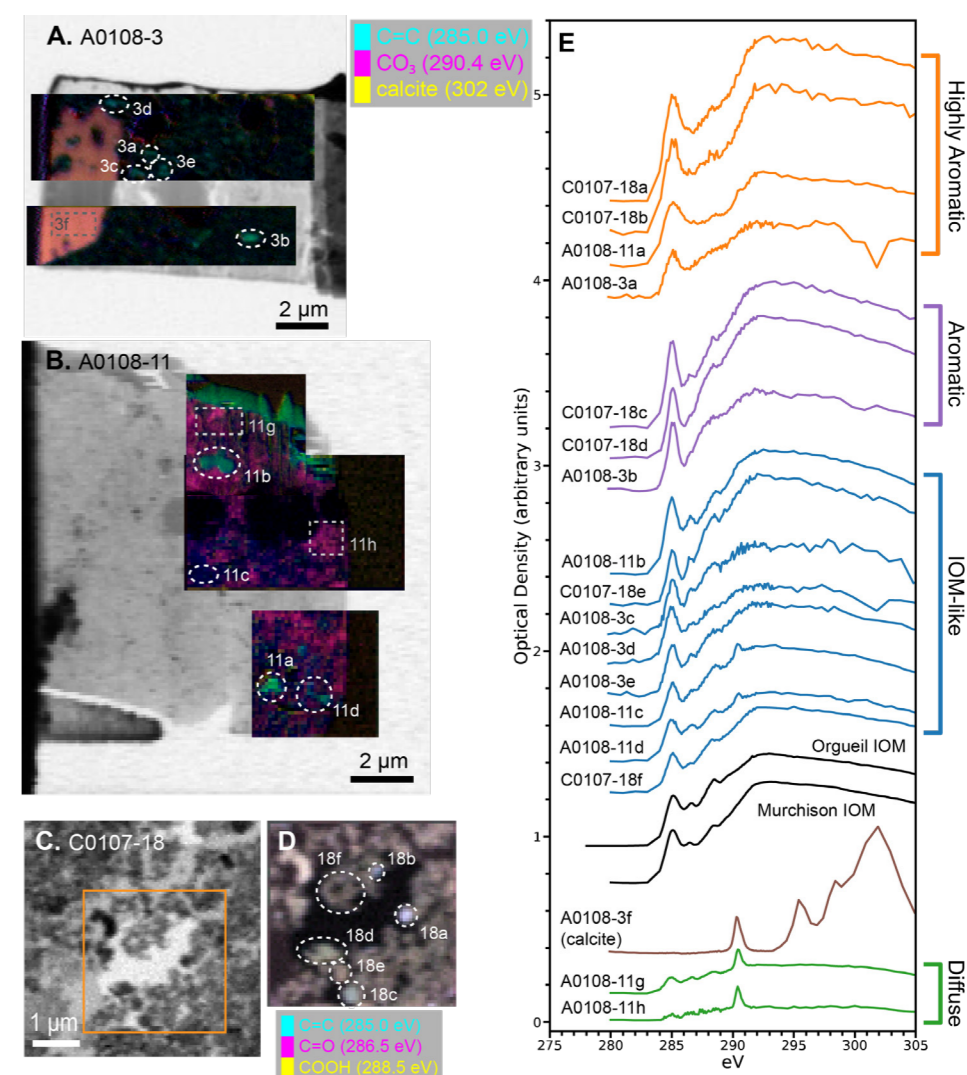
STXM-XANES, micro-FTIR, and micro-Raman measurements showed that macromolecular organic matter in Ryugu samples contained disordered, polyaromatic structures consisting of aromatic carbons, aliphatic carbons, ketones and carboxyls. The chemical structures are similar to that of insoluble organic matter (IOM) from primitive carbonaceous CI (Ivuna-type) and CM (Mighei-type) chondritic meteorites. NanoSIMS measurements showed that the bulk hydrogen and nitrogen isotopic ratios of carbonaceous grains in Ryugu samples were also similar to the bulk values and IOM of CI chondrites.

Combination of STXM-XANES and STEM-EELS-EDS revealed the chemical and morphological variations of organic matter in asteroid Ryugu. The carbon-XANES

spectra of Ryugu organic matter showed more diversity than those of meteorites, and they were classified into four types; i) highly aromatic (~25% of individual carbon grains), ii) aromatic (~35% of individual grains), iii) meteoritic IOM-like (~40% of individual grains), and iv) diffuse carbon (Fig. 1). These spectral patterns correlated with the morphologies of nano-sized organic matter. Organic nanoglobules are aromatic-rich, while organic matter mixed into Mg-rich phyllosilicate matrix and associated with carbonates were IOM-like or diffuse carbon containing molecular carbonate. Phyllosilicates and carbonates likely formed through aqueous alteration. The presence of organic matter associated with these minerals implies that a majority of the organic matter was chemically modified by various degrees of aqueous alteration on Ryugu's parent body. Progressive aqueous alteration causes: i) an increase in the amount of diffuse organic matter associated with phyllosilicates through hydrolysis of primordial macromolecular organic matter or intercalation and oxidation of soluble molecules, ii) an increase in the proportion of aromatic and oxygen-bearing functional groups in discrete organic particles and nanoglobules through aromatization and oxidation of macromolecular organic matter, and iii) an increase in macromolecular diversity.

According to NanoSIMS measurements, some of the carbonaceous grains in the Ryugu samples showed extreme deuterium (D) and/or nitrogen-15 ( $^{15}\text{N}$ ) enrichments or depletions, which are indicative of origin in an extreme cold environment below  $-200^\circ\text{C}$ , such as interstellar molecular cloud or solar nebula.

Our study has first proved the direct link between organic matter in the carbonaceous asteroid and that in primitive carbonaceous chondrites. The result provides further evidence that the organic matter formed in interstellar medium and solar nebula were modified by aqueous alteration on Ryugu's parent body. The dark, macromolecular organic matter could explain the low albedo of the asteroid Ryugu's surface. It could have contributed to the organic inventory available for the formation of habitable planetary environments.



**Figure 1:** (A and B) STXM images of ultrathin sections from the Ryugu grains. Color overlays on both sections are X-ray absorptions maps of individual functional groups. (C) STXM image of insoluble carbonaceous residue from Ryugu sample. (D) X-ray absorption map of individual functional groups. (E) Carbon-XANES spectra for carbonaceous grains and matrix regions identified in (A), (B), and (D). Carbon-XANES spectra show three major peaks, resulting from aromatic carbon (285 eV), aromatic ketone (286.7 eV), and carboxyl (288.5 eV). Some spectra contain a peak at 290.4 eV, corresponding to carbonate groups [8]. The data was acquired at beamline BL-19A, Photon Factory, and beamline 5.3.2.2, Advanced Light Source.

### REFERENCES

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BEAMLINE  
BL-19A

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