

VARIETY OF ORGANIC FUNCTIONAL CHEMISTRY IN RYUGU ORGANIC MATTER. B. T. De Gregorio¹, G. D. Cody², A. L. D. Kilcoyne³, R. M. Stroud¹, S. A. Sandford⁴, H. Yabuta⁵, H. Yurimoto⁶, T. Nakamura⁷, T. Noguchi⁸, R. Okazaki⁹, H. Naraoka⁹, K. Sakamoto¹⁰, S. Watanabe¹¹, Y. Tsuda¹⁰, and S. Tashibana¹² and the Hayabusa2 Organic Macromolecule Initial Analysis Team, ¹U.S. Naval Research Laboratory (Code 6366, 4555 Overlook Avenue SW, Washington, DC 20375; bradley.degregorio@nrl.navy.mil), ²Carnegie Institution for Science, Washington, DC, ³Lawrence Berkeley National Laboratory, Berkeley, CA, ⁴NASA Ames Research Center, Moffett Field, CA, ⁵Hiroshima University, Hiroshima, Japan, ⁶Hokkaido University, Sapporo, Japan, ⁷Tohoku University, Sendai, Japan, ⁸Kyoto University, Kyoto, Japan, ⁹Kyushu University, Fukuoka, Japan, ¹⁰Japanese Aerospace Exploration Agency, Sagami-hara, Japan, ¹¹Nagoya University, Nagoya, Japan, ¹²University of Tokyo, Tokyo, Japan.

Introduction: Analyses of regolith samples from asteroid 162173 Ryugu returned by the JAXA Hayabusa2 mission confirm the predicted connection between C-type asteroids and carbonaceous chondrite meteorites [1,2]. In addition, Ryugu samples enable measurement of pristine carbonaceous asteroid material, free from terrestrial contamination or shock-related effects from meteoroid ejection events. Characterization of the diversity of organic functional group chemistry in Ryugu carbonaceous grains, as well as its relation to grain morphology and local mineral composition, will provide a better understanding of synthesis and modification of organic macromolecules that occurred on asteroid parent bodies [3].

Samples and Methods: Several particles from Ryugu aggregate samples A0108 and C0109, along with grains from two acid-extracted insoluble organic matter (IOM) residues A0106 and C0107 were embedded in sulfur and ultramicrotomed. Letter designations “A” and “C” refer to samples from the first and second touchdown sites, respectively. Sections from the aggregate particles were placed on lacey C transmission electron microscopy (TEM) grids, while sections from the IOM residues were placed on Quantifoil TEM grids. An additional section was extracted from particle A0108-11 with a FEI Helios G3 focused ion beam (FIB) microscope.

Synchrotron-based x-ray absorption near-edge structure (XANES) spectroscopy was performed with the scanning-transmission x-ray microscopy (STXM) at beamline 5.3.2.2 at the Advanced Light Source, Berkeley, CA. Hyperspectral data stacks and line scans were acquired from carbonaceous grains and the surrounding fine-grained matrix at a spatial resolution of 50 nm/pixel and up to 0.1 eV energy resolution. Correlated STEM imaging and spectroscopy of selected C-rich features was performed with an aberration-corrected Nion UltraSTEM 200-X [4].

Results: *Carbonaceous Grains.* C-rich grains >200 nm were observed in C-STXM maps of the matrix sections (Fig. 1A). However, the maps also showed pervasive carbonaceous matter associated with

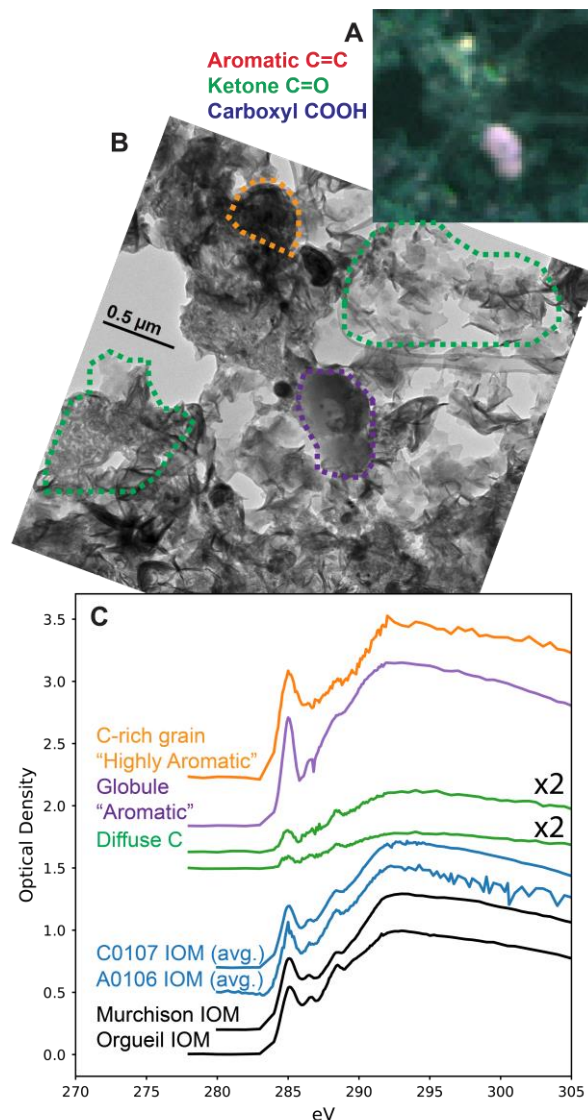


Figure 1. (A) False-color STXM image of two C-rich grains from C0109-11. The region outlined in purple is a compound nanoglobule. (B) Corresponding STEM image, dominated by matrix phyllosilicates. (C) C-XANES spectra of the two grains and diffuse carbon (outlined in green) in the matrix.

fine-grained matrix material, predominantly phyllosilicates [4]. This distribution of carbonaceous matter was also observed in the FIB liftout section (Fig. 2A). Many of the discrete C-rich grains have C-XANES spectra with three main pre-edge peaks (285.0 eV due to aromatic C=C bonding; 286.5 eV due to aromatic ketone -C=O functional groups; 288.5 eV due to carboxyl -COOH groups), consistent with previous studies of IOM [5] and *in situ* chondritic carbonaceous matter [6]. We designate this XANES spectral shape as *IOM-like*. In contrast, many C-rich grains in the Ryugu samples have a C-XANES spectrum with a dominant aromatic C=C peak (Fig. 1C). These spectra fall into two spectral categories—*Highly Aromatic*, having a broader aromatic peak and less intensity in the carbonyl photoabsorption bands, indicative of larger polyaromatic domains, and *Aromatic*, having little to no ketone peak but showing broad photoabsorption between 287–289 eV (Fig. 1C). Of 44 nanoglobules and other discrete compact carbonaceous grains in both sectioned particles and IOM samples, 57% have either an Aromatic or Highly Aromatic spectral shape (25% and 32% respectively). This appears to be a significantly higher abundance of aromatic carbonaceous material than that reported in previous studies of *in situ* carbonaceous matter and IOM in CM and CI chondrite meteorites [5,6]. N-XANES spectra indicate lower N abundance than CR IOM, similar to CI and CM IOM [7].

Diffuse Carbon. Diffuse organic matter is intimately mixed with fine-grained matrix phyllosilicates, sulfides, and oxides, which taken together contributes a significant amount of the total organic content of Ryugu samples. C-XANES spectra of this material typically shows IOM-like spectra, with significant variations in the relative intensity of the three characteristic pre-edge peaks. In some regions, a sharp peak at 290.4 eV was observed (Fig. 2). This would typically be assigned to the CO₃ functional groups in carbonates, but the lack of carbonate extended fine structure indicates that this is a molecular carbonate species. This spectral feature was occasionally noted in diffuse carbon in Type 1-2 chondrite matrices [6] and has been shown to originate from organic matter bound to clay interlayer sites [8]. This peak is noticeably absent from all IOM spectra, indicating this clay-bound carbon is lost or modified during the acid extraction process.

Discussion: Previous studies of aqueous alteration of the Tagish Lake meteorite [9] and CM chondrites [10] have shown that light to moderate hydrothermal processing results in an increase in the amount of diffuse organics and an increase in the relative proportion of aromatic and oxygen-bearing functional

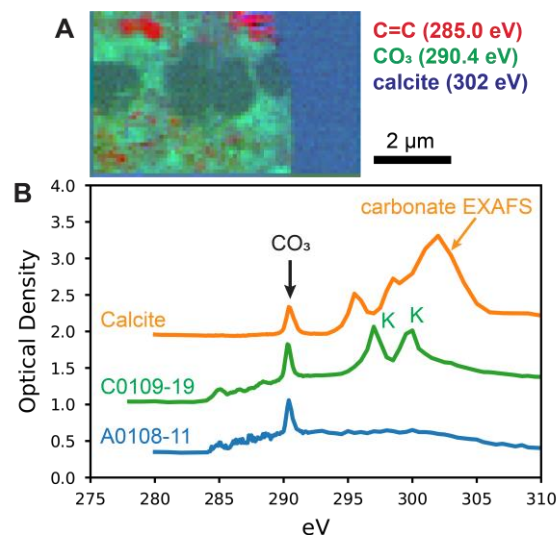


Figure 2. (A) False-color STXM image of a FIB section from A0108-11. Molecular carbonate is prevalent in the fine-grained matrix but is not associated with either the C-rich grains or carbonate minerals. (B) Some representative XANES spectra of clay-bound molecular carbonate in Ryugu.

groups. Ryugu organic matter fits these criteria, and therefore the high functional group diversity observed with STXM can be explained by parent body aqueous processing, culminating in both extensive diffuse C and Aromatic nanoglobules. The Highly Aromatic grains, on the other hand, could have an alternative origin from radiation processing in nebular or cold molecular cloud environments [5]. Ryugu organic matter could encompass both a component of primitive nebular material as well as highly evolved, aqueously altered material.

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