

FUNCTIONAL GROUP COMPOSITIONS OF MACROMOLECULAR ORGANIC GRAINS IN (162173) RYUGU IN RELATION TO CARBONACEOUS CHONDRITES.

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Introduction: The JAXA Hayabusa2 spacecraft collected surface regolith from C-type asteroid (162173) Ryugu during two separate touchdown events (stored in sample chambers A and C, respectively). Preliminary examinations of these samples by JAXA Curation [1] and Hayabusa2 Initial Analysis Teams [2,3] indicate a strong connection to Ivuna-type (CI) carbonaceous chondrites, in agreement with orbital-based near-infrared spectroscopy of the asteroid surface [4]. Scanning-transmission X-ray microscopy (STXM) and X-ray absorption near-edge structure spectroscopy (XANES) of Ryugu insoluble organic matter (IOM) residues also indicates a strong similarity with other aqueously-altered carbonaceous chondrites, specifically CI, CM, and the C-ungrouped Tagish Lake [3,5]. However, these studies also reported the presence of carbonaceous sub-grains with functional group distributions previously unseen in these chondrite groups. Here we further investigate the differences in organic macromolecular material between Ryugu and CI chondrites using correlated XANES, transmission electron microscopy (TEM), and nanoscale secondary ion mass spectroscopy (NanoSIMS).

Samples and Methods: Ryugu regolith grains were prepared from aggregate samples A0108 (from Chamber A) and C0109 (from Chamber C). Samples were either prepared by sulfur embedding and ultramicrotomy or by a focused ion beam (FIB) liftout procedure, and a corresponding suite of samples were prepared from fragments from the CI chondrite Orgeuil. STXM/XANES data were acquired at beamline 5.3.2.2 and 5.3.2.1 at the Advanced Light Source, or beamline BL-19 at the Photon Factory. Subsequently, TEM characterization was performed with an aberration-corrected Nion UltraSTEM 200-X at the U.S. Naval Research Laboratory using a 60 keV beam. Nitrogen and carbon isotopes of FIB section A0108-3 were also measured with a Cameca NanoSIMS 50L at the Carnegie Institution for Science.

Results and Discussion: The functional chemistry distribution of carbonaceous grains in Ryugu samples can be categorized into three main groups based on their XANES spectral shapes. The first two, IOM-like and Highly Aromatic, match the functional group diversity typically observed in nanoglobules from carbonaceous chondrites [6]. Likewise, carbonaceous grains in the Orgeuil samples also produced XANES spectra that matched either of these spectral “fingerprints”. In contrast, Ryugu samples contained carbonaceous grains with a third spectral shape, characterized by a large, narrow peak at 285 eV (due to C=C bonds), little to no peak at 286.7 eV (ketone C=O), and broad intensity at 288-289 eV (a combination of aliphatic C-C and carboxyl COOH). This Aromatic spectral shape could be consistent with a macromolecular structure composed of small, highly-modified, polyaromatic moieties connected by long aliphatic side chains, which could have been generated on the Ryugu parent body during aqueous alteration.

By correlating NanoSIMS, TEM and XANES data from FIB section A0108-3, we hope to glean information regarding the origin(s) of these three XANES spectral shapes. ¹⁵N/¹⁴N isotope ratios of most of the IOM-like and Aromatic carbonaceous grains in this FIB section were all anomalous relative to the bulk value of the section (i.e., diffuse organic matter interspersed within the fine-grained matrix). The two Highly Aromatic grains in the section contained slightly negative $\delta^{15}\text{N}/^{14}\text{N}$ values (-89±58 and -120±66), indicating these grains formed from distinct reservoirs of organic precursors, than the IOM-like and Aromatic grains. These data also suggest that the presence of the Aromatic functional chemistry profile is unlikely to come from addition of a separate population of organic precursor material, but rather was generated on the parent body in combination with IOM-like products.

References: [1] Yada T. et al. (2022) *Nature Astronomy* 6:214-220. [2] Yurimoto H. et al. (2022) *LPSCLIII*: 1377. [3] Yabuta H. et al. (2022), *LPSCLIII*: 2241. [4] Kitazato K. et al. (2019) *Science* 364: 272-275. [5] De Gregorio et al. (2022) *LPSCLIII*: 1634. [6] De Gregorio et al. (2013) *Meteoritics & Planetary Science* 48: 904-928.