

ANALYTICAL ELECTRON MICROSCOPY OF ORGANIC MATTER IN RETURNED SAMPLES FROM ASTEROID RYUGU.

R. M. Stroud^{1,*}, B. T. De Gregorio¹, K. D. Burgess¹, B. Cymes², J. Barosch³, L. R. Nittler³, T. Okumura⁴, M. Hashiguchi⁵, H. Yabuta⁶, T. Noguchi⁷ and the Hayabusa2 Macromolecular Organics and Sand Initial Analysis Teams. ¹Naval Research Laboratory, Washington, DC, USA (*current contact: rhonda.stroud@asu.edu), ²NRC Postdoctoral Fellow, Naval Research Laboratory, Washington, DC, USA, ³Earth and Planets Laboratory, Carnegie Institution of Washington, Washington, DC, USA, ⁴University of Tokyo, Tokyo, Japan, ⁵Nagoya University, Nagoya, Japan, ⁶Hiroshima University, Hiroshima, Japan, ⁷Kyoto University, Kyoto, Japan.

Introduction: Insoluble organic matter in carbonaceous chondrites has been studied extensively in order to constrain the history of the evolution of organic carbon in the solar system and the role of asteroids in delivery of prebiotic chemistry to the early Earth [1]. These studies have shown both that the organic matter can be considerably altered by hydrothermal processing on the asteroid, and that D and ¹⁵N isotopic composition indicators of outer nebula or molecular cloud origin can survive moderate levels of such parent body alteration. As revealing as the study of meteoritic organics has been, all such studies suffer from sampling biases associated with the factors necessary for meteorites to have reached Earth from the parent asteroid and survived atmospheric entry and the exposure to the terrestrial atmosphere. The direct laboratory study of organic matter in returned asteroid regolith, presently from C-type asteroid Ryugu, and in future from asteroid Bennu, provides an unprecedented opportunity to examine asteroid organic matter with established provenance and minimal artifacts from terrestrial alteration. As part of the Hayabusa2 initial analysis of Ryugu samples, we have used analytical transmission electron microscopy to study the microstructure, elemental composition, and functional chemistry of Ryugu insoluble organic matter, and the relationship to fine-grained minerals.

Methods: The samples for these studies included whole particles, extracted focused ion beam (FIB) cross-sections, microtomed slices of particles, and microtomed slice of insoluble organics isolates (IOM) from both the Chamber A and Chamber C collections. This range of samples and preparation methods allowed for investigation of a wide range of different aspects of the samples, such as the greatest preservation of mineral-organic textural relationships and possible soluble components in FIB sections, and observation of the few-nm to sub-nm features in the microtomed samples.

Transmission electron microscopy studies were performed with two microscopes: a JEOL 2200FS operated at 200 kV for bright field imaging, and a Nion UltraSTEM-X operated at 60 kV and 200 kV for annular dark field imaging, energy dispersive x-ray spectroscopy (EDS) of the elemental composition and electron energy loss spectroscopy (EELS) of the C K-edge fine structure and plasmon regions. The EDS and EELS data were collected with Bruker Xflash 100 and Gatan Enfium spectrometers attached to the UltraSTEM, respectively.

Results: The results of the electron microscopy studies of the organic matter confirm a strong link between the Ryugu regolith samples and carbonaceous chondrites in general and are most similar to observations of organic matter in CI chondrites such as Orgueil that have undergone low temperature aqueous alteration. Diffuse organic carbon is abundant, intermixed with μm to sub- μm minerals, including Mg-rich phyllosilicates, magnetite, carbonates and sulfides. Solid and hollow nanoglobules are present as isolated particles, most commonly < 400 nm diameter, and in clusters, with a few individual nanoglobules extending to as large as 2 μm . Nanodiamonds are also present in clusters surrounded by amorphous carbon. Two FIB sections revealed secondary minerals with interior vesicles. One of these sections, sample A0108-3, transected vesicles in a calcite grain that contain diffuse organics and nanoscale silicates and sulfides. The other (AP002-g01T5) preserved closed vesicles in a pyrrhotite grain that contain C-rich fluids. The EELS observations of the C bonding indicate that the diffuse carbon interspersed in Mg-rich phyllosilicates has a strong absorption feature at 290.4 eV associated with CO₃ groups, and varying amounts of other functional groups, including aromatic, ketone, aliphatic and carboxyl. The functional group chemistry of the nanoglobules includes particles that are dominated by aromatic groups (285 eV), and others with significant amounts of ketone (286.5) and carboxyl (288.5) groups. Finally, some aromatic carbon is present as coatings on nanoscale secondary minerals, including Fe and Cu-bearing sulfides. Taken together, the results demonstrate complex records of preaccretionary and parent body processing in the Hayabusa2 samples from Ryugu.

References: [1] Alexander, C. M. O'D. et al. *Chemie der Erde* 77, 227-256 (2007).

Acknowledgements: This work is funded by NASA awards 80HQRT19T0050, NNX16AK72G and 80NSSC20K0340.