2884
doi:10.1017/S1431927621010059
Microsc. Microanal. 27 (Suppl 1), 2021

Sample Preparation and Coordinated Analysis for Characterization of Organic Matter in Return Samples from the Carbonaceous Asteroids Ryugu and Bennu

Bradley De Gregorio[1] and Rhonda Stroud[2]

[1]U.S. Naval Research Laboratory, Washington, District of Columbia, United States, [2]U.S. Naval Research Laboratory, United States

Asteroid surface samples returned to Earth by the Hayabusa2 and OSIRIS-Rex space missions (to asteroids Ryugu and Bennu, respectively) will provide definitive evidence connecting C-type asteroids to carbonaceous chondrite meteorites. They will also be the most pristine samples available for the study of insoluble organic matter (IOM) and other carbonaceous materials that preserve a record of the early history of our solar nebula. Previous work on small (~10 μm) particles from comet 81P/Wild 2 returned by the Stardust spacecraft successfully utilized coordinated synchrotron-based STXM-XANES, TEM-EDS, and NanoSIMS to identify authentic cometary IOM and found that most of it shares functional group diversity and isotopic compositions with meteorite IOM [1]. However, because the sizes of many of the regolith particles in the Hayabusa2 sample canister are $>10^2$ μm, and the anticipated sampling from Bennu will likely contain similarly sized particles, sample preparation methods developed for Wild 2 samples need to be modified. Here, we describe a hybrid FIB-SEM + ultramicrotomy protocol to prepare sections for coordinated STXM/TEM analysis from a large (~350 μm) particle of crushed meteorite. This protocol is an improvement from previous approaches [2, 3] because it provides serial sections while preserving asteroidal organic matter. We selected the JbiletWinselwan carbonaceous meteorite as an analog sample for its similar IR spectral signature and heating history to Ryugu [4, 5]. Using a FEI Helios G3, a 15x15 μm "chunk" was extracted from the particle and attached to the tip of a wedge-cut Cu TEM grid (Figure 1A,B). The tip of this grid was then embedded in S to protect the chunk from organic contamination, and the entire grid wedge was embedded in epoxy (Figure 1C,D). Serial ultramicrotome sections were created for a variety of coordinated analysis techniques—thicker sections for NanoSIMS and IR measurements and 70 nm sections on lacey C grids for STXM/TEM—following the collaborative model set for Ryugu return samples. The S was removed by overnight heating at 60 °C.

The organic functional group composition of IOM in JbiletWinselwan was analyzed with the polymer STXM at beamline 5.3.2.2 at the Advanced Light Source. Several globular grains of IOM were located, showing C-XANES spectral features consistent with a kerogen-like, polyaromatic-rich, macromolecular structure containing ketone (C=O) and carboxyl (COOH) functional groups. The abundance of the O-bearing functional groups is similar to other members of the same meteorite class, but the aromatic carbon peak is increased by 40%, indicating a slightly elevated thermal history for JbiletWinselwan, most likely due to shock events on its parent asteroid [5]. Simultaneous imaging, EELS, and EDS spectrum images were acquired on the same section at 60 keV with the aberration-corrected Nion UltraSTEM200-X at NRL, equipped with a GatanEnfinium ER EEL spectrometer and a Bruker 0.7 sr windowless EDS system. Additional high-resolution EDS maps were also acquired using Bruker Esprit software. Both the lower resolution and high-resolution EDS datasets found variations in N content within the globular IOM, ranging from 0.7-2.3 at.%., which are correlated with subtle changes in C-EELS spectra consistent with inelastic scattering with aromatic C=N in pyrrole and pyridine functional groups. The IOM is also unexpectedly enriched in S (0.5 at.%), which is not common in other IOM samples that are S embedded, suggesting it is indigenous to the IOM. The variable N enrichment is likely due to a diverse assemblage of IOM precursor material, which was later modified into a single macromolecular grain during the hydrothermal alteration phase on its parent asteroid. The S enrichment could also have been formed at the same time, either in contact with a sulfide mineral or S-bearing amorphous silicate grain, or through reaction with dissolved S compounds [6].

In addition to these data providing a better understanding of the formation and evolution of IOM in meteorites and asteroid return samples, it is clear that a combination of analytical techniques is necessary to gain a more

complete picture. STXM-XANES provides the best spectral signature for characterizing the functional group composition of IOM but does not have the spatial resolution or sensitivity to identify variations at the ~10 nm scale that STEM-EELS-EDS can. Conversely, STEM-based characterization of IOM, even at 60 keV, can be complicated by effects of beam damage.

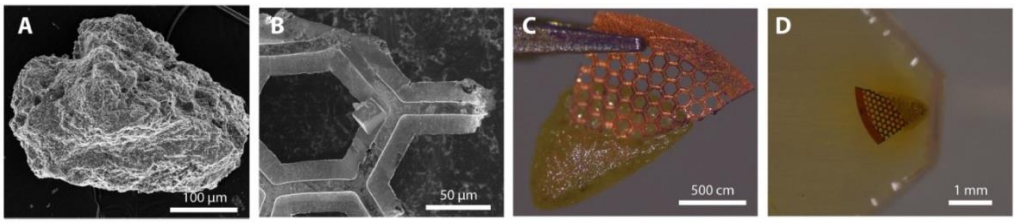

Figure 1.(A) Secondary electron (SE) image of JbiletWinselwan matrix particle. (B) SE image of extracted chunk after placement on cut grid. (C) Cut grid after coating in S. (D) Final double-embedded sample.

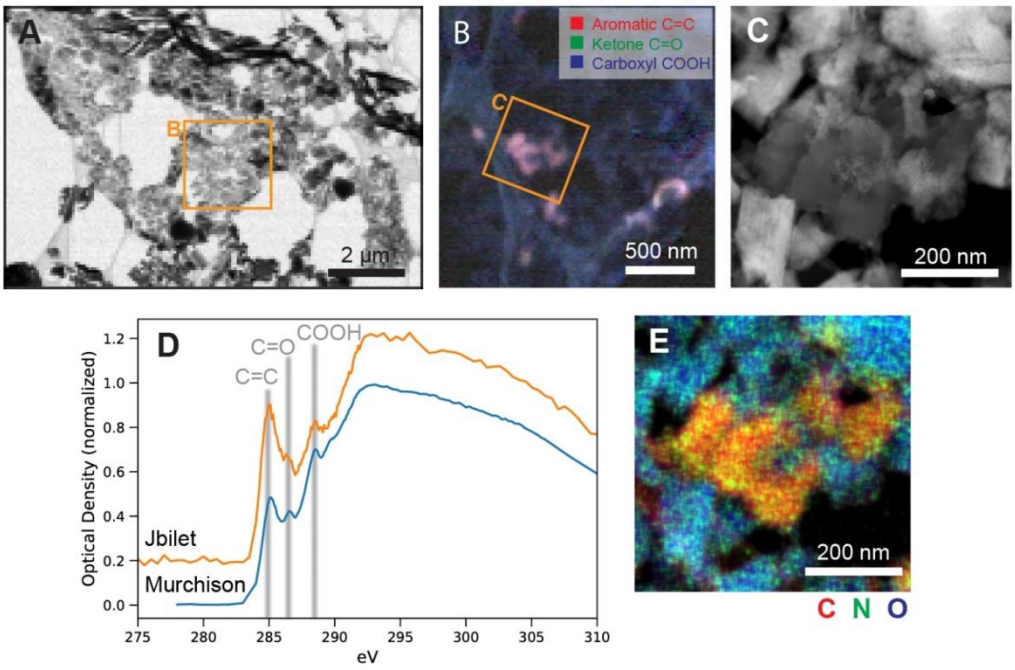

Figure 2. (A) STXM image of JbiletWinselwan section. (B) False-color RGB image of X-ray absorption for the three major organic functional groups. (C) STEM image of globular IOM. (D) C-XANES spectra of IOM grains compared with average Murchison IOM. (E) EDS map of IOM showing variations in N concentration.

References

[1] De Gregorio B. T. et al. (2011) Meteoritics & Planetary Science, 46, 1376-1396.
[2] Berger E. L. and Keller L. P. (2015) Microscopy Today, 23, 18-23.
[3] Ohtaki K. K. et al. (2019) Microscopy & Microanalysis, 26, 120-125.
[4] Kitazato K. et al. (2019) Science, 364, 272-275.
[5] King A. J. et al. (2019) Meteoritics & Planetary Science, 54, 521-543.
[6] Alexander C. M. O'D. et al. (2017) Chemie der Erde, 77, 227-256.

https://doi.org/10.1017/S1431927621010059 Published online by Cambridge University Press