

NANOSCALE HETEROGENEITY OF INSOLUBLE ORGANIC MATTER FROM PRIMITIVE CHONDRITES. B. T. De Gregorio¹, C. M. O'D. Alexander², and R. M. Stroud¹, ¹U.S. Naval Research Laboratory (Code 6366, 4555 Overlook Avenue SW, Washington, DC 20375; e-mail: bradley.degregorio@nrl.navy.mil), ²Earth and Planets Division, Carnegie Science (Washington, DC).

Introduction: Insoluble organic matter (IOM) is a macromolecular organic solid that comprises the majority of carbonaceous material in carbonaceous chondrite meteorites [1]. IOM from a given meteorite sample shows consistent macro-scale elemental, isotopic, and functional group composition (except for brecciated samples, which can contain a range of IOM characteristics [2]), creating a basis for comparative chondrite studies, e.g., [3]. However, recent work using synchrotron-based scanning-transmission X-ray microscopy (STXM) and state-of-the-art aberration-corrected scanning-transmission electron microscopy (STEM) with electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS) has shown that IOM contains significant heterogeneity at the sub- μm scale [4-6].

With regard to future sample returns from sampling missions to the carbonaceous asteroids 162173 Ryugu and 101955 Bennu, we are evaluating current methods for analyzing and characterizing meteoritic IOM in small samples, which will then be used to infer global characteristics of the entire asteroid. In particular, we seek to identify nanoscale heterogeneity that can affect larger-scale bulk measurements, and analysis conditions that may alter IOM.

Samples and Methods: Fresh, 35 nm ultramicrotome sections were created from S-embedded IOM powders from Dominion Range (DOM) 08006 (CO3) and Murchison (CM2). These hydrated and anhydrous IOM endmembers, while not direct analogs to Ryugu and Bennu, should represent the possible types of organic matter that could be returned from those asteroids. Sections were placed on C support films with regularly-spaced holes to aid in relocating analyzed regions between analyses.

Samples were first characterized by STXM and X-ray absorption near-edge structure spectroscopy (XANES) at beamline 5.3.2.2 at the Advanced Light Source, Berkeley, CA. Subsequently, the same areas were re-characterized using the Nion UltraSTEM 200 at the U.S. Naval Research Laboratory. To decrease potential beam damage from the 60 keV STEM probe, EELS spectrum images were collected with “sub-raster” mode, such that the beam is rastered over each 10x10 nm EELS pixel to spread out the electron dose. In addition, EDS using a 0.7 sr Bruker Quantax Si drift detector was simultaneously collected during each 5 s pixel acquisition.

Results: Variations in functional group chemistry were observed at the ~ 100 nm scale in STXM-XANES data, primarily between IOM with distinct textures (e.g., porous, non-porous, and/or globular). These variations were dominantly due to the relative proportions of large aromatic domains vs. smaller aromatic domains with attached carbonyl functional groups [1]. Restricting XANES data to only the nonporous IOM matched previous results. However, similar spectral variations were also observed at the ~ 10 nm scale with STEM-EELS within porous IOM textures, particularly

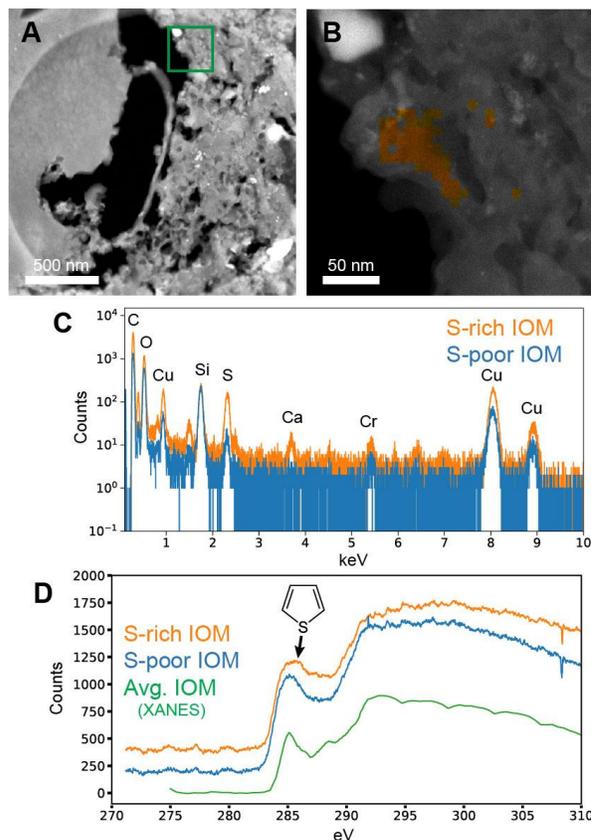


FIGURE 1. (A) HAADF-STEM image of IOM from DOM 08006 spanning a hole in the carbon support film. (B) HAADF-STEM image of 320x320 nm region located by the box in (A), with an overlay of S-rich analysis “spots”. (C) Summed EDS spectra of S-rich and S-poor IOM. (D) EELS spectra corresponding to the same areas in (C), indicating the presence of thiophene functionality in the S-rich areas.

in the Murchison sample, requiring several EELS spectrum images before a “bulk” spectrum could be determined.

Both DOM 08006 and Murchison contain nm-scale regions of IOM with detectable enrichments in S [Figure 1]. Although this S enrichment was too low to allow S-edge XANES or EELS at this scale, C-edge EELS indicates that in DOM 08006, S is primarily incorporated in aromatic thiophene groups. In Murchison IOM, however, this thiophene peak doesn't appear in spectra from S-bearing IOM, suggesting S is more likely located in monosulfide bonds like thiols, as observed in previous bulk measurements of Murchison [7-9]. Since these regions of S-enrichment are small, they are not observable by STXM-XANES, but specifically require high-resolution STEM-EELS-EDS for detection and characterization.

N enrichments were also observed in Murchison IOM. However, due to the prevalence of carbonyl functional groups in the IOM, a clear N-bearing functional group could not be identified using only C edge analysis. Previous work using N edge EELS had identified imine functional groups in 50-100 nm N-rich nanoglobule rims in the CR2 Northwest Africa (NWA) 852 [4] and in non-porous IOM fragments from CO3.0-3.4 chondrites [5].

Beam Damage. Unlike previous experiments using similar photon doses, Murchison IOM was clearly altered during STXM measurements in this study [Figure 2]. Since DOM 08006 IOM was not altered in this way, we believe this STXM damage is due to beam heating, which could not be effectively dissipated because of the lack of an underlying support film. Consequently, STEM-EELS analysis of STXM-exposed and unexposed areas reveal slight differences in functional group composition.

In contrast, we found that by carefully minimizing exposure to 60 keV electrons and using “sub-raster” mode while collecting EELS spectrum images, no significant visual changes were observed in either IOM. However, the broadened features in all EELS datasets indicates that some chemical changes are occurring. H loss is known to occur, even at these energies [10, 11].

Discussion: Because only small amounts of regolith material will be returned from the sampling missions to Ryugu and Bennu, asteroid-scale interpretations will be made from μm - and nm-scale measurements of individual carbonaceous grains. This study shows that combined STEM-EELS-EDS will be necessary to measure functional group composition of S and/or N that may be present in the return samples. However, STEM does induce changes in functional group chemistry, even using “low energy” 60 keV electrons. Ideally, a combination of STXM-XANES

and STEM-EELS-EDS will provide the best results. Thermal alteration of unsupported samples during STXM should be taken into account when planning experimental procedures, although this effect should be minimal in focused ion beam extracted samples, where the carbonaceous matter is surrounded by inorganic materials.

Acknowledgments: This work was funded by the NASA Emerging Worlds program.

References: [1] Alexander C. M. O'D. et al. (2017) *Chemie der Erde*, 77, 227-256. [2] Herd C. D. K. et al. (2011) *Science*, 332, 1304-1307. [3] Alexander C. M. O'D. et al. (2007) *GCA*, 71, 4380-4403. [4] Vollmer C. et al. (2014) *PNAS*, 111, 15338-15343. [5] De Gregorio B. T. et al. (2015) *LPSCXLVI*, 2951. [6] De Gregorio B. T. et al. (2013) *M&PS*, 48, 904-928. [7] Bose M. R. A. and Pizzarello S. (2017) *M&PS*, 52, 546-559. [8] Okumura F. and Mimura K. (2011) *GCA*, 75, 7063-7080. [9] Orthous-Daunay F. R. et al. (2010) *EPSL*, 300, 321-328. [10] De Gregorio B. T. et al. (2010) *GCA*, 74, 4454-4470. [11] Le Guillou C. et al. (2013) *Icarus*, 226, 101-110.

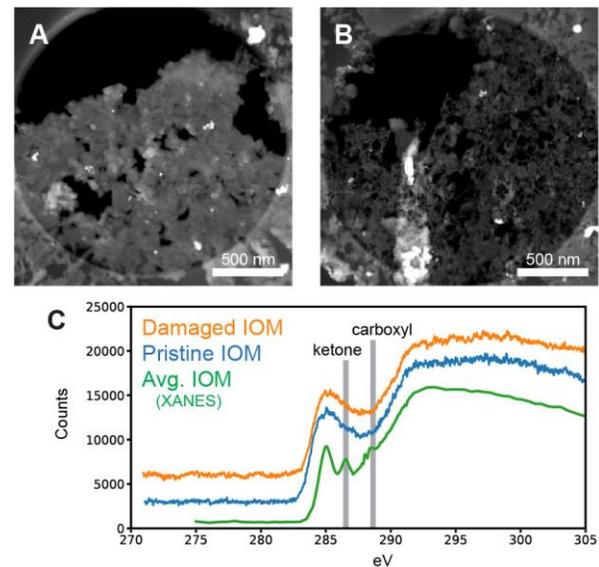


FIGURE 2. (A) HAADF-STEM image of Murchison IOM previously analyzed by STXM. (B) HAADF-STEM image of adjacent hole. (C) STEM-EELS comparison of STXM-damaged and pristine IOM. Only the pristine IOM shows visible evidence for ketone functional groups, which have been damaged during the STXM acquisition.