

ELEMENTAL COMPOSITION AND FUNCTIONAL CHEMISTRY VARIATION AT THE NANOSCALE IN INSOLUBLE ORGANIC MATTER FROM CARBONACEOUS CHONDRITES R. M. Stroud¹, B. T. De Gregorio¹, C. M. O'D. Alexander², ¹Materials Science and Technology Division, US Naval Research Laboratory, Washington, DC 20375, ²Carnegie Institution of Washington, Washington, DC 20015, USA (email: rhonda.stroud@nrl.navy.mil)

Introduction: Organic matter constitutes up to 3-4 wt.% of the matrices of carbonaceous chondrites (CCs), and the majority of that organic matter is acid-insoluble kerogen-like material. The insoluble organic matter (IOM) is distributed throughout the matrix as nanoscale coatings on grains, discrete sub-micron to micron sized particles, and occasionally in large veins extending several microns. The “bulk” elemental and isotopic composition, functional chemistry, and the microstructure of the IOM can vary significantly within and between the different CC groups. This is due to parent body alteration history, and to a lesser extent differences in the distribution of materials accreted. Despite the susceptibility of the IOM to chemical and physical alteration by processing in the parent asteroids, variations in the H and N isotopic compositions at the micron and smaller scales reveal some IOM retains signatures of primordial molecular cloud, interstellar or outer solar nebula origins [1].

Comparison of multi-technique analyses of IOM in different meteorite classes, in cometary samples, and in returned asteroid samples is the most insightful, though labor intensive, way to better decipher the formation and evolution of organic matter in the early solar system. Coordinated IOM studies often involve X-ray absorption near edge spectroscopy (XANES) for determination of C functional chemistry variations at ~ 50+ nm scale, secondary ion mass spectrometry (SIMS) for determination of C, H, O and N isotope compositions at 100+ nm, transmission electron microscopy (TEM) for elemental compositions and structure at 1+ nm scale, and FTIR spectroscopy for molecular speciation (1,000+ nm). A multimodal approach is necessary in order to distinguish preserved primordial from heavily altered components. Despite concerns of beam damage, electron energy loss spectroscopy (EELS) is an attractive alternative to XANES for determination of C functional chemistry, because it can be carried out as part of routine TEM analysis along with high-resolution imaging and energy dispersive x-ray (EDX) elemental analysis. In this study, we compare coordinated C-K edge XANES and EELS data from a range of CCs groups. Our data show the importance of coordinated EELS-EDX scanning transmission electron microscopy (STEM) measurements for revealing the variation in N elemental abundance and functional groups. These methods will be

critical for maximizing the science return for analysis of organic matter in Ryugu and Bennu samples.

Methods: The preparation of IOM samples, and their bulk properties were reported previously [2]. For this coordinated STXM-STEM study, we prepared ultramicrotome sections of sulfur-embedded IOM from Elephant Moraine (EET) 94024 (CR2), Allan Hills (ALH) 77307 (CO3), and Murchison (CM2). The thickness of the sections was varied (50 to 100 nm) in order to determine an optimum trade-off between minimizing multiple scattering effects for 60 kV STEM analysis and maintaining a nominal X-ray scattering cross-section for adequate STXM signal-to-noise. The sections were placed on Quantifoil™ TEM grids to allow measurement of sample over holes in the support film, to further minimize multiple scattering. Microtomed sections of a focused -ion-beam extracted chunk of Jbilet Winselwan (CM2) for in situ analysis were also prepared. The XANES measurements were carried out at the Advanced Light Source beam line 5.3.2.2, as 25 nm/px stacks. The STEM-EELS-EDX and imaging were performed on the same samples at the Naval Research Laboratory with the Nion UltraSTEM200-X, operated at 60 keV. The STEM SI data were obtained as simultaneous EELS-EDX spectrum images, with nominal resolutions of 20 nm/px. Higher resolution EDX SIs were subsequently obtained with the Bruker Esprit system.

Results: Multiple STXM and STEM datasets from EET 92042, ALH 77307, Murchison and Jbilet were obtained. One example dataset from EET 92042 is illustrated in Figs. 1-3. The high angle annular dark field (HAADF) STEM image (Fig. 1) reveals abundant nanoglobules, and mineral grain inclusions. The C, N, O RGB elemental map extracted from the STEM-EDS SI clearly reveals that the 400 nm nanoglobule in the bottom right is N rich, compared to the material in the center of the ROI (Fig. 2). Extracted EDX sum spectra from the N-rich globule (ROI 1), the N-poor region (ROI 2), and the full SI, quantitatively demonstrate that N, but not O, is enriched in ROI 1 compared to the “bulk” value of the full SI sum spectra. This enrichment is critical to the interpretation of the simultaneously acquired STEM-EELS C-K edge data (Fig. 3), and corresponding XANES data. The extracted EELS spectrum from N-rich ROI 1 reveals that the N is incorporated in aromatic C=N bonds, which are less

pronounced in the full sum spectrum and ROI 2. No increase in peak intensity at 286.7 is observed, for which nitrile ($C\equiv N$) can be ruled out in favor of a constant abundance of ketone ($C=O$) groups. The XANES sum spectrum from approximately the same area provides higher energy resolution (0.1 eV compared to 0.4 eV), but poor signal, due to the thinness of the sample (~ 50 nm) and collection time limitations. Sub-regions of the C XANES data do not have sufficient signal to spatially resolve the $C=N$ variations, and N XANES could not be obtained with sufficient signal to detect the N. Another important difference between the EELS and XANES data, is that the intensity of the carboxyl (COOH) feature is significantly reduced in the EELS spectra compared to the XANES. This was also observed for datasets obtained from ALH 77307, which show more prominent carboxyl features.

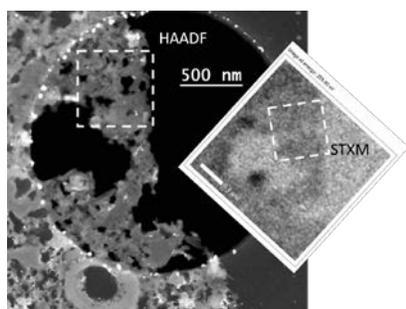


Figure 1. HAADF image and 285.6 eV STXM image of EET 92042 IOM isolate over a hole in the TEM support film. The dashed white boxes indicate the area of the STEM-EDX-EELS acquisition.

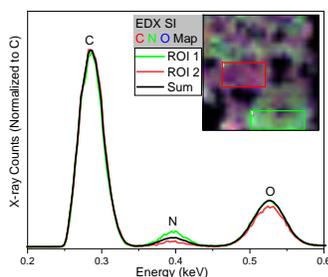


Figure 2. STEM-EDX-SI data from EET 92042 IOM.

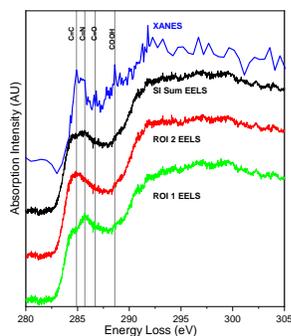


Figure 3. Comparison of STEM-EELS-SI and XANES C-K edge data from EET 92042.

Discussion: Cometary and asteroidal organic matter has been studied extensively with synchrotron XANES, in order to map C functional chemistry distributions, e.g., [3]. When performed on a soft X-ray beamline, these measurements are generally less prone to induce alteration of the IOM than are comparable STEM-EELS measurements. More recent use of lower voltage, cold-FEG UHV STEM techniques, i.e., ‘gentle-STEM’, has been suggested as a possible way to reduce, though not completely eliminate, the electron beam alteration of the organics and allow important high-spatial resolution discoveries [4]. In addition, when combined with STEM-EDX, these measurements have the potential to resolve ambiguity in the assignments of features in the C-K edge spectra, e.g., nitriles and ketone, or sulfur-bearing groups, and allow for straight forward quantitative determination of C:N:O:S abundances. So far, no detailed assessment of the degree of reduction of damage, or range of applicability to IOM of different levels of damage susceptibility has been published.

Our analysis indicates that the low voltage STEM methods preserve the aromatic functional groups, but that significant loss of aliphatic groups that contain H occurs, even for heated meteorites such as ALH 77307 (CO3) and Jbilet Winselwan (CM2). For future Ryugu and Bennu sample analysis, this indicates continued reliance on a combination of XANES and STEM-EDX-EELS is the best approach, along with complementary SIMS and optical spectroscopies is the best approach. Additional strategies, such as the use of a cryogenic STEM sample holder, and more efficient EELS detectors can offer additional improvements, but introduce other trade-offs.

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References: [1] Alexander C. M. O’D. et al. (2017) *Chemie der Erde*, 77, 227-256. [2] Alexander, C. M. O’D., et al.. *GCA*, 71, 4380–4403 (2007). [3] Le Guillou C. et al. (2014) *GCA*, 131, 368-392. [4] Vollmer, C. et al. (2020) *Sci. Rep.*, 10, 20251.