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Nanoscale Variation in Carbonaceous Matter from Primitive Meteorites Revealed by Aberration-Corrected STEM.

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The majority of the organic matter (OM) at the surface of the early Earth was delivered by primitive meteorites and comets. By studying the characteristics of OM in meteorites and/or cometary dust, we can gain insight into the overall galactic pathway(s) of organic precursor molecules present in the early Solar Nebula (and in the collapsed molecular cloud from which it formed) that eventually provided components for prebiotic chemistry on Earth. In particular, we are interested in robustly distinguishing the signatures of OM that are representative of various asteroidal, nebular, and pre-nebular (e.g., molecular cloud) processes [1]. However, distinguishing these signatures is non-trivial and requires analysis of fine-scale heterogeneities to separate features with unique chemical signatures [2, 3]. To achieve the required spatial and spectral resolution, previous work has mostly relied on coordinated, multi-instrument analysis, such as XANES (characterization of C bonding at 0.1 eV energy resolution) + TEM (observation of sub-nm morphology) [3, 4]. TEM-based EELS is generally not suitable for these studies as typical operating conditions (e.g., 200 keV with a 200pA probe) can cause observable changes in the organic functional chemistry of meteorite OM. The feasibility of using an alternative "gentle" STEM approach (i.e., 60 keV in a UHV aberration-corrected microscope) was recently demonstrated [5]. In this study, we demonstrate the advantages of using the "gentle" STEM approach with both EELS and EDS for faster, more complete characterization of meteorite OM.

Three insoluble organic matter (IOM) residues, created by acid dissolution of silicate minerals from the DOM08006, EET92042, and Murchison meteorites [1], were selected to represent different asteroidal processing regimes. Particles of IOM were embedded in S and then ultramictrotomed to obtain 30 nm sections, which were placed on lacey C TEM grids. Analyses were carried out at 60 keV with the Nion UltraSTEM200 at NRL, equipped with a Gatan Enfinium ER EEL spectrometer and a Bruker window-less, SDD x-ray spectrometer (~0.6 sr). Hyperspectral EELS datasets at the C K-edge were acquired from 250 nm × 250 nm regions at 8 nm/pixel, with a measured resolution (FWHM) of 0.30 eV. Subsequently, hyperspectral EDS maps were collected from the same region. The combined analysis time for both techniques was less than 45 min, with no detectable changes to the sample chemistry. With this EDS setup, we were able to quantify a 50% N enrichment in a 5 nm rind surrounding a spherical organic globular feature [Figure 1A, B].

The most primitive IOM sample, DOM08006, contains two main textural components, a "fluffy" material composed of connected carbonaceous nanoparticles, forming a porous network with high surface area, and a "compact" material of dense, non-porous carbonaceous matter, some of which forms large pieces extending several μm^2 in size [Figure 1C]. The EDS data reveal that the compact IOM has a high S abundance (6 at.%) [Figure 1D]. Furthermore, EELS data indicate the two textures contain distinct organic functional group chemistry [Figure 2]. Specifically, the fluffy IOM spectra show high intensity of the 285.0 eV π^* peak (due to aromatic C=C bonding) and of the 290.1 eV σ^*_1 peak (due to graphitic ordering), consistent with poorly graphitized C. This is consistent with the overall petrologic history of the meteorite, which has experienced heating on the parent asteroid at ~200 °C [6]. However, the compact, S-rich IOM lacks these heating spectral features, but rather has increased intensity at 286.7 eV and at 288.5 eV, which are indicative of carbonyl-bearing (C=O) modification of aromatic C [Figure 2]. This S-rich IOM appears to be absent in EET92042, and therefore may be a unique component in DOM08006 (and its related meteorites from the same parent asteroid). Whether this S-rich IOM is due to variation in precursor chemistry or is related to the particular processing history of the parent asteroid will be determined by its S bond distribution. Measurements of S-EELS and simultaneous C+S-EELS using the DualEELS are planned to address these questions [7].

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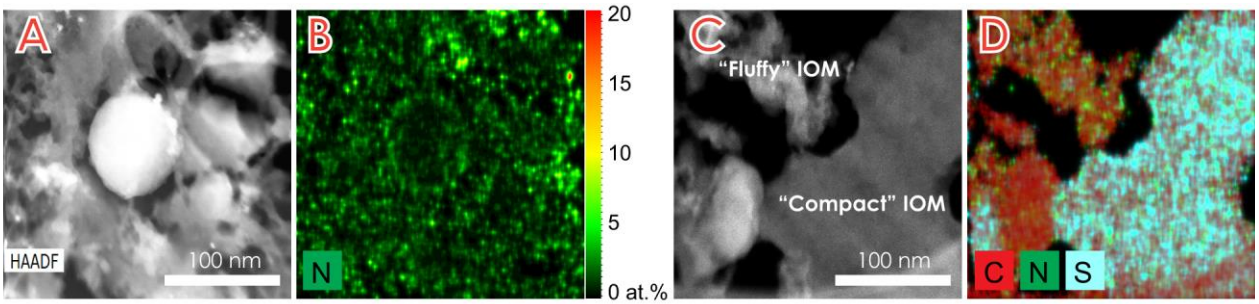

Figure 1. Meteorite IOM from DOM08006. (A) HAADF image and (B) EDS N abundance map of a 95 nm organic nanoglobule with a 5 nm N-rich rind. (C) HAADF image and (D) EDS hyperspectral map of "fluffy" and "compact" IOM textures.

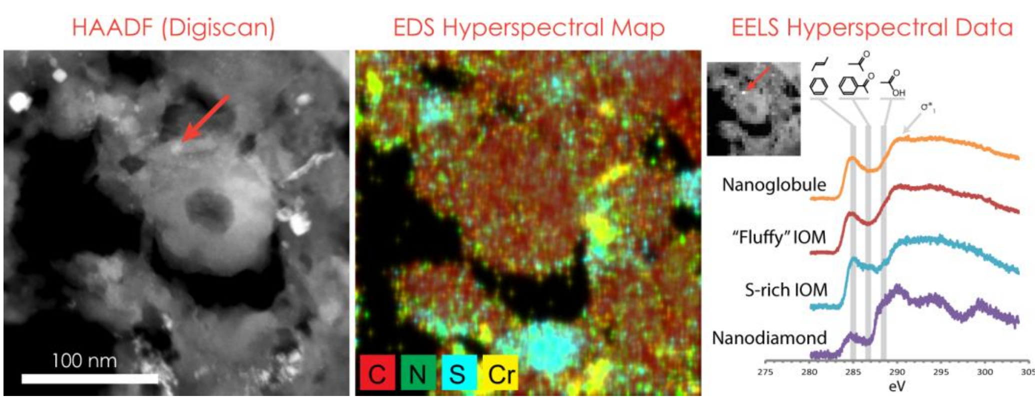

Figure 2. Hyperspectral EELS/EDS dataset from a hollow organic nanoglobule in DOM08006. A 7 nm nanodiamond is also present (red arrows and purple spectrum).

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