DETECTION OF ORGANIC COMPOUNDS WITH ONE-NANOMETER SPATIAL RESOLUTION.
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Introduction: The nature of meteoritic organic matter is highly relevant to astrobiology and the origin of prebiotic matter on the early earth [1-3]. Identification of organics in general and specific classes of organic compounds in particular is limited by low abundances, molecular heterogeneity and the nanometer-scale distribution of organics among meteoritic lithic components. Features due to organic compounds occur in the 1-5 eV region in electron energy-loss spectra, but they are difficult to resolve because of poor energy resolution and overlap with the broad tails on the zero-loss electron beam. Using a monochromated electron beam with improved energy resolution (~0.1-0.2 eV) we are able to detect features in organic and inorganic materials with energy losses ≤5 eV and spatial resolution of ~1 nanometer [3,4]. We used this new capability to detect a 5.7 eV (220 nm) feature in organic carbon-rich IDPs, thereby solving a half-century-old mystery in observational astronomy, the origin of the ~220 nm UV extinction feature, the strongest feature from dust in the interstellar medium [5]. Here we report new low-loss data from organic compounds as well as our first data in the near-IR, a region where multiple classes of organic compounds have characteristic spectral features.

Experimental Techniques: Experiments were performed using monochromated FEI Tecnai and Titan monochromated and aberration-corrected microscopes at Lawrence Livermore National Laboratory (LLNL) and the National Center of Electron Microscopy (NCEM), Lawrence Berkeley National Laboratory (LBNL). Spectra were acquired at 80, 200 and 300 keV in monochromated STEM mode using the Gatan Tridiem electron energy loss image filters (GIFs). Sub-nanometer resolved probes were used with full-width half-maxima (FWHM) on the zero-loss peak (ZLP) between 0.08 and 0.18 eV. For the 80 and 300 keV experiments, 30 spectra were collected, each with 0.5 seconds acquisition times using a 1 mm opening aperture on the GIF, and then summed to resolve low-loss fine structure between 0 and 20 eV. Over the course of acquiring 30 individual spectra, a small 1 eV offset was applied to the drift tube and, if low loss signal bounced outside the specified drift bounds, the spectrum was rejected and another spectrum was taken.

Results: Low-loss features from coronene ($C_{24}H_{12}$), pyrene ($C_{16}H_{10}$) and 1-pyrene carboxaldehyde ($C_{17}H_{10}O$) are shown in Figure 1. They indicate that the low-loss ~5.7 eV (220 nm) feature is characteristic of polyaromatic hydrocarbons (PAHs). (Interstellar PAHs are the most widely accepted carrier of the astronomical 220 nm feature [6]). Variation in the strengths of the features are likely PAH abundance-dependent. Since the features are from pure compounds, variation in their positions and shapes is likely related to the number of rings in the aromatic chromophores and side-chain functionalities.

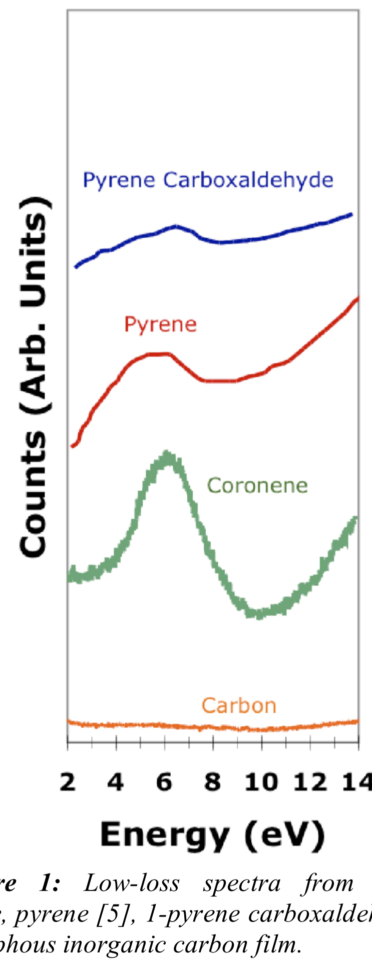

Figure 1: *Low-loss spectra from the PAHs coronene, pyrene [5], 1-pyrene carboxaldehye [5] and an amorphous inorganic carbon film.*

Figure 2 shows low-loss features from carbonaceous matter in Orgueil acid residue, an HF-etched IDP (W7207A-8), and carbonaceous matrix unetched IDPs

(W7013E17) and sub-grains in three unetched IDPs (L2047 D23, L2036-C18-F4 and L2047 D23 [5]). The features confirm that PAHs are present in meteorite acid residues and in etched and unetched chondritic IDPs. Non-solar $^{12}C/^{13}C$and $^{14}N/^{15}N$ abundances in IDPs L2047 D23 and L2036 C18 F4 suggest that the carriers of the 5.7 eV feature may be outer nebular or interstellar PAHs [7].

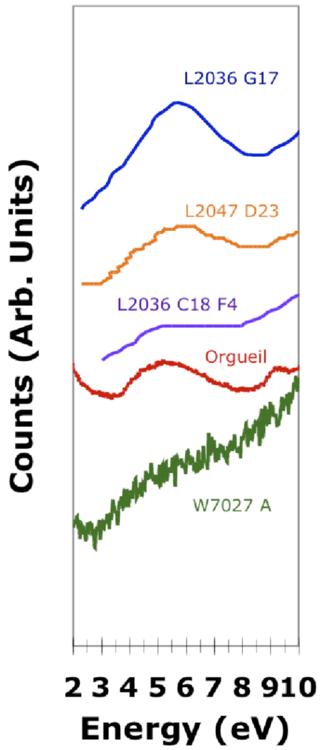

Figure 2: *Low-loss features from organic matter in meteorite and IDP acid residues and unetched IDPs.*

The low-loss region also contains features from inorganic species. Figure 3 shows features from amorphous silicates (GEMS) in IDP L2036-G16. The non-solar oxygen isotopic composition of these GEMS establishes that they are interstellar amorphous silicates [7]. Features at 1.3 eV (953 nm), 1.9 eV (653 eV) and 10.2 eV (122 nm) are detected. The 1.3 eV feature is consistent with Fe^{2+} in silicates [8], the 10.2 eV is a (silicate) exciton and the 1.9 eV feature remains unidentified.

Discussion: Improved energy resolution made possible using monochromated STEM enables detection of features from a variety of organic and inorganic species in the low-loss region with ~1 nm spatial resolution. We have confirmed that meteoritic PAHs exhibit a strong 5.7 eV feature consistent with the astronomical 220 nm UV extinction feature (Fig. 1). Preliminary evidence suggests that the position and shape of the feature is sensitive to the molecular architecture of PAHs (Fig. 2).

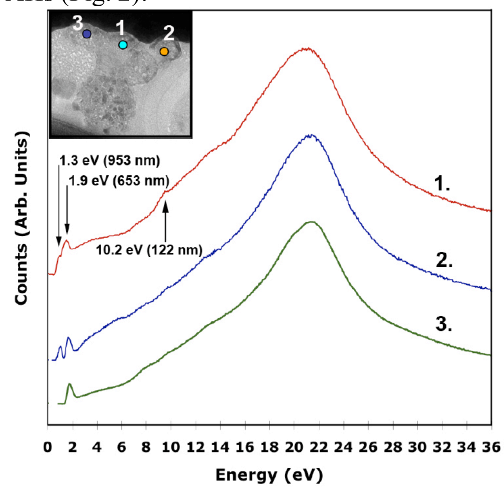

Figure 3: *Low-loss features from inorganic matter (amorphous silicate in GEMS) in chondritic IDPs. Inset, upper right, shows a brightfield TEM image and the spots from which the spectra were acquired.*

A primary goal of this research is to identify low-loss features that are characteristic and ideally unique "fingerprints" of specific types of molecular compounds in meteoritic materials. Towards this end we are assembling a low-loss spectral database of organic compounds. In a parallel effort, we are developing a zero-loss deconvolution algorithm based on multivariate statistical analysis. The algorithm will allow us to deconvolute the ZLP peak from acquired low-loss spectra and assign statistical significance to the spectral analysis. The combination of ZLP deconvolution and well-resolved aberration corrected monochromated STEM will enable us improve the energetic information limit associated with low-loss spectrocopy and the detection of organic functionality at the nanoscale.

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