Functional chemistry of minimally altered organic matter in the meteorite Winchcombe probed by monochromated EELS

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Background incl. aims

The composition of organic matter (OM) in meteorites such as carbonaceous chondrites is a useful indicator for the type of organic matter present on early, prebiotic earth [1]. This OM can be extracted with solvents and analysed with mass spectrometers, but these techniques lose local petrographic context, and the sometimes harsh chemical processes involved in the extraction have the potentially to unintentionally alter the detailed functional chemistry of the OM. Here, careful preparation of thin lamellas using focused ion beam (FIB) techniques, and correlative analysis by high-resolution electron energy loss spectroscopy (EELS) and scanning transmission x-ray microscopy (STXM) of the very same samples, allow for a detailed OM characterization at the nanoscale [2] within the OM's native petrographic context and with minimal alteration.

Methods

Using a Hitachi Ethos NX5000 triple-beam FIB system, several lamellas were prepared containing OM from the meteorite Winchcombe, with special care taken to minimize the impact from sample preparation and enable the study of minimally altered OM. Steps taken to minimize alteration include minimizing the use of protection layers where possible to avoid carbon contamination, backside milling to ensure FIB-deposited material is downstream of the thinned area, and rocking milling to improve uniformity. Where FIB deposition was necessary, metal-containing deposits only (Pt, W) were used, ensuring that any redeposition could be easily identified. Most lamellas were thinned to ≤ 40 nm, a thickness optimised both for sufficient EELS signal at low kV as well as for complementary STXM analysis of the same lamella. To minimize surface damage, crucial for thin samples, Ga+ milling was followed by 1 kV Ar+ polishing using the 'third beam' of the NX5000. Careful, targeted broad-beam low-energy Ar+ polishing, with repeated short exposures and multiple incident angles proved highly effective at reducing surface amorphization and Ga-implantation-related damage. The application of Ar+ polishing directly in the FIB offers here an additional degree of control during the final thinning procedure while minimizing sample handling, thus further lowering any risk of alteration to the OM. SEM imaging of thin areas was also limited and performed at low beam energies to mitigate electron beam alteration of the OM.

Monochromated EELS was carried out at 60 kV in a Nion UltraSTEM100MC-Hermes equipped with a Nion IRIS spectrometer and a DECTRIS ELA direct electron detector. With the samples in ultra-high vacuum, a probe size of 0.1 nm with low beam current of < 5pA, together with an energy resolution of 50-90 meV, makes it possible to distinguish local variations in the different bonds in carbon- and nitrogen-containing OM. Both nanoglobules (~ 300 nm) and 'diffuse' carbon infiltrated into the phyllosilicate matrix (< 100 nm) were analysed. Complementary X-ray absorption near-edge structure (XANES) analysis in the STXM was carried out at the I08 beam-line of Diamond Light Source, UK with a nominal beam size of ~ 40 nm and energy step sizes of 0.1 to 0.5 eV. Where possible, both XANES and EELS were carried out on the same lamella, allowing for direct comparison and highlighting the complementarity of these related techniques.

Results

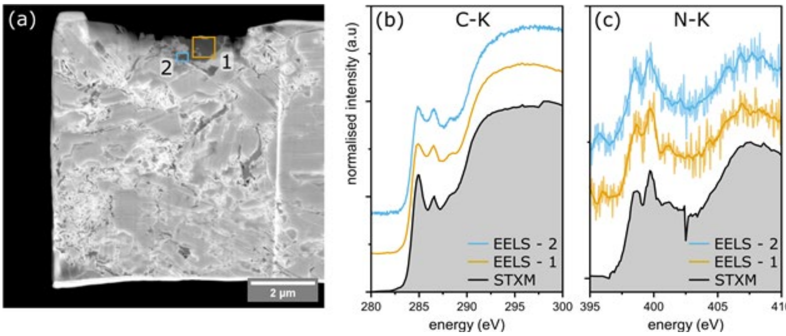
Both STXM-XANES and STEM-EELS reveal distinctive C K absorption bands at 285 and 286.5 eV across all lamellas, relating to aromatic carbon and aromatic ketone/aldehyde bonds. The superior spatial resolution of the STEM probe highlights local variations in the 285 eV aromaticity-linked peak, with a generally higher ratio of aromatic/aliphatic content compared to CM chondrites, indicative of higher alteration. The low noise of direct electron detector-based EELS also enables probing the functional chemistry of the less abundant nitrogen (atomic N/C ratios of only a few %). N K distinct bands are at 398.8 eV and 399.8 eV, associated with C-N double and triple bonds, respectively. Applying statistical denoising methods enables the detection of energy bands beyond those distinguishable in the STXM data, pointing to the presence in nanoscale areas of amino acids such as L-alanine, which had been previously detected by soluble OM studies [3]. Here, the variation of this 402-403 eV fine structure at small length scales, together with the care taken to provide as unaltered a view of the OM as possible within its petrographic context, suggest these functional groups can be linked unambiguously to fluid processes within the OM.

Conclusion

The combination of STXM-XANES and high-resolution STEM-EELS on carefully prepared, minimally altered FIB lamellas allows for the analysis of OM at the smallest length scales. Different nanoscale textures such as nanoglobules and diffuse OM can be distinguished and compared to learn about the evolution and alteration mechanics of organics in carbonaceous chondrites. The direct correlation and excellent match between STXM and 60 kV STEM-EELS results demonstrate how this approach provides a powerful characterization tool for complex extraterrestrial samples with a unique combination of high spatial and energy resolutions.

Figure: (a) scanning electron micrograph of an extracted FIB lamella. The top is thinned to electron transparency and exhibits both a bigger irregular OM grain and smaller patches of OM. (b-c) STEM-EELS + STXM data of the C-K and N-K edges. EELS – 1 and 2 correspond to regions indicated in (a). Subtle changes in the EELS spectrum can be observed for OM areas, even in close proximity.

Graphic:



Keywords:

EELS, meteorite, Winchcombe, FIB

Reference:

[1] Vollmer, C., Kepaptsoglou, D., Leitner, J. et al. High-spatial resolution functional chemistry of nitrogen compounds in the observed UK meteorite fall Winchcombe. Nat Commun 15, 778 (2024). doi: 10.1038/s41467-024-45064-x
[2] Vollmer, C., Kepaptsoglou, D., Leitner, J. et al. Fluid-induced organic synthesis in the solar nebula recorded in extraterrestrial dust from meteorites. PNAS 111.43, 15338-15343 (2014). doi: 10.1073/pnas.1408206111
[3] Chan, Q. H. S., Watson, J. S., Sephton, M. A. et al. The amino acid and polycyclic aromatic hydrocarbon compositions of the promptly recovered CM2 Winchcombe carbonaceous chondrite. Meteor. Planetary Sci. 1-30 (2023). doi: 10.1111/maps.13936