

EX SITU ANALYSES OF CHEMICAL HETEROGENEITY IN INSOLUBLE ORGANIC MATTER FROM PRIMITIVE CHONDRITES

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Introduction: Insoluble organic matter (IOM) is present in the matrices of chondritic meteorites at concentrations of 0 to 4 wt.%. The bulk elemental and isotopic composition and C functional group chemistry of IOM from different meteorites varies with parent body grouping and petrographic grade [1], demonstrating the strong influence of hydrothermal parent body alteration. However, some IOM has sub-regions with large deviations in N and/or H isotopic compositions from solar values that are most easily explained as the product of low temperature (10s of K) ion-molecule reactions in the outer solar nebula or proto-solar molecular cloud. Measurements of the average IOM composition and functional chemistry can be used to constrain the parent body alteration of an unclassified sample and help identify the appropriate classification, whereas measurements of isotopically anomalous regions can inform our understanding of nebular and molecular cloud chemistry. X-ray absorption near-edge spectroscopy (XANES) of the C K edge in a scanning transmission x-ray microscope (STXM) is the most trusted method for determination of the functional group chemistry, due to the high energy resolution and minimal alteration imparted to sensitive IOM samples when performed at a soft x-ray beam line. However, XANES is limited in spatial resolution and in the ability to detect minor element variations. Electron energy loss spectroscopy (EELS) of the C K near edge structure combined with energy dispersive x-ray spectroscopy (EDS) in a scanning transmission electron microscope (STEM) is an attractive alternative to XANES, if the electron-beam damage can be minimized. In order to establish protocols for applying STEM-EELS-EDS to returned samples of Ryugu, and eventually Bennu, we have begun a systematic comparison of STXM and STEM-EELS-EDS to IOM from primitive meteorites in the CM, CR and CO groups.

Methods: We prepared ultramicrotome sections of S-embedded IOM from Elephant Moraine (EET) 92042 (CR2), Allan Hills (ALH) 77307 (CO3), and Murchison (CM2). Details of the bulk properties of these samples are reported elsewhere [2, 3]. The XANES measurements were carried out at the Advanced Light Source (ALS) beam line 5.3.2.2, as 25 nm/px stacks. Simultaneous EELS-EDS spectrum images (SIs) were collected from the same sample regions as the XANES with the Nion UltraSTEM200-X at the Naval Research Laboratory, operated at 60 kV and at a nominal resolution of 20 nm/px. Higher resolution EDS SIs were subsequently obtained with the Bruker Esprit system. A sub-set of the samples was remeasured at ALS after the STEM measurements in order to assess the extent of electron beam alteration.

Results: Comparison of the XANES and STEM-EELS sum spectra show good qualitative agreement. Consistent with prior STXM studies [3], our EELS sum spectra from ALH 77307 have predominantly aromatic and carboxyl functionality, and those from Murchison and EET 92042 have a mixture of aromatic, ketone, and carboxyl groups. However, the STEM-EELS-EDS data from EET 92042 reveal nanoscale variations in both functional groups and elemental compositions not resolved in the STXM data, including nitrile and aliphatic groups, and the presence of N-rich and N-poor nanoglobules. In addition, the coordination of the EELS and EDS data sets can resolve potential ambiguity in the assignment of near edge features to functional groups with overlapping energy ranges, such as ketone and nitrile, through an association with increased O or N EDS counts, respectively. For EET 92042, repeat STXM measurements after the STEM show only limited alteration due to electron beam exposure, mostly as loss of carboxyls. Our results indicate that low voltage STEM-EELS-EDS will be an important complement to more targeted synchrotron XANES analyses, and coordinated isotopic analyses, for understanding the diversity of Ryugu and Bennu organic matter and the relationship to processing history.

References: [1] Alexander, C. M. O'D. et al. *Chemie der Erde* 77, 227-256 (2007). [2] Alexander, C. M. O'D., et al. *GCA*, 71, 4380-4403 (2007). [3] De Gregorio, B. T., et al. *M&PS* 48, 904-928 (2013).

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