

MODIFICATION OF THE MURCHISON INSOLUBLE ORGANIC MATTER (IOM) BY ACID EXTRACTION. G. J. Flynn¹, S. Wirick², L. P. Keller³, and C. Jacobsen². ¹Dept. of Physics, SUNY-Plattsburgh, Plattsburgh NY 12901 USA (george.flynn@plattsburgh.edu). ²Dept. of Physics and Astronomy, SUNY- Stony Brook, Stony Brook, NY 11794 USA, ³NASA Johnson Space Center, Houston TX 77058 USA.

Introduction: A large fraction of the total carbon in the carbonaceous chondrite meteorites is organic rather than elemental carbon. In the CO, CV, and CK classes of carbonaceous meteorites this organic carbon is almost exclusively an acid Insoluble Organic Material (IOM). In the CI, CM and CR classes of carbonaceous chondrites the organic matter consists of IOM as well as numerous water and acid soluble organic compounds, but the IOM constitutes >70% of the total organic matter in the CI, CM and CR classes [1].

Nonetheless, organic matter is a minor component of these meteorites, which are dominated by silicates and contain other minerals. The IOM is frequently extracted by dissolving the silicates and most other minerals in a sequence of HF and HCl acid treatments (described in [2]). The concentrated IOM can then be analyzed by conventional laboratory techniques.

The characterization of solid species in the interstellar and protostellar regions of space is performed mainly by infrared spectroscopy because many solids have diagnostic bending, wagging or stretching modes in the infrared. The 3.3 μm aromatic and aliphatic C-H features of interstellar organic matter are very similar to these features in the IOM extracted from the Murchison CM2 meteorite [3], causing speculation that these organic phases share a similar origin.

However, the repeated exposure of organic matter to HF and HCl, sometimes at elevated temperatures, has the potential to alter that organic matter. To determine if the acid extraction alters meteoritic IOM, we have compared the organic matter we find in-situ in Murchison with IOM that was acid extracted from Murchison using the same analytical techniques we have applied to the analysis of organic matter in interplanetary dust particles (IDPs) [4].

Instruments and Analytical Procedures: We determine the types and abundance of organic matter using two synchrotron-based instruments at the National Synchrotron Light Source (Brookhaven National Laboratory, Upton, New York, USA). These instruments have the high spatial resolution and high sensitivity required to locate and analyze the meteoritic organic matter without acid concentration, allowing identification of the organic functional groups at the micron and sub-micron scale. We employ:

1) a Scanning Transmission X-ray Microscope (STXM) with a spatial resolution ~ 35 nanometers to

determine the C, N and O abundance and characterize the organic functional groups by X-ray Absorption Near-Edge Structure (XANES) spectroscopy, and,

2) a microscope-based Fourier Transform InfraRed (FTIR) spectrometer with a spatial resolution of ~ 3 to $5 \mu\text{m}$ to determine the organic functional groups.

We use two sample preparation techniques. In some cases, ultramicrotome sections, ~ 70 to 100 nm thick, were cut from chips of Murchison that were embedded in elemental S [as described in 4]. Some sections were deposited on TEM grids with SiO substrates for carbon analyses, while other sections were deposited on TEM grids with conducting substrates for mineralogical characterization. Other samples were prepared by crushing several small pieces, approximately 1 to 2 mm in size, of the Murchison meteorite between two cleanglass slides. Tapping the slides removed large particles. The meteoritic material that remained on the glass slide was suspended in a 600 ml sterilized water droplet (Sigma no. W3500). A copper TEM grid, backed with silicon monoxide was used to collect material from the surface and near surface of the droplet. Any soluble material formed a thin film on the grid substrate and the rest of the particles were randomly distributed over the whole TEM grid. This technique selects for particles less than $\sim 1 \mu\text{m}$ in size with most of the particles in the sub-micron size range. It biases against large crystals, which our prior analyses show to contain little or no detectable organic matter. Thus, we concentrate the organic matter in a process that subjects the sample only to gentle crushing and water.

Results: The STXM has a monochromatic x-ray beam focused to an $\sim 35 \text{ nm}$ spot using a zone plate (described by Flynn et al. [4]). By rastering the sample through the fixed beam, we obtain x-ray absorption maps of each sample at the selected energy. We collect a sequence of absorption maps by stepping the monochromator over the range from 280 to 310 eV, typically in 0.1 eV steps over the critical range from 294 to 300 eV, where the distinctive molecular features occur. The maps in this image stack are then aligned, and X-ray Absorption Near-Edge Structure (XANES) spectra are derived by comparing the absorption at a pixel in the image with the absorption in a reference area located on the substrate.

In XANES spectroscopy x-rays induce electron transitions from the ground state to unoccupied, higher-

energy molecular orbitals, which have transition energies characteristic of specific functional groups. This probes the molecular structure. Carbon-XANES spectroscopy is particularly useful in distinguishing elemental carbon, such as graphite, amorphous carbon, and fullerenes, from organic carbon by detecting the carbon to H, N, or O bonding characteristic of organic matter.

C-XANES spectra vary significantly from spot to spot on the Murchison in-situ samples. A few examples are shown in Figure 1. In most cases these spectra differ significantly from C-XANES spectra of the acid extracted IOM, with the ratio of the C=C to C=O peak heights sometimes being higher in-situ than in the extracted material, possibly indicating the formation of C=O functional groups during the extraction process. In addition, the C=C peak is broader in the acid extracted IOM than in many of the in-situ analyses, suggesting that the extraction technique bonds something, possibly H, on the C-ring macromolecule.

We also characterized the samples by infrared spectroscopy. Again, despite the variation in spectra from spot to spot in Murchison, there were clear differences between the in-situ organic matter and the acid extracted IOM (Figure 2). The aromatic C-H feature is easily detectable in the acid extracted IOM while it is below the detection limit in most in-situ analyses. In addition, the aliphatic C-H₃ to C-H₂ ratio is significantly higher in the acid extracted IOM than in the in-situ analyses.

Preliminary results comparing in-situ organic and acid extracted IOM from the Orgueil CI1 carbonaceous meteorite show differences as well. Thus it appears that the acid extraction of IOM results in significant alteration to the organic matter initially present in the meteorite. We recently tested this result by examining IOM extracted from Murchison using a more gentle extraction technique described by Alexander et al. [5]. This new sample of Murchison IOM, provided by Conel Alexander, has both IR and C-XANES spectra that are much closer to those of the material we analyzed in-situ in Murchison and to the material we find in the hydrous IDPs. These measurements confirm our result that the earlier IOM material was substantially altered by the acid extraction process.

Conclusions: The organic matter in-situ in Murchison differs significantly in both its C-XANES and its infrared spectra from samples of Murchison IOM analyzed in the same instruments. This suggests that the acid extraction produces aromatic C-H, possibly because large C-ring structures are broken up into smaller molecules, providing more sites for H attachment, 2) acid extraction increases the aliphatic C-H₃ to C-H₂ ratio, presumably by breaking and shortening aliphatic chains, and, 3) acid extraction seems to reduce the C=C

to C=O ratio. These results suggest that the agreement between the infrared spectra of interstellar organic matter and the IOM from Murchison may simply be fortuitous, since we see no such agreement when comparing the in-situ infrared spectra of organic matter in Murchison with published interstellar spectra.

References: [1] Pizzarello, S. et al. (2006) in *Meteorites and the Early Solar System II*, Univ. of Arizona Press, 625-651. [2] Alexander, C. M. O.'D. (1998) *Meteorit. Planet. Sci.*, **33**, 603-622. [3] Pendleton, Y. (1995) *Planetary and Space Science*, **43**, 1359-1364. [4] Flynn, G. J. et al. (2003) *Geochim. Cosmochim. Acta*, **67**, 4791-4806. [5] Alexander, C. M. O.'D. (2007) *Geochim. Cosmochim. Acta*, **71**, 4380-4403.

Figure 1: C-XANES spectra at three spots on Murchison organic matter separated by crushing and selecting fine-grained material that floated on sterilized water (red) and acid extracted IOM (black).

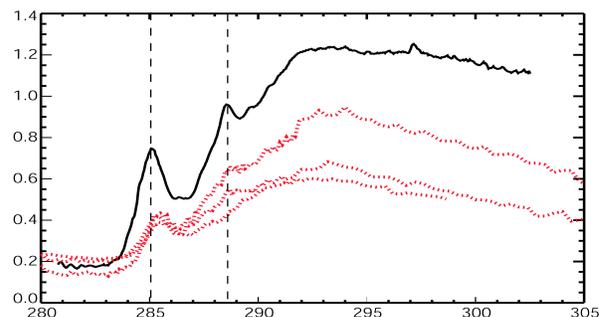


Figure 2: Comparison of the IR spectrum of Murchison IOM with spectra taken of organic rich spots in material dispersed directly from crushed samples of Murchison. Note the deeper C-H₃ absorption in the acid residue (in red) than in the in-situ analyses (blue).

