MICRO-SCALE CHARACTERISTICS OF INSOLUBLE ORGANIC MATTER IN CHONDRITES: A COORDINATED TEM, STXM AND SIMS STUDY. L. R. Nittler[1], C. M. O'D. Alexander[1], G. Cody[2], B. T. De Gregorio[3], A. L. D. Kilcoyne[4], R. M. Stroud[3], and A. Tiwari[3,5]. [1]Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington DC 20015, lnittler@ciw.edu. [2]Geophysical Laboratory, Carnegie Institution of Washington, Washington DC 20015. [3]Materials Science and Technology Division, Naval Research Laboratory Washington DC, USA, [4]Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, USA. [5]Sidwell Friends High School, Washington DC.

Introduction: Primitive chondrites contain up to several wt. % C, mostly in the form of an insoluble organic matter (IOM). Isotopic anomalies (mainly D and/or ^{15}N excesses) in the IOM have long been taken as evidence for partial preservation of presolar material from the Sun's parental molecular cloud [1-3], where chemical reactions are predicted to cause large isotopic fractionations [4]. A connection to interstellar organic matter has also been argued on the basis of spectral similarities [5]. More recent work has argued for an origin within the early Solar System for D-rich IOM [6], though it is not clear whether the proposed scenario can also explain ^{15}N enrichments.

Previous studies have shown that the bulk properties of IOM vary between different meteorites, and that at the micro-scale IOM is highly heterogeneous in morphology and isotopic composition. Of particular interest is recent work that has shown the common presence of sub-micron to micron-sized, often hollow, carbonaceous spheres ("globules") in the IOM in carbonaceous chondrites, interplanetary dust particles and comet Wild-2 samples [7-11]. Coordinated transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS) studies have shown that these globules are typically highly enriched in D and/or ^{15}N relative to bulk IOM [9, 10]. A key question is whether there are also chemical differences among meteoritic globules.

A better understanding of the synthesis, molecular structure, and alteration history of extraterrestrial organic matter should lead to an improved understanding of chemical processes in space and on meteorite parent bodies. To this end, we are performing spatially coordinated microanalytical studies of purified IOM extracts from a number of primitive meteorites, with a goal of characterizing the same organic grains for their molecular chemistry, morphology, structure and isotopic compositions. Here we report TEM and synchrotron transmission X-ray microscope (STXM) results for IOM from the Orgueil (CI1), Bells (CM2), Tagish Lake (C-ung), and Elephant Moraine 92042 (CR2) chondrites and SIMS isotopic imaging of IOM from the Queen Alexandra Range 99177 (CR2) meteorite. SIMS measurements of the materials analyzed by TEM and STXM are planned for the near future.

Methods: We studied IOM residues produced by CsF/HCl dissolution of meteorites [3]. Small fragments of IOM were embedded in elemental S, sliced with an ultramicrotome and placed on SiOx sample support films. TEM studies of the microtomed residues were performed at the Naval Research Laboratory with a JEOL 2200FS 200 kV field-emission microscope. A ~ 10 nm carbon coat was applied to the backside of the support films prior to TEM examination to prevent sample charging. The TEM measurements were limited to parallel illumination, low magnification bright-field imaging to minimize radiation dose. STXM analyses were made at the soft X-ray beamline 5.3.2 (optimized for ~250-600 eV) of the Advanced Light Source in Berkeley (resolution ~40 nm), in both stack image and linescan modes. We obtained spectra from carbon and nitrogen X-ray Absorption Near-edge Structure (C-/N-XANES) Spectroscopy. XANES allows the determination of the relative elemental abundances as well as the functional characterization of the C- and N-bearing molecules [12]. H, C and N isotopic ratio images were made with a NanoSIMS 50L ion probe in raster imaging mode on 10-40 μm fragments of IOM pressed into gold foil. For C and N, the data were internally normalized to the known bulk composition of the IOM [3]; for the H measurements, a terrestrial organic standard was used to quantify the data.

Note that in order to understand potential effects of damage from the different techniques, we vary the order in which we perform the analyses. Thus, to rule out the possibility of electron-beam induced sample damage affecting the chemical data, STXM measurements were performed before TEM studies on EET and Bells residues. To ensure the possibility of observing globules by STXM, TEM imaging was carried out first on Tagish Lake residues and on one area of Bells. In addition, material identified as unusual by the NanoSIMS measurements of bulk IOM will be extracted by FIB lift-out to enable TEM and STXM analyses.

Results: *TEM.* As seen in previous work [8], the IOM from all studied meteorites was found to primarily consist of porous fluffy amorphous material and varying amounts of spherical globules. Although the appearance of the globules is similar from meteorite to meteorite, there do appear to be systematic differences in their abundance and/or size for different meteorites. Bells IOM, which has the highest bulk $^{15}N/^{14}N$ ratio of any carbonaceous chondrite, has far more numerous globules than the other residues. Preliminary TEM data suggest a correlation between average globule diameter and wall thickness with bulk $^{15}N/^{14}N$ ratio for Orgueil, Tagish Lake, and EET 92042.

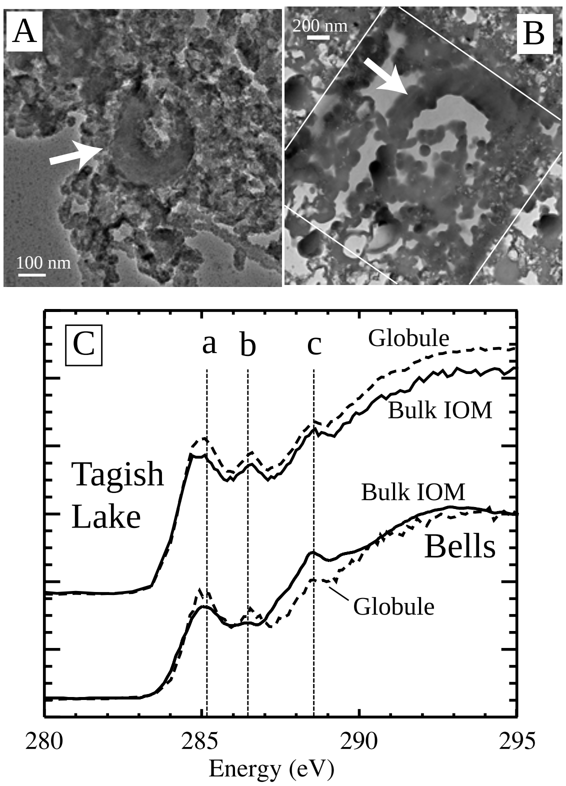

Fig. 1: A) TEM image of Tagish Lake IOM; arrow indicates carbonaceous globule. B) TEM image of Bells IOM following STXM analysis. Arrow indicates a globule; square encloses area of X-ray beam damage. C) C-XANES spectra of globules from A and B and nearby non-globular IOM from same meteorites.

TEM examination of IOM samples first analyzed by STXM indicates significant damage from the X-ray beam, especially for Bells IOM. For example, Fig. 1B shows a TEM image of Bells IOM; within the STXM raster square the IOM, including a globule, appear melted. Less extreme modification is seen for Tagish Lake IOM. We believe that most of the damage occurs during acquisition of N-XANES data, since these measurements often entail long dwell times to improve the signal.

STXM. For globules without apparent beam damage from Tagish Lake and Bells, C-XANES spectra appear very similar to those of non-globule IOM nearby in the same sections (Fig. 1). The spectra exhibit strong absorptions at 285.0, 286.7 and 288.5 eV, due to a) C-C double bonds in aromatic domains, b) vinyl-ketone functional groups and c) carboxyl functional groups, respectively. IOM from different meteorites shows significant differences in the relative peak heights that are attributed to parent body processing [13]. On the microscale within a single meteorite, we see some variation in peak heights from region to region, but it is not yet clear how the chemical variability in the globules compares to that of the IOM on the whole. For one cluster of globules in Bells, prior TEM analysis appears to have induced significant damage to the material. Compared to other IOM and globule spectra, the carboxyl intensity is greatly decreased and the aromatic signal at 285 eV enhanced. IOM in Bells appears to be very sensitive to beam damage by both TEM and STXM; IOM in Tagish Lake less so.

NanoSIMS: H, C and N isotopic images of purified IOM from CR2 QUE 99177 indicates a very similar range of isotopic compositions to that found by similar measurements *in situ* in this meteorite [14]. Namely, we find that a few percent of the analyzed area consists of D and/or ^{15}N hotspots, with $\delta^{15}N$ values up to 2200 ‰ and δD values up to 20,000 ‰. Many hotspots are clearly associated with globule-like morphologies, but many are not. A few small regions with moderate (10–20%) ^{13}C depletions are also seen, usually associated with enhanced ^{15}N. Future TEM and STXM analyses of isotopic hotspots both in situ and in the IOM samples of this meteorite will allow investigation of the effects of the acid dissolution on the molecular structure of the organic matter.

Acknowledgements: This work is supported by NASA grant NNX07AI75G to LRN. AT was supported by the ORN/NRL SEAP program.

References: [1] Alexander C. M. O' D., et al. (1998). *Meteoritics & Planet. Sci., 33,* 603-622. [2] Busemann H., et al. (2006). *Science, 312,* 727-730. [3] Alexander C. M. O'D., et al. (2007). *GCA, 71,* 4380-4403. [4] Ehrenfreund P. and Charnley S. B. (2000). *A&A, 38,* 427-483. [5] Pendleton Y. J., et al. (1994). *ApJ, 437,* 683-696. [6] Remusat L., et al. (2006). *EPSL, 243,* 15-25. [7] Garvie L. A. J. and Buseck P. R. (2004). *EPSL, 224,* 431-439. [8] Garvie L. A. G. and Buseck P. R. (2006). *Meteoritics & Planet. Sci., 41,* 633-642. [9] Nakamura-Messenger K., et al. (2006). *Science, 314,* 1439-1442. [10] Messenger S., et al. (2008). *LPS XXXIX, 39,* Abstract #2391. [11] De Gregorio B. T., et al. (2009). *LPS XL, 40,* submitted. [12] Cody G. D., et al. (2008). *Meteoritics & Planet. Sci., 43,* 353-365. [13] Cody G. D., et al. (2008). *EPSL, 272,* 446-455. [14] Nguyen A. N., et al. (2008). *Meteoritics & Planet. Sci., 43 (supp),* abstract #5277.