

**COORDINATED ANALYSIS OF *IN SITU* ORGANIC MATERIAL IN THE CR CHONDRITE QUE 99177.** Z. Peeters<sup>1,3</sup>, H.G. Changela<sup>2</sup>, R.M. Stroud<sup>2</sup>, C.M.O'D. Alexander<sup>1</sup>, L.R. Nittler<sup>1</sup>; <sup>1</sup>Dept. of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd, Washington DC, 20015, <sup>2</sup>Naval Research Laboratory, Code 6366, 4555 Overlook Ave SW, Washington DC, 20375; <sup>3</sup>zpeeters@ciw.edu.

**Introduction:** Organic matter (OM) in the fine-grained matrix of primitive meteorites has traditionally been studied in extracted form, where the insoluble organic matter (IOM) was purified by dissolving away the surrounding material [1]. *In situ* studies are required, however, to better understand the origin and processing history of extraterrestrial OM. We report here the results of an ongoing [2] *in situ* study of OM in Queen Alexandra Range (QUE) 99177, a primitive CR3 chondrite with little evidence for parent body alteration [3]. Previous NanoSIMS isotopic mapping of sections of QUE 99177 [4, 5] revealed carbon to be distributed throughout the matrix as sub- $\mu\text{m}$  sized particles with a wide range of H, C, and N isotopic compositions. Coordinated analysis of several focused ion-beam (FIB) lift-out sections by X-ray absorption near-edge spectroscopy (XANES), TEM, and NanoSIMS allows detailed investigation of the chemical, structural, and isotopic nature of OM and its geochemical setting.

**Experimental:** An unusually large ( $\sim 8 \times 3 \mu\text{m}$ ), C-rich vein was previously discovered in a section of QUE 99177 [4]. We have mapped a large area ( $300 \times 600 \mu\text{m}$ ) of the same thin-section in C and N isotopes at low resolution to identify additional large, isotopically anomalous, C-rich inclusions. The large vein and several inclusions from the new maps, as well as a random area of the matrix, were targeted for FIB lift-out. Sections  $\sim 100 \text{ nm}$  thick were extracted with a Zeiss Auriga FIB-SEM at the Carnegie Institution and taken to the scanning transmission X-ray microscope (STXM) on beamline 5.3.2.2 at the Advanced Light Source (ALS, LBNL) for XANES analysis. After XANES mapping, the sections were analyzed with the JEOL 2200FS TEM equipped with a Noran EDS system at the Naval Research Laboratory. BFTEM, STEM imaging, HRTEM, STEM-EDX, and selected area diffraction were performed on the FIB sections. Two of the sections were measured with the Carnegie NanoSIMS 50L. The analyses were performed in order of increasing energy impact on the sample.

**Results and discussion:** The large vein, as measured by NanoSIMS from the top of the inclusion (i.e. before lift-out) was enriched in D ( $\delta\text{D} = +6000 \text{ ‰}$ ) and  $^{15}\text{N}$  ( $\delta^{15}\text{N} = +500 \text{ ‰}$ ), significantly higher than the bulk IOM composition for this meteorite ( $\delta\text{D} = +3139 \text{ ‰}$ ,  $\delta^{15}\text{N} = +187 \text{ ‰}$ ) [1]. Measurement of the FIB section by NanoSIMS following STXM and TEM analysis confirmed the  $^{15}\text{N}$  and D enrichment values, see Fig. 2. In addition, we found that the vein was homogeneous in its  $^{15}\text{N}$  enrichment, displaying no hotspots within

the vein.  $^{15}\text{N}$  hotspots were found outside the vein, however, with enrichments as high as  $+1800 \text{ ‰}$ .

TEM images of the FIB sections (Fig. 1 and 2) showed a range of morphologies in the C-rich inclusions, also seen in IOM extracts [6, 7]. The large vein (Fig. 2) was found to consist mainly of nanoglobules and also showed an alkali-rich, fine-grained material that has seeped into the interstitial volume between the nanoglobules, almost certainly carried by a liquid from the surrounding matrix. The FIB section in Fig. 1 showed a number of smaller ( $0.5\text{--}2 \mu\text{m}$ -size) carbonaceous inclusions, including isolated solid and hollow nanoglobules, nanoglobule aggregates in ‘pockets’, as well as non-globular ‘fluffy’ material. One nanoglobule with a ‘crushed’ appearance is surrounding an Fe-oxide grain, possibly goethite. The TEM observations of all studied sections clearly indicate the presence of liquid water at some point and that QUE 99177 is somewhat aqueously altered.

C-edge XANES mapping of carbonaceous inclusions revealed three bands commonly seen in chondritic IOM (aromatic or vinylic carbon bonds, aromatic or vinylic ketone bonds, and carboxyl bonds) as well as a feature at  $290.3 \text{ eV}$  originating from carbonate, see Fig. 3. The most prominent band is the aromatic or vinylic C=C-bond peak at  $\sim 285 \text{ eV}$ . Most inclusions, including individual solid nanoglobules, pockets of nanoglobules, and ‘fluffy’ OM, as well as OM from the FIB section of a randomly selected part of the matrix, show this peak at  $284.9 \text{ eV}$ , slightly lower than observed in the extracted IOM ( $285.1 \text{ eV}$ ). In the large vein, the aromatic

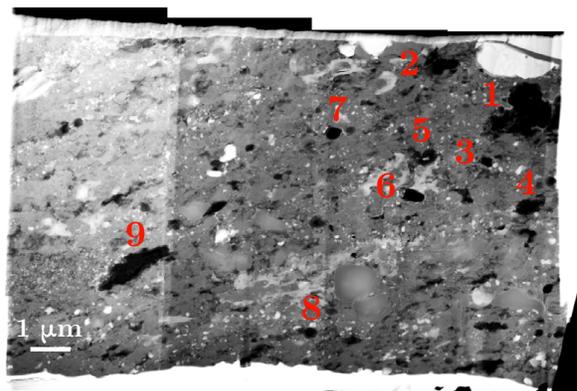


Figure 1: HAADF STEM image of a FIB section showing C-rich inclusions with different morphologies. 1, 2, pockets of nanoglobules; 3, 4, 9, fluffy OM; 5, crushed nanoglobule; 6, 7, solid nanoglobules; 8, hollow nanoglobule.

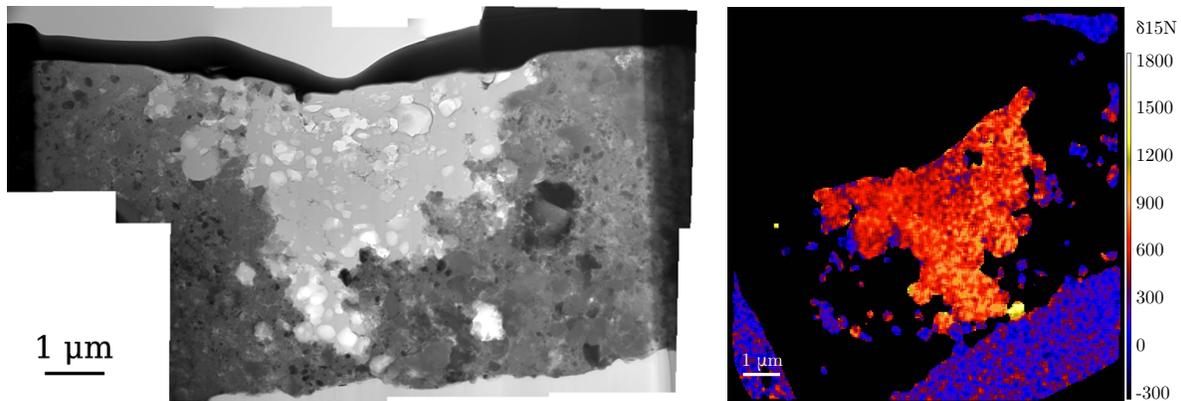


Figure 2: Bright field TEM image (left) and NanoSIMS  $^{15}\text{N}/^{14}\text{N}$  ratio image (right) of the FIB section containing the large, C-rich vein. Vein dimensions  $\sim 8 \times 6 \mu\text{m}$ .

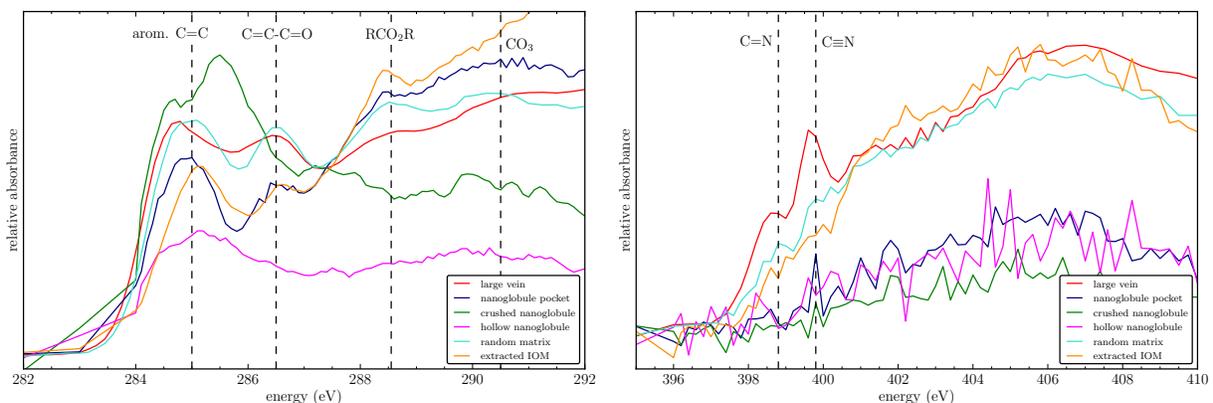


Figure 3: C-edge (left) and N-edge (right) XANES spectra.

C=C peak is shifted to lower energy (284.7 eV) and appears asymmetric. The XANES spectrum of the crushed nanoglobule with the Fe-oxide grain is very different from the rest in that the aromatic C=C peak appear diminished while a new, as yet unidentified, peak appears at 285.5 eV. The other two peaks present in most of the other spectra, aromatic ketone bond and carboxyl bond, are absent from the crushed nanoglobule spectrum. The spectrum of an isolated, hollow nanoglobule resembles those of the aromatic-type nanoglobules observed in several chondrites [6].

**Conclusion:** We have studied the OM *in situ* in FIB lift-out sections of QUE 99177 using XANES, TEM, and NanoSIMS. The OM is present in QUE 99177 as isolated,  $\mu\text{m}$  to sub- $\mu\text{m}$ -sized inclusions, as well as in larger (up to  $10 \mu\text{m}$ ) veins, with a range of morphologies including clusters of nanoglobules. Chemical variability among the different morphologies is revealed by XANES analysis. One large vein of nanoglobules is remarkably homogeneous in H and N isotopic compositions, relative to the range observed for isolated grains, and also shows homogeneous C-

and N-XANES spectra that are distinct from typical IOM from QUE 99177. These observations indicate that the nanoglobules within the vein likely formed together from common precursors and not as a random collection of typical nanoglobules. There is clear evidence for the past presence of liquid water making the CR3 classification of QUE 99177 uncertain.

**Acknowledgement:** The authors wish to acknowledge David Kilcoyne of the ALS for his help with XANES measurements. ALS beamline 5.3.2.2 is supported by the Director of the Office of Science, Department of Energy, under Contract No. DE-AC02-05CH11231.

**References:** [1] Alexander C. M. O'D. et al. (2007) *Geochim. Cosmochim. Acta.* 71, 17, 4380–4403. [2] Peeters Z. et al. (2011) *Meteorit. Planet. Sci.* 46, A185. [3] Abreu N. M. et al. (2010) *Geochim. Cosmochim. Acta.* 74, 1146–1171. [4] Nguyen A. N. et al. (2008) *Meteorit. Planet. Sci.* 43, A5277. [5] Floss C. et al. (2009) *Astrophys. J.* 697, 2, 1242–1255. [6] Herd C. D. K. et al. (2011) *Science.* 332, 1304–1307. [7] Changela H. G. et al. (2012) in *LPS XLIII* A2745.