

ORGANIC MATERIAL IN THE MATRICES OF UNEQUILIBRATED ORDINARY CHONDRITES: A COORDINATED STXM-TEM STUDY. H. G. Changela¹, C. Le Guillou² and A. J. Brearley¹ ¹Department of Earth and Planetary Sciences, MSC03-2040, 1University of New Mexico, Albuquerque, NM87131, USA. ²Ruhr-Universität Bochum, Inst. für Geologie, Mineralogie and Geophysik, 44780, Bochum, Germany. (Email:changela@unm.edu).

Introduction: Organic material (OM) in carbonaceous chondrites (CCs) makes up to ~2 wt. % carbon and is mostly found in their matrices [1]. Solid OM inclusions are randomly distributed in CC matrices as discrete sub-micron inclusions with various morphologies, displaying IOM-like aromatic (C=C) - ketone (C=O) - carboxylic (COOH) functional chemistry [2]. In contrast, less than 0.4 wt. % carbon is found in unequilibrated ordinary chondrites (UOCs) [1]. Matrices of UOCs make up much smaller volumes than CCs, ranging from ~10-15 % compared to ~volume 30-99 % in CCs [3]. However, because most of the OM in the UOCs is concentrated in their matrices [4], the likelihood of finding discrete OM inclusions in random locations of UOC matrix should be high.

In situ observations of OM in UOC's will constrain the spatial context and distribution of the OM and allow the evaluation of the effects of aqueous alteration and thermal metamorphism at demonstrably higher temperatures than CCs [5, 6]. Some modifications of OM related to progressive aqueous alteration are apparent in CCs, such as the redistribution of OM that is enriched in aliphatic and carboxylic functional groups [7].

Samples & Methods: Hand-picked fragments of matrix from Semarkona LL 3.0, Bishunpur LL3.1, Chainpur LL3.4, and Lewis Hills LEW 87284 L3.6 UOCs were pressed into indium foil. Focused ion beam (FIB) sections were extracted from the matrices of these fragments. In addition, a FIB section was extracted from a carbon-coated thin section of Queen Alexander Range QUE 97008 L3.05. Scanning transmission X-ray microscopy (STXM) was performed at Berkeley ALS Beamline 5.3.2 and the Canadian Light Source Beamline 10 ID-1, Saskatoon prior to TEM. The distribution of aromatic/olefinic C was initially obtained by subtracting the optical density of each pixel at the energy of aromatic/olefinic C (285.6 eV) from that of the pre C-edge (280 eV). Multiple energy X-ray absorption images from ~270 – 340 eV were collected to form stacks, enabling XANES spectra to be extracted from any regions of the images. The distribution of distinctive spectra were then obtained from the stacks using a linear fit procedure with the STXM data reduction software *AXIS-2000*, which searches for initially defined spectra extracted from the stacks. The relative functional group abundances were obtained by fitting background subtracted and normalized spectra using *Athena* software and methods described in [7,8]. The morphologies of the OM particles and their relationship with surrounding matrix material were then characterized by Scanning/TEM at the University of New Mexico using a JEOL 2010 TEM and a JEOL 2010F FEGSTEM, operating at 200 kV.

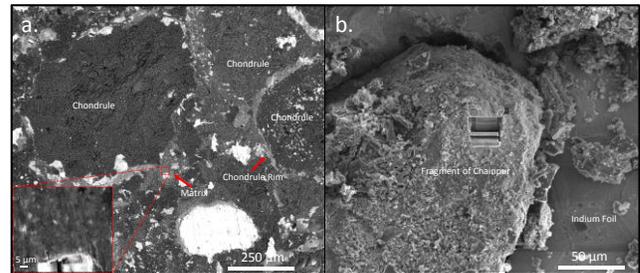


Figure 1. Images of UOC fragments (a) BSE image of Bishunpur showing a polished chip pressed in indium foil. Matrix regions are interstitial to chondrules and their rims. (b) Fresh matrix fragment from Chainpur pressed in indium foil. Trenches made for the FIB section are shown in the figures.

Results: Discrete sub-micron inclusions and more uniformly distributed, diffuse OM were detected in the UOC FIB sections, similar to the CCs (Fig. 2) [e.g. 8]. OM inclusions are typically less abundant than those in the CCs. The matrix mineralogy consists of finer scale crystalline silicate minerals than in the CC matrices (Fig 2b). Replacement textures of amorphous silicate by Fe-rich crystalline silicates, probably fayalitic olivine, were found in Bishunpur. Larger crystalline aggregates appear to have been fragmented into material similar to the fine grained silicates which dominate some samples (e.g. Fig 2b). LEW 87284 L3.6 has coarser grained silicate crystals in its targeted matrix location.

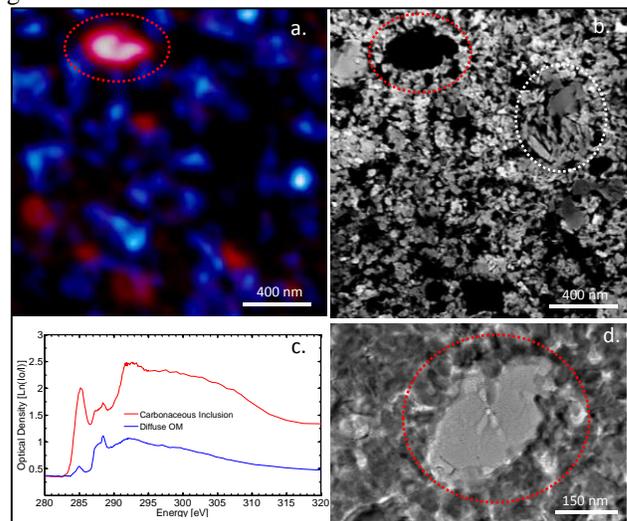


Figure 2. STXM-TEM analysis of Semarkona. (a) Stack fit showing the distribution of 2 spectral populations. (b) Coordinated DF STEM montage. Circled white region is a large fragmented crystalline silicate aggregate. (c) Unnormalised XANES spectra of 2 populations showing the difference in their optical densities. (d) BF-TEM image of OM inclusion (red circle).

All of the spectra except for a tentative peak in Semarkona lack the C=O ketone peak at 286.5 eV. A carboxylic peak was identified in all of the inclusions from the samples except for in LEW 87284 L3.6, which has just a large aromatic peak (Fig. 3). One globular-shaped grain was found in LEW 87284. A distinctive hollow nanoglobule was found in Chainpur. The aromatic peaks in the normalised XANES of the inclusions show an increase in intensity from the lowest to highest UOC petrologic types (Fig. 3). Around the fine-grained matrix material, more widely distributed, ubiquitous OM is also found in the UOCs, similar to the CCs. This diffuse OM [7] is also always aromatic poorer and carboxylic richer than the discrete inclusions. It is less dense than the OM inclusions, as shown by its lower optical density (Fig 2c) but occurs in a much larger volume of the samples. The resulting contribution of this diffuse component to the total organic carbon is therefore far less than that of the discrete OM inclusions. Semarkona diffuse OM has the highest carboxylic fraction with a carboxylic peak area close to QUE 97008, whereas Chainpur has a slightly less intense carboxylic peak (Fig. 3). The CO₃ peaks of the diffuse OM are highly variable among the UOCs studied. Semarkona diffuse OM lacks a CO₃ peak, Chainpur has a detectable CO₃ peak, and the QUE 97008 XANES is anomalously high in the CO₃ when compared to the other meteorites.

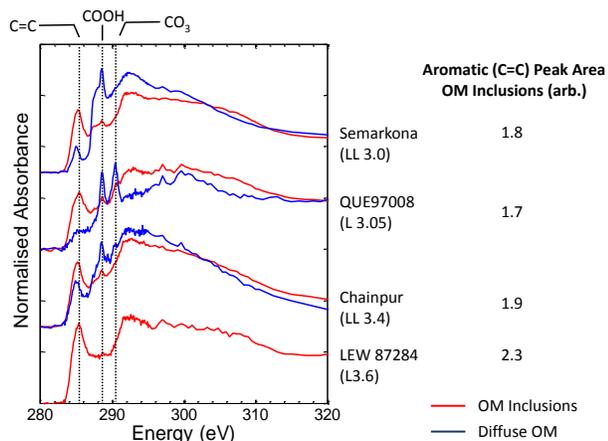


Figure 3. C-XANES spectra of OM in representative UOC samples. The organic inclusions (red) are overlaid with the representative diffuse spectra (blue) from the same sample. The lower aromatic and higher carboxylic peak areas are more pronounced in the diffuse spectra in the UOCs when compared with the type 2/3 CR chondrites [4].

Discussion: Thermal maturity of OM in the UOCs has previously been documented by *in situ* Raman analyses [6] and changes in a 1s-σ* bond (291.7 eV) in C-XANES spectra of IOM [9]. Our results also suggest these thermal effects by the higher aromatic peaks of the carbonaceous inclusions when compared to those, for instance, in the CR chondrites [8]. The areas of the aromatic/olefinic normalised peak in the UOC inclusions are higher than those in the CRs, with an average peak area in the UOCs ~40 %

higher than those in the type 2/3 CRs [8]. The most aromatic OM is seen in the pure aromatic XANES of a single globule-like inclusion in LEW 87284. The loss of other functional groups reflected in these spectra may also suggest a higher degree of thermal processing. The functional groups of the carbonaceous inclusions are different to the characteristic IOM-like aromatic, ketone and carboxylic 3-peak spectra found in CCs in that the ketone peaks are typically lacking. The XANES spectra of the inclusions also show a close similarity to the XANES spectra of UOC IOM [9] which have broad aromatic peaks, lacking ketones and containing carboxylic peaks. The more widely distributed, but far less massive diffuse OM, has the same property as the diffuse OM found in the CCs [7,8] in being always aromatic poor and carboxylic richer when compared to the discrete inclusions in the samples. However, the carboxylic component is more abundant in the UOC diffuse OM, compared with the type 2 and 3 CR chondrites, and the aromatic component is lower. The average carboxylic peak area in the UOC diffuse OM is 30 % higher than the average diffuse carboxylic peak in the type 2/3 CRs [8]. Only the most altered CR1 chondrite has a carboxylic component that compares in abundance with the UOCs. This may imply that higher temperatures and/or slower cooling rates experienced in the UOCs have been preferentially increasing this carboxylic fraction of OM.

Summary & Conclusions: Organic inclusions with XANES spectra reminiscent of IOM residues (2-peak broad aromatic and slight carboxylic peak spectra) [9] have been identified *in situ* in random locations within samples of UOC matrix from petrologic types 3.0 up to at least type 3.6. Carbonaceous inclusions in the UOCs are more aromatic in character than in the CCs, and typically lack any ketone functional groups. This is consistent with higher temperatures experienced by the UOCs when compared with the CCs. The low abundance, but ubiquitous diffuse OM [7] in the UOC matrices is both aromatic poorer and carboxylic richer than the discrete inclusions in UOCs, similar to the CCs. The carboxylic peaks in the diffuse OM are more pronounced than the diffuse OM of CCs from previous studies, suggesting that elevated temperatures during metamorphism may have enhanced the formation of the carboxylic fraction, relative to other functional groups.

References: [1] Alexander C. M.O.'D. et al. (2007) *GCA*, 74, 4417-4437. [2] Cody G. et al. (2011) *Proc. Nat. Acad. Sci.* 108, 19171-19176. [3] Weisberg, M.K et al. (2006) In *Treatise on Geochemistry*. Elsevier. pp. 19-52. [4] Michel-Levy M. C. & Lautie A. (1981) *Nature* 291, 321-322. [5] Grossman L. & Brearley (2005) *MaPS* 40(1), 87-122. [6] Quirico E. et al. *MaPS* 38(5), 795-81. [7] LeGuillou C. et al. (2013) *GCA* in press. [8] Changela H. G. et al. (2014) *LPS This meeting*. [9] Cody G. D. et al. (2008) *EPSL* 272: 446-455.

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