

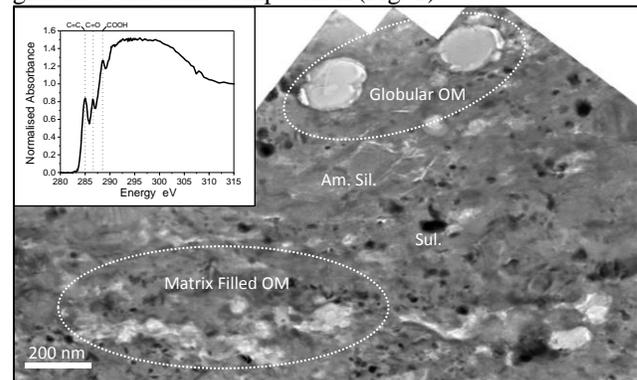
**ANALYTICAL CONSTRAINTS ON THE FORMATION AND EVOLUTION OF ORGANIC MATERIAL BY PROCESSES ON PRIMITIVE CHONDRITE PARENT BODIES.** H. G. Changela<sup>1</sup>, C. Le Guillou<sup>2</sup> and A. J. Brearley<sup>1</sup> <sup>1</sup>Department of Earth and Planetary Sciences, MSC03-2040, 1University of New Mexico, Albuquerque, NM87131, USA. <sup>2</sup>Natural History Museum, Paris, France. (Email:changela@unm.edu).

**Introduction:** Organic material (OM) pervades the matrices of primitive chondrites [1,2]. Carbonaceous chondrites (CCs) contain up to ~ 1.5-4 wt.% organic carbon, with the highest concentration of OM found in the most water-rich CCs: Average CI > average CM > average CR [3]. OM has traditionally been divided into soluble and insoluble types. The acid insoluble fraction – insoluble organic matter (IOM) makes up the highest fraction of OM, ranging from 70-99% of total organic carbon in CCs [4]. Solid OM inclusions exist in chondrite matrices as discrete micron-submicron inclusions with various morphologies and displaying CC IOM-like aromatic (C=C) - ketone (C=O) - carboxylic (COOH) functional chemistry by C K-edge XANES [5]. In contrast, less than 0.4 wt.% insoluble carbon is found in unequilibrated ordinary chondrites (UOCs) whose matrices make up smaller volumes than CCs, ranging from ~10-15 vol% compared to ~30-99 vol% in CCs [6]. They display more distinctive 2-peak (C=C) – (COOH) spectra (286.5 eV lacking peaks) and graphitization features than IOM in CCs [7].

A detailed study of OM *in situ* across a range of primitive chondrites has been performed. Different primitive chondrite groups and classes represent different processing histories of their primary components. By understanding the microscopic environments that OM exists in and its sensitivity to varying degrees of parent body processing, we have gained insights into its formation and evolution. CCs display a diverse range of alteration by the action of water whereas the UOCs show petrologic variations controlled by the degree of thermal metamorphism, sometimes in the presence of aqueous fluids [8].

**Samples & Methods:** Hand-picked fragments of matrix from the following CRs: QUE 99177 (CR3), EET 87770 (CR2), EET 92042 (CR2), GRA 95229 (CR2), Renazzo (CR2), LAP 02342 (CR2) and GRO 95577 (CR1) and the following UOCs: Semarkona (LL 3.0), QUE 97008 (L3.05), Bishunpur (LL3.1), Chainpur LL (3.4), and LEW 87284 (L3.6) were pressed into indium foil. Twenty five focused ion beam (FIB) sections were prepared from their matrices with typically 2-3 FIB sections per chondrite. Scanning transmission X-ray microscopy (STXM) was performed at Berkeley ALS Beamline 5.3.2 and the Canadian CLS Beamline 10 ID-1 prior to TEM analysis. X-ray absorption images from ~270 – 340 eV were collected to form stacks, enabling C K-edge XANES spectra to be extracted from them. The relative functional group abundances were obtained by fitting background subtracted and normalized spectra using methods described in [1]. The morphologies of the OM particles and their microscopic environments were then characterized by TEM at UNM using the JEOL 2010 and 2010F instruments.

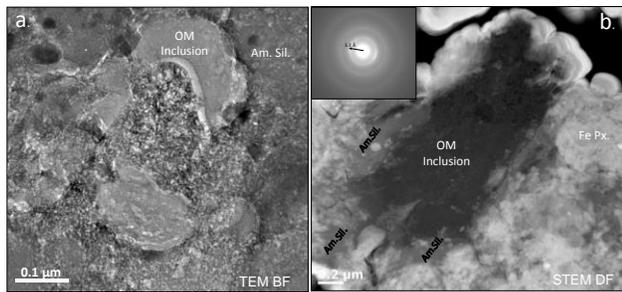
**Results:** Discrete micron-submicron inclusions and more uniformly distributed, ‘diffuse’ OM were observed in the CC and UOC FIB sections (e.g. Fig.1). OM inclusions are typically less abundant in the UOCs than in the CCs. In the CR chondrites, they exist in discrete globular form but also to have texturally filled the matrix (Fig. 1). They mostly display the 3-peak (C=C)-(C=O)-(COOH) functional chemistry of IOM. These different morphologies have the same composition (Fig. 1).



**Figure 1** BF TEM montage of EET 92042 (CR2). In the CR3/2 chondrites, Discrete globular and matrix filled inclusions locally have identical C K-edge XANES spectra (see inset). Am. Sil = Amorphous Silicate, Sul. = Fe,Ni Sulphide.

Much rarer 2-peak (C=C)-(COOH) inclusions were also found in 3 of the 14 FIB sections of the CR3/2CRs. Most of these inclusions have textures suggestive of post formation alteration (e.g. Fig 2a). In GRO 95577 (CR1), OM inclusions in 2 out of 3 FIB sections studied also display these ketone-poor peaks at 286.6 eV. They also contain the most aromatic inclusions of all the CRs and are the most carboxylic rich. Solid OM in GRO 95577 is, on average, coarser-grained than the OM inclusions in the type 3/2s [9]. These 2-peak OM inclusions have spectral characteristics that are also typical of the OM inclusions found in the lower petrologic type UOCs. The aromatic peaks in the normalised XANES of the UOC OM inclusions show an increase in intensity from the lowest to highest UOC petrologic types (Fig. 3a). A carboxylic peak was identified in all of the inclusions from the UOCs except for an inclusions in LEW 87284 L3.6, which only has a large aromatic peak (Fig. 3a).

In the CRs, OM is ubiquitously present in and around both amorphous silicate grains which dominate the matrices of the type 3/2s, and the coarser phyllosilicates found in GRO 95577 (CR1). In these phases, the OM is always poorer in aromatics and richer in carboxyl functional groups than the OM inclusions. This diffuse OM has been found in all of the CCs studied [1]. In the UOCs, the surrounding mineralogy consists of fine-scale crystalline



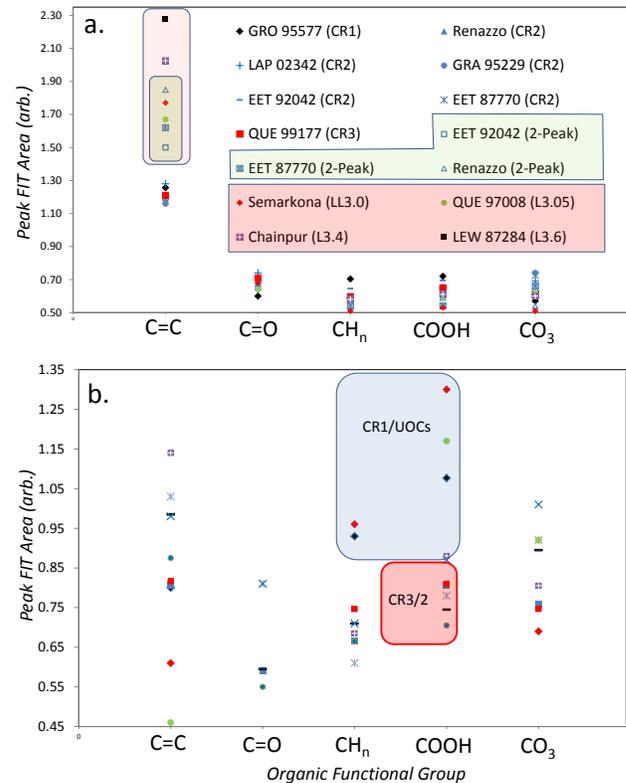
**Figure 2** (a) BF TEM of a 2-peak (286.6 eV ketone peak lacking) OM inclusion from EET 87770 (CR2). (b) A coarser graphitized inclusion from Bishunpur (UOC 3.2). Inset shows SAD of the inclusion and most intense 3.3 Å rings indicating a polycrystalline structure of graphite - (002) reflections.

silicate minerals compared with abundant amorphous silicates in the CR3/2 matrices and coarser phyllosilicates in the CR1. Around the fine-scale minerals and OM inclusions, diffuse OM is also present in the UOCs but in less abundance than the CR chondrites. Its aliphatic and carboxylic fraction are, however, more similar to those found in the most altered CR chondrite GRO 95577 (CR1). 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 in its diffuse OM (Fig. 3b). Unlike the OM inclusions, the diffuse OM also displays CO<sub>3</sub> peaks in both the CCs and some of the lower petrologic type UOCs. Semarkona diffuse OM lacks a CO<sub>3</sub> peak, Chainpur has a detectable CO<sub>3</sub> peak but QUE 97008 is anomalously high in this component when compared to the other meteorites. GRO 95577 (CR1) is the only CR chondrite which lacks this CO<sub>3</sub> peak in its diffuse OM.

**Discussion:** In the least altered CCs, evidence of matrix filling of 3-peak OM suggests the formation of these inclusions by the presence of fluids that filled pores in their matrices. Alteration textures of OM inclusions associated with 2-peak OM suggest that they are the product of alteration post formation, possibly of the 3-peak OM. This is further supported by the presence of coarse, texturally altered, vinyl ketone poor (C=C-C\*=O) OM inclusions found in GRO 95577 (CR1) [9]. However, carbonyl functional chemistry could still exist as aryl ketone (C=C\*-C=O), whose absorption features by XANES could be convoluted by the broader aromatic peaks in the 2-peak inclusions [10]. The increase in aromaticity and reduction in vinyl ketone correlates with more pervasive degrees of alteration in the CR1 and UOCs where the aromaticity of the OM inclusions increases and absorption at 286.6 eV from C K-edge XANES decreases. This is consistent with elevated temperatures associated with alteration [7]. The loss of other functional groups in the XANES spectra of LEW 87284 (3.6) demonstrates the effects of increasing devolatilization of OM at higher degrees of thermal pro-

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**Figure 3** Average peak FIT areas of C-XANES spectra of OM. (a) OM Inclusions. (b) Diffuse OM. Spread of individual FIB sections in [9,11].

cessing. The uniformly distributed, diffuse OM in the CCs contains a higher fraction of aliphatics and carboxyl functional chemistry and is more abundant in the more aqueous altered CCs [1,9]. This carboxyl and aliphatic group enrichment may be the result of modification of OM inclusions via an oxidation process [12] with aqueous fluids. The carboxylic fraction is higher in the UOC diffuse OM, compared with the type 2 and 3 CR chondrites, and the aromatic component is lower (Fig. 3b) upto Chainpur (UOC 3.4). Only the most altered CR1 chondrite has a carboxylic fraction that compares with the UOCs, suggesting that a similar type of oxidation process may have occurred in the lower petrologic type UOCs.

**Conclusions:** OM inclusions with 3-peak (C=C)-(C=O)-(COOH) C K-edge XANES spectra occurs interstitially in the matrices of most primitive CCs. With increasing aqueous alteration and elevated temperatures, the aromaticity of the OM inclusions increases, vinyl ketone content decreases and the carboxyl content increases. Further thermal processing leads to 2-peak (C=C)-(COOH) OM, where the aromaticity increases with the onset of graphitization. The diffuse OM around inclusions reduces in aromaticity and increases carboxyl fractions up to the conditions recorded in petrologic type 3.4 (Chainpur).