

**ORGANIC MATTER IN THE UNIQUE CARBONACEOUS CHONDRITE MILLER RANGE 07687: A COORDINATED IN SITU NANOSIMS, FIB-TEM, AND XANES STUDY.** J. Davidson<sup>1\*</sup>, L. R. Nittler<sup>1</sup>, R. M. Stroud<sup>2</sup>, A. Takigawa<sup>3</sup>, B. T. De Gregorio<sup>4</sup>, C. M. O'D. Alexander<sup>1</sup>, A. L. D. Kilcoyne<sup>5</sup>, and G. D. Cody<sup>6</sup>, <sup>1</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington (CIW), Washington DC 20015, <sup>2</sup>Naval Research Laboratory, Washington DC 20375, <sup>3</sup>Department of Mineralogy and Geology, Kyoto University, Kyoto 606-8502, Japan, <sup>4</sup>Nova Research Inc., Alexandria VA 22308, <sup>5</sup>Advanced Light Source, LBNL, Berkeley CA 94720, <sup>6</sup>Geophysical Laboratory, CIW, Washington DC 20015. \*E-mail: jdavidson@ciw.edu

**Introduction:** The organic matter (OM) present in primitive chondrites may have supplied early Earth with prebiotic molecules that were crucial for the origin of life [e.g., 1]. While OM can be identified by its isotopically anomalous compositions via secondary ion mass spectrometry (SIMS), analysis of OM via techniques such as X-ray absorption near edge structure (XANES) spectroscopy and transmission electron microscopy (TEM) allows investigation of its chemistry and microstructure. The analysis of OM located *in situ* also allows us to investigate its relationship to the surrounding matrix material. Miller Range (MIL) 07687 is a unique ungrouped Antarctic carbonaceous chondrite that shows minimal evidence of thermal metamorphism [2], but it exhibits a unique type of partial, localized aqueous alteration [3]. It also shows petrographic similarities to the ungrouped C3 Acfer 094 [4]. As a result, MIL 07687 provides us with the opportunity to investigate the effects of aqueous alteration on OM in a single sample at the sub- $\mu\text{m}$  scale. We report the results of coordinated NanoSIMS–XANES–TEM analyses of OM located *in situ* in MIL 07687.

**Experimental Methods:** Areas of matrix were identified in a thin section of MIL 07687 via secondary electron imaging with a JEOL JSM-6500F field emission scanning electron microscope (SEM) at the Carnegie Institution of Washington (CIW). Multiple matrix areas were then subjected to raster ion imaging via high-resolution SIMS (NanoSIMS 50L at CIW) using automated mapping routines. A  $\sim 2$  pA  $\text{Cs}^+$  primary ion beam was used to image  $10 \times 10 \mu\text{m}^2$  areas with a spatial resolution of  $\sim 150$  nm. Three sets of measurements were performed: (i) to locate C-anomalous carbonaceous material, and O- and C-anomalous presolar grains ( $^{16,17,18}\text{O}^-$ ,  $^{12}\text{C}_2^-$ ,  $^{12}\text{C}^{13}\text{C}^-$ ,  $^{28}\text{Si}^-$ ,  $^{27}\text{Al}^{16}\text{O}^-$  and secondary electrons), (ii) to determine the C and N isotopic compositions of carbonaceous material ( $^{16,17}\text{O}^-$ ,  $^{12}\text{C}_2^-$ ,  $^{12}\text{C}^{13}\text{C}^-$ ,  $^{12}\text{C}^{14}\text{N}^-$ ,  $^{12}\text{C}^{15}\text{N}^-$ ,  $^{28}\text{Si}^-$  and secondary electrons), and (iii) to determine the H isotopic compositions of carbonaceous material ( $^1\text{H}^-$ ,  $^2\text{H}^-$ ,  $^{12}\text{C}^-$ ,  $^{13}\text{C}^-$ ,  $^{16}\text{O}^-$  and secondary electrons). The abundances of presolar grains were previously reported [4, 5]. In total,  $\sim 43,000 \mu\text{m}^2$  of fine-grained matrix were analyzed. Three cross-sections ( $\sim 100$  nm thick) of matrix including isotopically anomalous carbonaceous material were extracted for further analysis by focused ion beam

(FIB) lift-out using an FEI Nova 600 FIB-SEM at the Naval Research Laboratory (NRL) and a Zeiss Auriga FIB-SEM at CIW. C, N, and O K-edge XANES analyses were performed on two of the three extracted sections and on a microtomed section of insoluble organic matter (IOM) using the scanning transmission X-ray microscope on beamline 5.3.2.2 [6] at the Advanced Light Source (ALS, LBNL). After XANES spectroscopy, TEM analysis was performed with a JEOL JEM 2200FS at NRL.

### Results and Discussion:

**NanoSIMS analysis.** NanoSIMS ion image mapping identified abundant carbonaceous regions with anomalous H/C/N isotopic compositions, with  $\delta^{13}\text{C}$  up to  $\sim 200$  ‰,  $\delta^{15}\text{N}$  up to  $\sim 2,000$  ‰ and  $\delta\text{D}$  up to  $\sim 5,000$  ‰ (Fig. 1).

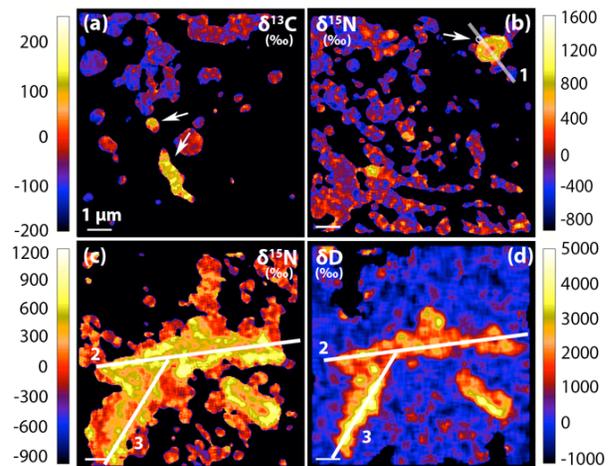


Fig. 1. NanoSIMS ion image maps ( $10 \times 10 \mu\text{m}^2$  raster areas) of isotopically anomalous OM in the matrix of MIL 07687, with the location of three FIB-extracted sections marked (numbered white lines). (a) Isotopically anomalous OM ( $\delta^{13}\text{C} = \sim 200$  ‰) not associated with Si indicated by the two arrows, (b) OM with isotopically normal C but isotopically anomalous N ( $\delta^{15}\text{N} = \sim 1400$  ‰) adjacent to a Group 4 presolar silicate grain (outline indicated by arrow), and (c, d) N- and H-isotopically anomalous OM in a vein ( $\delta^{15}\text{N} = 700$  ‰;  $\delta\text{D} = 2540$  ‰). All scale bars are  $1 \mu\text{m}$ .

Regions with anomalous C-isotopic compositions do not always exhibit anomalous N- and/or H-isotopic compositions, and vice versa. The majority of isotopi-

cally anomalous OM grains in MIL 07687 are round submicron hotspots; one N-anomalous region ( $\sim 700$  nm in diameter;  $\delta^{15}\text{N} = 804 \pm 22$  ‰) is adjacent to an  $^{18}\text{O}$ -rich presolar silicate grain [4] (Fig. 1b). However, a large ( $\sim 8 \times 6$   $\mu\text{m}$  diameter), isotopically anomalous ‘vein’ of carbonaceous material was also identified (Fig. 1c,d). The vein is isotopically anomalous in both N (average  $\delta^{15}\text{N} = 700 \pm 8$  ‰; Fig. 1c) and H ( $\delta\text{D} = 2540 \pm 40$  ‰; Fig. 1d), but not C. The isotopic composition is variable across the vein with some hotspots seen (up to  $\sim 2,000$  ‰ in  $\delta^{15}\text{N}$  and  $\sim 5,000$  ‰ in  $\delta\text{D}$ ). The MIL 07687 vein is similar to C-rich inclusions previously seen in the CR chondrites QUE 99177 [7] and GRA 95229 [8], demonstrating the presence of such material in chondrite groups other than the CR chondrites.

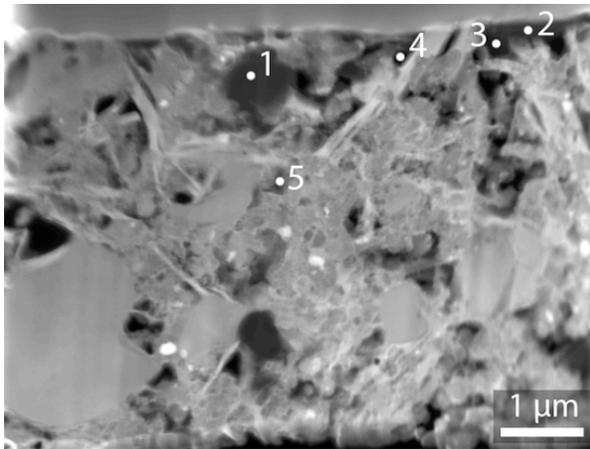


Fig. 2. TEM HAADF image of Section 2 (vein; Fig. 1c and 1d) showing the distribution of C (darker regions). See Fig. 3 for XANES spectra of marked locations.

**XANES and TEM analysis.** Carbon K-edge XANES mapping of Section 1 did not detect significant amounts of C adjacent to the supernova silicate grain. However, TEM analysis revealed that a thin layer ( $\sim 25$  nm thick) of OM remains at the surface. Section 3 contains a wedge of carbonaceous material at the surface but the section could not be studied by XANES due to the sample geometry (future TEM analyses are planned). Sections 1 and 2 contain pockets of OM throughout (e.g., Fig. 2), indicating that OM is pervasive throughout the matrix of MIL 07687. Carbon K-edge XANES spectra from OM in these sections exhibit three spectral bands that are commonly seen in chondritic IOM [9]. These bands are associated with the presence of aromatic and olefinic carbon bonds (at  $\sim 285$  eV), vinyl-keto bonds (at  $\sim 286.5$  eV), and carboxyl bonds (at  $\sim 288.4$  eV; Fig. 3) [9]. Spectral features associated with the presence of carbonate were also seen (at  $\sim 290$  eV). Spectra from carbonaceous material show variability in the position of the aro-

matic peak ( $\sim 285$  eV), similar to what was seen in the OM of QUE 99177 [7]. The carbon K-edge XANES spectra indicate that the carbonaceous material is chemically variable. No nanoglobules were seen either *in situ* or in the extracted IOM via TEM analysis in contrast to what is seen in the CR chondrites [e.g., 7, 8, 10]. The presence of carbonate is consistent with the aqueously altered nature of MIL 07687. Thus, MIL 07687 should be considered to be a type 2 carbonaceous chondrite.

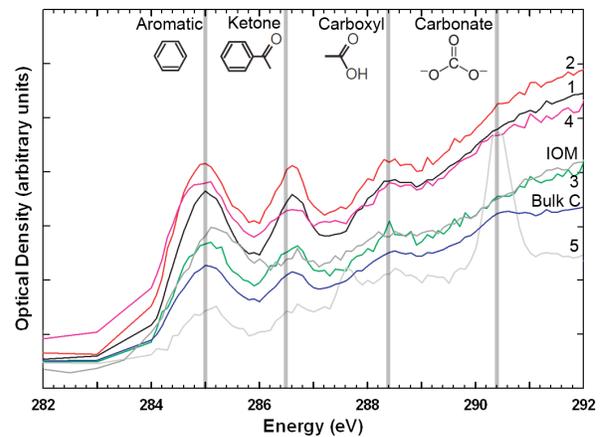


Fig. 3. Carbon K-edge XANES spectra from OM and carbonate in Section 2 (Fig. 2) and microtomed IOM. Chemical bonds associated with specific peaks are shown (after [10]).

**Summary:** We performed coordinated NanoSIMS isotopic analysis, XANES spectroscopy, and TEM microscopy on the OM in sections of matrix from the unique carbonaceous chondrite MIL 07687. The carbonaceous material appears to be spectrally similar to IOM from this and other primitive carbonaceous chondrites, but is morphologically different as it contains no nanoglobules. The OM is present as abundant, isolated, sub-micron inclusions but also as larger, albeit much rarer, veins of material. Further NanoSIMS analyses are planned.

**References:** [1] Busemann H. et al. (2006) *Science* 312, 727–730. [2] Davidson J. et al. (2014) *LPS XLV*, 1384. [3] Brearley A. (2012) *LPS XLIII*, 1233. [4] Davidson J. et al. (2014) *LPS XLV*, 1376. [5] Davidson J. et al. (2014) *Goldschmidt*, 503. [6] Kilcoyne A. L. D. et al. (2003) *J. Synchrotron Rad.*, 10, 125–136. [7] Peeters Z. et al. (2012) *LPS XLII*, 2612. [8] Peeters Z. et al. (2012) *Meeting of the Met. Soc.*, A5283. [9] Cody G. D. et al. (2008) *MAPS* 43, 353–365. [10] De Gregorio B. T. et al. (2013) *MAPS* 48, 904–928.

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