

Carbonaceous material in the unique carbonaceous chondrite Miller Range 07687: A coordinated NanoSIMS, FIB-TEM, and XANES study. J. Davidson^{1*}, L. R. Nittler¹, R. M. Stroud², A. Takigawa³, C. M. O'D. Alexander¹, A. L. D. Kilcoyne⁴, and George D. Cody⁵,
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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 [1]. While OM can be identified by its isotopically anomalous compositions via secondary ion mass spectrometry (SIMS) analysis [e.g., 1], analysis of OM via techniques such as transmission electron microscopy (TEM) and X-ray absorption near edge structure (XANES) spectroscopy allows us to investigate its microstructural and chemical nature. The extraction of OM located *in situ* also allows us to investigate its relationship to the surrounding chondritic matrix material.

Miller Range (MIL) 07687 is a unique ungrouped Antarctic carbonaceous chondrite that shows minimal evidence of thermal metamorphism [2] but exhibits a unique type of partial, localized aqueous alteration that has resulted in two apparent matrix lithologies [3]. 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-mm scale. We report the results of coordinated NanoSIMS–XANES analysis of carbonaceous material located *in situ* in MIL 07687.

Experimental methods:

Areas of matrix were identified in a thin section of MIL 07687 with a JEOL JSM-6500F field emission scanning electron microscope (SEM) imaging 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 ~ 2 pA Cs^+ primary ion beam was used to image $10 \times 10 \mu\text{m}^2$ areas with a spatial resolution of ~ 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 area was analyzed. Three cross-sections (~ 100 nm thick) of matrix areas including isotopically

anomalous carbonaceous material were extracted for further analysis using focused ion beam (FIB) lift-out with two SEMs, an FEI Nova 600 FIB-SEM equipped with an Ascend Extreme Access micromanipulator at the Naval Research Laboratory and a Zeiss Auriga FIB-SEM equipped with an Omniprobe micromanipulator at CIW. The entire lengths of the sections were covered in Pt straps by ion beam deposition to protect the samples during milling. C-, N-, and O-XANES analyses were performed on the extracted sections using the scanning transmission X-ray microscope (STXM) on beamline 5.3.2.2 [6] at the Advanced Light Source (ALS, LBNL).

Results and discussion:

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

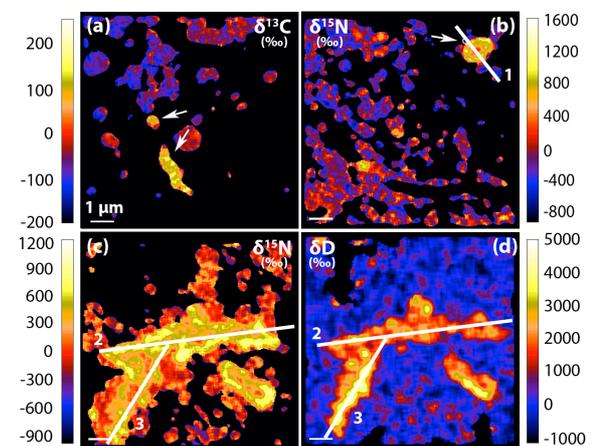


Fig. 1. NanoSIMS ion image maps ($10 \times 10 \mu\text{m}^2$ raster areas) of (a–d) isotopically anomalous carbonaceous material in the matrix of MIL 07687, with the location of three FIB-extracted sections marked (numbered white lines). (a) Isotopically anomalous carbonaceous material ($\delta^{13}\text{C} = \sim 200$ ‰) not associated with Si indicated by the two arrows, (b) carbonaceous material 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 carbonaceous material ($\delta^{15}\text{N} = 700 \pm 8$ ‰; $\delta\text{D} = 2540 \pm 37$ ‰). All scale bars are $1 \mu\text{m}$.

Regions with anomalous C-isotopic compositions do not always exhibit anomalous N-isotopic compositions, and vice versa. Similarly, N-anomalous regions are not always also H-anomalous, and vice versa. The majority of isotopically anomalous carbonaceous grains are round submicron hotspots; one N-anomalous region (~ 700 nm in diameter; $\delta^{15}\text{N} = 804 \pm 22$ ‰) is adjacent to an ^{18}O -rich presolar silicate grain [4] (Fig. 1b). However, a large ($\sim 8 \times 6$ μm diameter), isotopically anomalous ‘vein’ of carbonaceous material was also identified (Fig. 1c,d). The vein is isotopically anomalous in both N ($\delta^{15}\text{N} = 700 \pm 8$ ‰; Fig. 1c) and H ($\delta\text{D} = 2540 \pm 37$ ‰; 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 δD). 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.

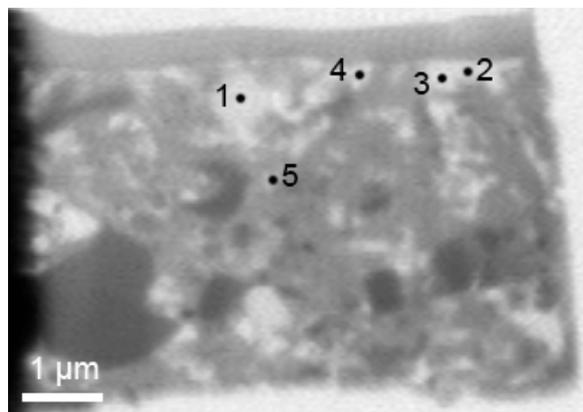


Fig. 2. XANES map of Section 2 (Fig. 1c and 1d) showing the distribution of C (brighter regions) in the section at 280 eV. Spectra of the marked locations are shown in Fig. 3.

Carbon K-edge XANES mapping of Section 1 revealed that the carbonaceous material adjacent to the supernova silicate grain appears to have been sputtered away during NanoSIMS analysis. Section 2 (Fig. 2) contains pockets of carbonaceous matter throughout, indicating that carbonaceous material is pervasive throughout the matrix of MIL 07687. Section 3 contains a wedge of carbonaceous material similar to that seen in Section 2.

Carbon K-edge XANES spectra from carbonaceous material in all 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 ~ 285 eV), vinyl-keto bonds (at ~ 286.5 eV), and carboxyl bonds (at ~ 288.4 eV; Fig. 3) [9]. Spectral features associated with the presence of carbonate were also seen (at ~ 290 eV). Spectra from carbonaceous material show variability in the position of the aromatic peak (~ 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. Future TEM analysis will determine if this variability correlates with specific morphologic features such as nanoglobules [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.

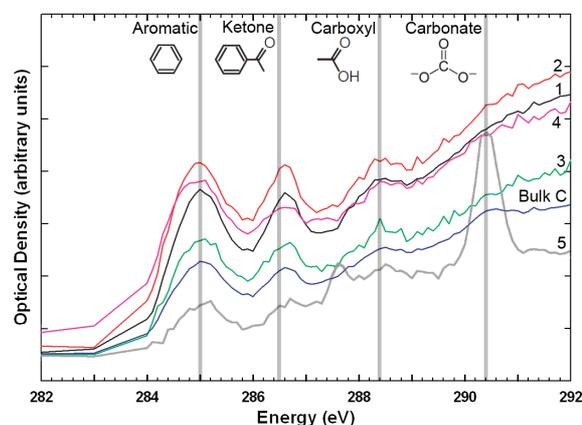


Fig. 3. Carbon K-edge XANES spectra from OM and carbonate in Section 2 (Fig. 2). Chemical bonds associated with specific peaks are shown (after [10]).

Summary: We performed coordinated NanoSIMS isotopic analysis and XANES spectroscopy on the carbonaceous material in sections of matrix from the unique carbonaceous chondrite MIL 07687. The carbonaceous material appears to be similar to IOM from other primitive carbonaceous chondrites, and is present as abundant, isolated, sub-micron inclusions but also as larger, albeit much rarer, veins of material. Further TEM and NanoSIMS analyses are planned.

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