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SECONDARY ION MASS SPECTROMETRY AND X-RAY ABSORPTION NEAR-EDGE STRUCTURE SPECTROSCOPY OF ISOTOPICALLY ANOMALOUS ORGANIC MATTER FROM CR1 CHONDRITE GRO 95577. H. Busemann^{1,2}, T. J. Zega³, C. M. O'D. Alexander², G. D. Cody⁴, A. L. D. Kilcoyne⁵, L. R. Nittler², R. M. Stroud³, H. Yabuta⁴, ¹Planetary & Space Science Research Institute, The Open University, Milton Keynes, MK7 6AA, UK, h.busemann@open.ac.uk, ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, USA, ³Materials Science and Technology Division, Naval Research Laboratory Washington DC, USA, ⁴Geophysical Laboratory, Carnegie Institution of Washington, USA, ⁵Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, USA.

Introduction: Primitive meteorites contain abundant (2–5 wt%) carbonaceous material. At least some of this, mostly insoluble organic matter (IOM), is likely to have originated in the protosolar molecular cloud, based on its spectral properties and H and N isotope characteristics [1–4]. The complete characterization of this IOM will hence improve our understanding of: (i) chemistry in interstellar space, (ii) processes that occurred during incorporation of interstellar IOM into the first solar system bodies, and (iii) parent-body processing of the IOM.

The synthesis, molecular structure and alteration mechanisms of the IOM are mostly unknown and difficult to assess. Particularly helpful in this regard may be spatially correlated studies, where isotope anomalies in H and N, detected with Secondary Ion Mass Spectrometry (SIMS), locate interstellar material that can then be analyzed with Micro-Raman Spectroscopy, Scanning Transmission X-Ray (STXM) and Transmission Electron (TEM) Microscopy.

Samples: Here we discuss correlated examinations of IOM from the CR1 chondrite GRO 95577. This meteorite contains the as-yet most primitive IOM of any chondrite we have studied, based on Micro-Raman Spectroscopy, bulk IOM H and N isotopic analyses and isotope mapping [4–6]. See [5] for the method of IOM extraction.

SIMS Analyses: We mapped the H, C, and N (as CN⁻) isotopic compositions of 10 fragments of the GRO 95577 IOM, pressed into Au substrates, with the Cameca NanoSIMS 50L at the Department of Terrestrial Magnetism (nominal resolution 100 nm). All fragments show large positive D and ¹⁵N isotope anomalies in bulk and in hotspots comparable and exceeding those found in the IOM of EET 92042 (CR2) and in the matrix of Bells (anomalous CM) [4]. One fragment (Fig. 1A) has the largest directly measured δD value (41,000±9000 ‰) reported for any extraterrestrial material in the laboratory and approaches the ~50,000 ‰ value inferred for a hotspot in one interplanetary dust particle (IDP) [7]. Fig. 1B shows a small “region of interest” (ROI) with a large $\delta^{15}N$ value of ~1800 ‰. Many other ROIs have anomalies

in δD in the range 5000–20,000 ‰. The fragment in Fig. 1C contains five ROIs that show spatially correlated enrichments in D and ¹⁵N. Three of them also show depletions in ¹³C (not shown). We selected these three, isotopically most interesting, aggregates for Focused Ion Beam lift out (FIB) and x-ray spectroscopy.

FIB extraction: The ROIs discussed above have been lifted out with the Naval Research Laboratory FEI Nova 600 FIB-SEM microscope equipped with an Ascend Instruments Extreme Access lift-out tool [8]. Five sections of ~3–15 μm (Fig. 1) were extracted with a 30 keV Ga⁺-ion beam, thinned to ~200 nm and lifted out with micro-tweezers fabricated in situ. The protective Pt straps covering the IOM are visible in Figs. 1A–C. Fig. 1D shows the excavated sections of the fragment in Fig. 1C before lift out.

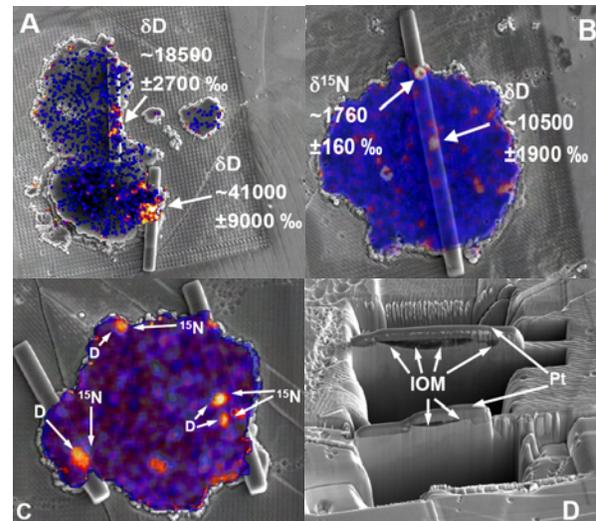


Fig. 1A–C: SEM micrographs (15 keV, mag 2500–5000) of 3 fragments of GRO 95577 IOM, showing the Pt protective straps and overlaying NanoSIMS δD and $\delta^{15}N$ distribution maps. Various isotopically anomalous ROIs are indicated. **D:** Excavated sections from fragment in Fig. 1C with IOM sandwiched between Pt and Au substrate, prior to lift out. The STXM image of the section in front (~3 μm IOM) is shown in Fig. 2. The section in the back was lost during sample handling.

XANES Analyses: We analyzed the four surviving sections shown in Fig. 1 with the scanning x-ray transmission microscope (STXM) at the soft x-ray beamline 5.3.2 (optimized for ~250-600 eV) of the Advanced Light Source in Berkeley (resolution ~40 nm), both in stack image and line modes. We obtained spectra from carbon, nitrogen, and oxygen X-ray Absorption Near-edge Structure (C-, N-, and O-XANES) Spectroscopy. XANES allows the determination of relative elemental abundances, as well as the functional group characterization of C-, N-, and O-bearing molecules [9].

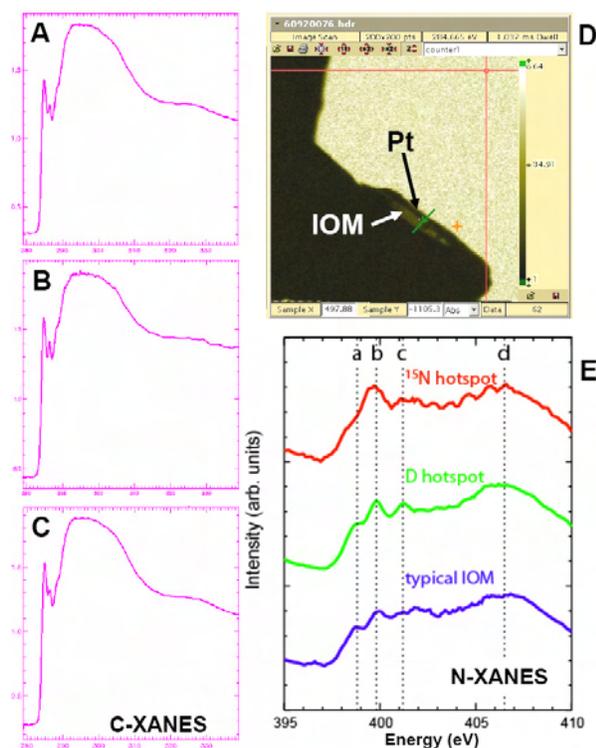


Fig. 2A-C: C-XANES spectra of D-rich (top), ^{15}N -rich and “typical” (bottom) IOM. **D:** STXM image (above C-edge) of fragment shown in front of Fig. 1D. **E:** N-XANES of D and ^{15}N hotspots and typical IOM: a=imine, b=nitrile, c= amidyl(?), d=ionization edge.

Analysis of the XANES data is ongoing, but Fig. 2 illustrates some preliminary results. Figs. 2A-C show examples of C-XANES spectra of D (top) and ^{15}N hotspots, as well as “typical” IOM (bottom). Most spectra are very similar and show features at ~285 and 289 eV, typical for aromatic and carbonyl functional groups. Fig. 2D shows a STXM image of the section in the foreground of Fig. 1D. Fig. 2E compares the spatially integrated N-XANES spectra (fragment from Fig. 1B) for D (green) and ^{15}N (red) hotspots and “typical” IOM (blue). The three spectra show signifi-

cant variations. In particular the ^{15}N hotspot shows much higher abundance of nitrile than the other IOM regions and the D hotspot shows a stronger feature at ~401 eV, possibly due to amidyl. All O-XANES spectra (not shown) were similar, showing a carbonyl feature at ~532 eV.

Discussion: The better spatial resolution of the NanoSIMS compared to the 6f used in earlier studies reveals that the anomalies in D reported for meteoritic IOM of up to $\delta\text{D} \sim 20,000 \text{ ‰}$ [4] are still lower limits. The highest δD value of 41,000 ‰ found in this study approaches the values in gaseous deuterated molecules in the cold interstellar medium [10], providing further evidence for the pristine character of the IOM and its likely origin in the protosolar cloud or outer regions of the protoplanetary disk. The IOM in GRO 95577 (CR1) appears similarly primitive to that of EET 92042 (CR2) [4–6], implying that the more extensive aqueous alteration experienced by this type 1 CR chondrite did not significantly alter the pristine characteristics of the IOM. The spatially correlated positive anomalies in D and ^{15}N , and negative anomalies in ^{13}C resemble closely the properties recently reported for nanoglobules in the Tagish Lake meteorite [e.g., 11, 4], suggesting that these, probably presolar, aggregates are also present in the primitive CR chondrites. The apparent lack of significant variations in C-XANES spectra may indicate that the most extreme D anomalies are not associated with any specific functional groups. Variations in the N-XANES spectra suggests, however that the ^{15}N enrichments, originating from interstellar environments, do appear to be associated with a noticeable increase in nitrile functionality; i.e. that there exists in the case of ^{15}N a molecular carrier for this isotopic anomaly.

Further analyses of the FIB sections by TEM are planned and will be presented at the meeting.

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