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CORRELATED MICROSCALE ISOTOPE AND SCANNING TRANSMISSION X-RAY ANALYSES OF ISOTOPICALLY ANOMALOUS ORGANIC MATTER FROM THE CR2 CHONDRITE EET 92042. H. Busemann¹, C. M. O'D. Alexander¹, L. R. Nittler¹, T. J. Zega², R. M. Stroud², G. D. Cody³, H. Yabuta³, P. Hoppe⁴, ¹Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5421 Broad Branch Road NW, Washington DC 20015-1305, USA, busemann@dtm.ciw.edu, ²Naval Research Laboratory Washington DC, USA, ³Geophysical Laboratory, Carnegie Institution of Washington, USA. ⁴Max-Planck-Institut für Chemie Mainz, Germany.

Introduction: Insoluble carbon-rich residues extracted from primitive meteorites contain abundant macromolecular organic matter (OM) that yields important information about the earliest stages of solar system evolution. Extraterrestrial OM was potentially also an important source of prebiotic precursors of the complex molecules that were essential for the formation of life on Earth [1]. Based on its spectral properties and H and N isotope characteristics, it is believed that at least parts of the OM in meteorites and interplanetary dust particles (IDPs) originates from the protosolar cloud [2, 3]. The complete characterization of this OM is therefore important to understand (i) chemistry in interstellar space, (ii) processes that occurred during incorporation of interstellar OM into the first solar system bodies and (iii) alteration of the OM due to parent-body processing. However, synthesis, molecular structure and alteration reactions of the interstellar OM are mostly unknown and difficult to assess. Particularly important are spatially correlated examinations, where isotope anomalies in H and N, detected with Secondary Ion Mass Spectroscopy (SIMS), indicate interstellar OM, which is then analyzed with, e.g., Micro-Raman Spectroscopy, Scanning Transmission X-Ray (STXM) or Transmission Electron (TEM) Microscopy.

Here we discuss correlated examinations of OM, using multiple analytical methods, from the CR2 chondrite EET 92042. Of all carbonaceous chondrites, the OM from this meteorite is the most primitive, as shown with Micro-Raman Spectroscopy [4], bulk OM H and N isotopic analyses [5] and isotope mapping [6, 7].

Analyses and Results: We mapped the distributions of ^{1,2}H, ^{12,13}C, ^{14,15}N, O and Si in >100 aggregates of meteoritic OM, unprocessed matrix particles of various primitive chondrites as well as entire IDPs (~20-3000 μm²) [e.g., 6-11]. The samples were pressed into Au substrates and analyzed with SIMS (Cameca ims 6f, Carnegie Institution, and NanoSIMS 50, MPI Mainz) in order to identify the most pristine interstellar OM and other isotopically anomalous matter. The OM extraction procedure is given in [5]. Some of the most isotopically anomalous “regions of interest” (ROIs)

have been lifted out and thinned in situ down to ~100 nm with the Focused Ion Beam-Scanning Electron Microscope (FIB-SEM, [12]) for further examination with STXM and TEM.

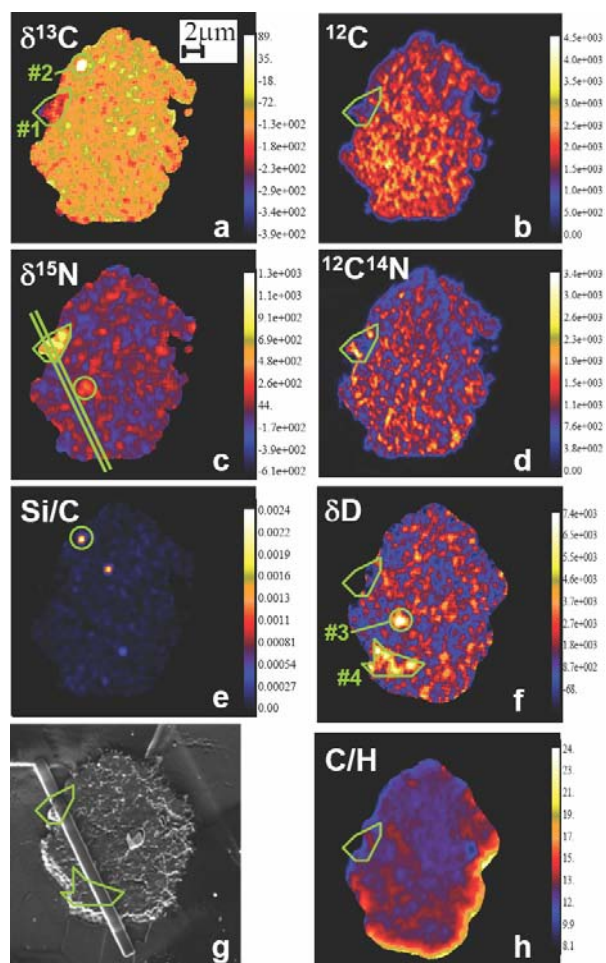


Fig. 1: Distribution maps of an assemblage of OM from the CR2 chondrite EET 92042. **Fig. 1a-c:** ims 6f, **Fig. 1f-h:** NanoSIMS. Four isotopically anomalous ROIs are indicated. **Fig. 1g:** SEM micrograph showing where an electron-transparent section was created and lifted out for analyses with STXM and TEM. Elemental abundances and ratios are in non-calibrated units.

SIMS Analyses. ^{12}C , $^{14,15}\text{N}$ (as $^{12}\text{C}^{14,15}\text{N}$) and Si have been mapped with the NanoSIMS at a nominal resolution of 100 nm. ^1H , C and O have been mapped with the ims 6f at a resolution of $\sim 1.5\ \mu\text{m}$.

SIMS and NanoSIMS revealed four large isotopically anomalous ROIs that are labeled in Figs. 1a+f.

ROI #1 is $\sim 5\ \mu\text{m}^2$, shows a positive ^{15}N anomaly ($\delta^{15}\text{N} \sim 1150 \pm 40\ \text{‰}$, Fig. 1c) and a negative $\delta^{13}\text{C}$ value of $-113 \pm 14\ \text{‰}$ (Fig. 1a). Smaller areas within this ROI show larger $\delta^{15}\text{N}$ values of up to $1590 \pm 90\ \text{‰}$. Carbon and N are heterogeneously distributed. The region is C-poor, partially very N-rich and devoid of Si (Figs. 1b, d, e), compared to the bulk OM. ROI #1 does not show any anomalous D/H (Fig. 1f), and is generally C- and H-poor. The C/H ratio is similar to the neighboring OM (Fig. 1h).

ROI #2 ($\sim 0.12\ \mu\text{m}^2$) has a $\delta^{13}\text{C}$ of $1810 \pm 120\ \text{‰}$ ($^{12}\text{C}/^{13}\text{C} = 32$, solar value: 89, Fig. 1a) and is highly enriched in Si (Fig. 1e), while N and H are isotopically normal (Figs. 1c+f).

ROI #3 ($2.6\ \mu\text{m}^2$) is enriched in ^{15}N ($\delta^{15}\text{N} = 560 \pm 60\ \text{‰}$, Fig. 1c) and shows element abundances that are typical for this OM. The ^{15}N hotspot is spatially correlated with a D-rich hotspot ($\delta\text{D} = 5200 \pm 700\ \text{‰}$, Fig. 1f).

ROI #4 ($8\ \mu\text{m}^2$) is D-rich with an average $\delta\text{D} = 4800 \pm 600\ \text{‰}$ (Fig. 1f) and is not related to any ^{15}N hotspot (Fig. 1c).

STXM Analyses. The section through the most anomalous ROI #1 and parts of ROI #4, which has been lifted out with FIB-SEM [12], is shown in Figs. 1c+g. It has been analyzed with STXM at a resolution $< 50\ \text{nm}$ (Advanced Light Source Berkeley).

Spectra from Carbon X-ray Absorption Near-edge Structure (C-XANES) Spectroscopy (see, e.g., [13]) are shown in Fig. 2b. For comparison, a spectrum of microtomed OM from EET 92042 is shown. The spectrum of the ^{15}N -rich and ^{13}C -poor ROI #1 significantly differs from those of the remaining OM in this section. ROI #1 does not show signs of abundant C, in agreement with the SIMS analyses. Differences between the FIB and the microtome sections can be explained by saturation effects due to the presence of Pt nanoparticles incorporated to protect the section during the milling process [12].

Results from TEM and Micro-Raman Spectroscopy [see, e.g., 4, 10, 11] will be shown at the meeting.

Discussion: The OM of EET 92042 contains significant amounts of isotopically heterogeneous and very pristine material. Correlations of the “interstellar matter pathfinders” D and ^{15}N are rare, rendering it difficult to define “components”, as found in IDPs

[14]. The already performed examinations of the unusual ^{15}N -rich and ^{13}C -poor ROI #1 do not allow its identification. However, known presolar grains such as graphite or SiC can be excluded, because C and Si are depleted in ROI #1. Nevertheless, a presolar origin is likely, because of the large isotope anomalies in ^{15}N and ^{13}C . The C/H ratio, which is comparable to average C/H in this OM (Fig. 1f), might originate from thin coatings of “common” OM present during the SIMS measurements. The highly unusual C-XANES spectrum of this region emphasizes its unique character. TEM analyses are ultimately necessary to identify this C-poor, acid resistant and isotopically highly anomalous material. ROI #2 is clearly a presolar SiC grain.

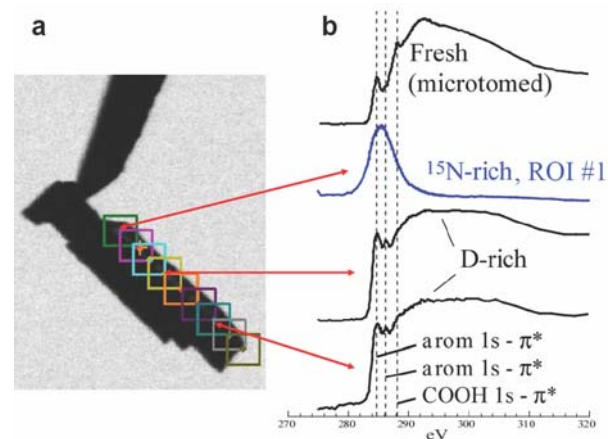


Fig. 2a: Section lifted out from the OM aggregate of EET 92042 (Figs. 1c+g). The OM lies under the squares and is sandwiched between Pt and the AU substrate. A “microtweezer” holds the section [11, 12]. **Fig. 2b:** Some of the (averaged) C-XANES spectra obtained along the section of OM.

References: [1] Pizzarello S. et al. (2006) in *Meteorites and the Early Solar System II*, in press. [2] Alexander C. M. O’D. et al. (1998) *Meteorit. Planet. Sci.*, 33, 603–622. [3] Messenger S. (2000) *Nature*, 404, 968–971. [4] Busemann H. et al. (2005) *LPS XXXVI*, Abstract #1975. [5] Alexander C. M. O’D. et al. (in preparation) *GCA*. [6] Busemann H. et al. (2005) *Meteorit. Planet. Sci. Suppl.*, 40, A26. [7] Busemann H. et al. (submitted) *Science*. [8] Young A. F. et al. (2004) *LPS XXXV*, Abstract #2097. [9] Nittler L. R. (2005) *Meteorit. Planet. Sci.*, 40, A114. [10] Nittler L. R. et al. (2006) *LPS XXXVII*, this volume. [11] Zega T. J. et al. (2006) *LPS XXXVII*, this volume. [12] Zega T. J. and Stroud R. M. (2006) *LPS XXXVII*, this volume. [13] Flynn G. J. et al. (2003) *GCA*, 67, 4791–4806. [14] Aléon J. and Robert F. (2004) *Icarus*, 167, 424–430.