

**ORGANIC ANALYSIS IN THE MILLER RANGE 090657 CR2 CHONDRITE: PART 3 C AND N ISOTOPIC IMAGING** S. Messenger<sup>1</sup>, K. Nakamura-Messenger<sup>1</sup>, J. E. Elsila<sup>2</sup>, E. L. Berger<sup>3</sup>, A. S. Burton<sup>1</sup>, S. J. Clemett<sup>4</sup>, and T. Cao<sup>5</sup> <sup>1</sup>Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX, [scott.r.messenger@nasa.gov](mailto:scott.r.messenger@nasa.gov), <sup>2</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, <sup>3</sup>GeoControl Systems Inc – Jacobs, NASA Johnson Space Center, Houston, TX, USA, <sup>4</sup>ERC Inc – Jacobs, NASA Johnson Space Center, Houston, TX, USA, <sup>5</sup>University of California, Merced, CA,

### Introduction:

Primitive carbonaceous chondrites contain a wide variety of organic material, ranging from soluble discrete molecules to insoluble nanoglobules of macromolecular carbon [1-3]. The relationship between the soluble organic molecules, macromolecular organic material, and host minerals are poorly understood. Large H, C and N isotopic anomalies suggest some organic components formed in low-T interstellar or outer Solar System environments [4-5]. The highest isotope anomalies occur in  $\mu\text{m}$ -scale inclusions in the most primitive materials, such as cometary dust and the least altered carbonaceous chondrites [6]. Often, the hosts of these isotopically anomalous ‘hotspots’ are discrete organic nanoglobules that probably formed in the outermost reaches of the protosolar disk or cold molecular cloud [7].

Molecular and isotopic studies of meteoritic organic matter are aimed at identifying the chemical properties and formation processes of interstellar organic materials and the subsequent chemical evolutionary pathways in various Solar System environments. The combination of soluble and insoluble analyses with *in situ* and bulk studies provides powerful constraints on the origin and evolution of organic matter in the Solar System. Using macroscale extraction and analysis techniques as well as microscale *in situ* observations we have been studying both insoluble and soluble organic material in primitive astromaterial samples. Here, we present results of bulk C and N isotopic measurements and coordinated *in situ* C and N isotopic imaging and mineralogical and textural studies of carbonaceous materials in a CR2 carbonaceous chondrite. In accompanying abstracts we discuss the morphology and distribution of carbonaceous components [8] and soluble organic species of this meteorite [9].

**Samples and Analysis Methods:** The CR2 carbonaceous chondrite Miller Range (MIL) 090657 was selected for this study. This chondrite has not been extensively characterized, but based on previous isotopic and petrographic descriptions, it appears to have experienced minimal aqueous alteration [10]. This meteorite also has a relatively high presolar silicate abundance (~112 ppm) and bulk  $\delta\text{D}$  (814 ‰) indicating that this meteorite is highly primitive [11]. To prepare samples for coordinated TEM-isotopic study, fine grained dark fragments (50 – 100  $\mu\text{m}$ ) were carefully selected from the matrix and embedded in pure S. Thin

sections of 70-100 nm-thickness were prepared using ultramicrotomy and deposited on TEM grids. Bright-field and dark-field images were obtained using a JEOL 2500SE field-emission scanning TEM at Johnson Space Center (JSC). This instrument is equipped with an energy-dispersive X-ray detector (EDX) analysis system, capable of nanometer-scale compositional mapping. Carbon and N isotopic imaging studies were carried out with the JSC NanoSIMS 50L ion microprobe. Isotopic images of  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{16}\text{O}$ ,  $^{12}\text{C}^{14}\text{N}$ ,  $^{12}\text{C}^{15}\text{N}$  and  $^{28}\text{Si}$  were acquired in multidetection mode with electron multipliers (EMs). Images were obtained by rastering a ~1 pA, ~100 nm  $\text{Cs}^+$  beam over 10 – 20  $\mu\text{m}$  fields of view. Imaging runs consisted of repeated (20 – 100) scans over the same area. Electrostatic charging was mitigated with an  $\text{e}^-$  flood gun. Carbon and N isotopic images from a terrestrial kerogen were used as an isotopic standard. Images were corrected for EM dead-time, QSA, and instrumental mass fractionation with custom software.

Bulk C and N abundances and isotopic ratios of MIL were measured at Goddard Space Flight Center. Measurements were acquired using a Costech ECS 4010 combustion elemental analyzer (EA) connected by a Thermo ConFlo III interface to a Thermo MAT 253 isotope ratio mass spectrometer (IRMS). Three aliquots of powdered sample (~10 – 22 mg each) were weighed in tin cups, folded into sealed packets, and loaded into the Costech zero-blank autosampler of the EA, which was purged with ultra-pure He for 5 min. The tin cups were flash combusted in the EA at 1000°C and subsequently oxidized and reduced to  $\text{CO}_2$  and  $\text{N}_2$ . These gases were separated on a GC column and passed into the IRMS for isotopic measurement. An L-alanine standard was used to calibrate the bulk isotopic measurements. Errors for abundances and isotopic values are standard deviations for triplicate measurements.

**Results:** The MIL matrix samples show three distinct silicate lithologies: 1) submicron polycrystalline, 2) amorphous and 3) hydrated silicates. The dominant lithology (#1) is composed of sub- $\mu\text{m}$  euhedral polycrystalline olivine and pyroxene grains. Networks of spongy to granular carbonaceous material occur between grains. In the amorphous silicate lithology, the carbonaceous material appears to be larger and smoother than the that found in lithology 1. The volume ratio of carbonaceous matter to mineral grains is

1:1 in lithologies 1 and 2. Isotopic images were obtained from MIL sections that were essentially free of hydrated silicates.

Bulk composition measurements yielded results of  $0.8 \pm 0.2$  wt% C and  $0.067 \pm 0.006\%$  N. Bulk isotopic analysis by EA-IRMS gave a  $\delta^{13}\text{C}$  value of  $-0.5 \pm 0.8$  ‰ that was indistinguishable from that determined by NanoSIMS isotopic imaging ( $\delta^{13}\text{C} = 1 \pm 2\%$ ). However, the bulk  $\delta^{15}\text{N}$  determined by EA-IRMS of  $+186.0 \pm 0.4$  ‰, was significantly higher than that measured by isotopic imaging ( $\delta^{15}\text{N} = 57 \pm 7$  ‰) and a previous bulk measurement ( $\delta^{15}\text{N} = 132$  ‰; [11]).

Isotopic imaging of MIL showed significant  $\mu\text{m}$ -scale variability in  $\delta^{15}\text{N}$ , with anomalies similar in magnitude to that observed in other carbonaceous chondrites and cometary dust particles (Fig. 1, 6,7,12). The  $\delta^{15}\text{N}$  anomalies in these  $\mu\text{m}$ -scale hotspots were typically 400 – 600 ‰, reaching a maximum of 1,100 ‰. Subdivision of the images into equivalent 500 nm diameter bins showed that ~5 % of the matrix in these samples was isotopically anomalous (Fig. 2). By contrast, no regions in these images showed significant C isotopic anomalies.

**Discussion:** The bulk  $\delta^{15}\text{N}$  value of 186 ‰ is relatively high among carbonaceous chondrites, suggestive of an abundant primordial (cometary or interstellar) component. This is borne out by isotopic imaging studies that revealed numerous  $\mu\text{m}$ -scale areas with significantly greater anomalies. The lower bulk  $\delta^{15}\text{N}$  measured by isotopic imaging, relative to EA-IRMS, suggests that other areas of MIL have still higher abun-

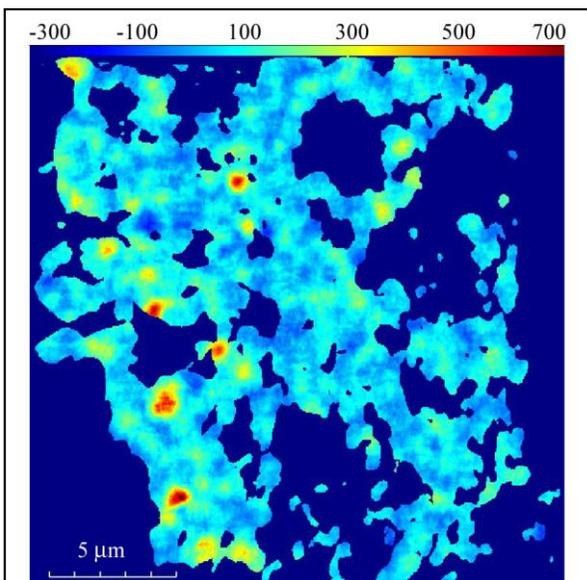


Fig. 1:  $\delta^{15}\text{N}$  image of a microtome section of the Mil 090657 CR2 chondrite. The image has been smoothed by a spatially variable  $n \times n$  binning procedure that results in  $\leq 5\%$   $1\sigma$  counting statistical error in each pixel. Areas lacking sample have been masked out (dark blue).

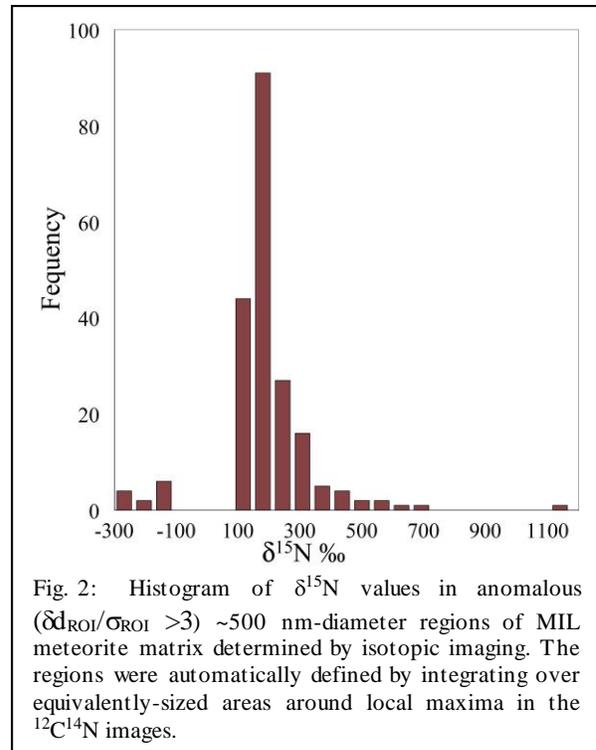


Fig. 2: Histogram of  $\delta^{15}\text{N}$  values in anomalous ( $\delta_{\text{ROI}}/\sigma_{\text{ROI}} > 3$ ) ~500 nm-diameter regions of MIL meteorite matrix determined by isotopic imaging. The regions were automatically defined by integrating over equivalently-sized areas around local maxima in the  $^{12}\text{C}^{14}\text{N}$  images.

dances of  $^{15}\text{N}$ -rich carriers. Such spatial heterogeneity in isotopic compositions (Fig 1 & 2) provides a quantitative measure of how well primordial organic matter has been preserved in various parent bodies. This preliminary study suggests that MIL possesses a high concentration of preserved isotopically anomalous organic grains, in accord with previous studies of very primitive meteorites [6]. Even a single parent body may possess significantly different chemical environments and histories of thermal and aqueous processing. Forthcoming organic chemical measurements by two-step laser mass spectrometry ( $\text{L}^2\text{MS}$ ) of MIL are planned to investigate its micro-scale chemical heterogeneity to constrain pre-accretionary, interstellar properties and/or imprints of secondary chemical processes.

**References:** [1] Sephton (2002) *Phil. Trans. R. Soc. A* 363:2729-2742. [2] de Gregorio et al. *MAPS* 48: 904-928 [3] Garvie & Buseck *MAPS* 41:633-641. [4] Geiss J. and Reeves H. (1981) *Astron. Astrophys.* **93**, 189-199. [5] Zinner E. (1988) In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 956-983. Univ. Ariz. Press, Tucson. [6] Busemann, H. et al. *Science* 312, 727–730 (2006). [7] Nakamura-Messenger, K. et al. *Science* 314, 1439–1442 (2006). [8] Cao T. et al. (2016) LPS (this volume). [9] Burton et al. (2016) LPS (this volume) [10] Alexander C. M. O'D. et al. (2013) *GCA* 123, 244 [11] Davidson, J. et al., (2015). *LPSC XLVI*, Abstract #1603. [12] Messenger S. (2000) *Nature* 404, 968