

## ORGANIC ANALYSIS IN THE MILLER RANGE 090657 CR2 CHONDRITE: PART 2 AMINO ACID ANALYSES

A. S. Burton<sup>1</sup>, T. Cao<sup>2</sup>, K. Nakamura-Messenger<sup>1</sup>, E. L. Berger<sup>3</sup>, S. Messenger<sup>1</sup>, S. J. Clemett<sup>4</sup>, J. C. Aponte<sup>5,6</sup>, and J. E. Elsila<sup>6</sup>. <sup>1</sup>Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX ([aaron.burton@nasa.gov](mailto:aaron.burton@nasa.gov)), <sup>2</sup>University of California, Merced, CA, <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>Catholic University of America, NASA Goddard Space Flight Center, Greenbelt, MD, USA, <sup>6</sup>Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD, USA.

**Introduction:** Primitive carbonaceous chondrites contain a wide variety of organic material, ranging from soluble discrete molecules to insoluble, unstructured kerogen-like components, as well as structured nanoglobules of macromolecular carbon. The relationship between the soluble organic molecules, macromolecular organic material, and host minerals are poorly understood. Due to the differences in extractability of soluble and insoluble organic materials, the analysis methods for each differ and are often performed independently [1,2]. The combination of soluble and insoluble analyses, when performed concurrently, can provide a wider understanding of spatial distribution, and elemental, structural and isotopic composition of organic material in primitive meteorites. Using macroscale extraction and analysis techniques in combination with *in situ* microscale observation, we have been studying both insoluble and soluble organic material in the primitive CR2 chondrite Miller Range (MIL) 090657. In accompanying abstracts (Cao et al. and Messenger et al.) we discuss insoluble organic material in the samples. By performing the consortium studies, we aim to improve our understanding of the relationship between the meteorite minerals and the soluble and insoluble organic phases and to delineate which species formed within the meteorite and those that formed in nebular or presolar environments.

In this abstract, we present the results of amino acid analyses of MIL 090657 by ultra performance liquid chromatography with fluorescence detection and quadrupole-time of flight mass spectrometry. Amino acids are of interest because they are essential to life on Earth, and because they are present in sufficient structural, enantiomeric and isotopic diversity to allow insights into early solar system chemical processes. Furthermore, these are among the most isotopically anomalous species, yet at least some fraction are thought to have formed by aqueously-mediated processes during parent body alteration [4,8,9]

**Samples and Analysis Methods:** MIL 090657 has not been extensively characterized, but based on available data and its petrographic description, it appears to have experienced minimal aqueous alteration [3]. There have been no previous organic studies reported in the literature. Sample processing for amino acid analyses was performed as described in depth elsewhere [4], and is briefly described here. Procedural blank samples were processed in parallel with a crushed meteorite sample

(153 mg) that was placed in an ampoule with 1 mL ultrapure water. The ampoules were sealed, and placed in an oven at 100 °C for 24 h. For each sample, the supernatant was removed, divided into two equal aliquots, and dried down in separate vials. One aliquot of each sample was set aside for the analysis of free amino acids. The other aliquot was subjected to acid vapor hydrolysis (6N HCl) at 150 °C for 3 h, to convert amino acid precursors to free amino acids (total amino acids = free + acid-labile). The samples were then purified by cation-exchange chromatography (BioRad AG50W X-8 resin) and eluted with aqueous ammonia (2M). The samples were dried down under vacuum, then brought up in water. Aliquots of the sample were derivatized immediately prior to analysis by OPA/NAC derivation. The data presented herein are reported from analyses by liquid chromatography – UV fluorescence detection, though subsequent analyses are being performed by liquid chromatography with fluorescence detection and hybrid quadrupole time-of-flight mass spectrometry.

Amino acid	GRO 95577 (CR1)	EET 92042 (CR2)	MIL 090657 (CR2)	QUE 9917 (CR3)
Amino acid abundances				
Total of listed amino acids (ppb)	1,160	240,000	213,000	51,400
D+L aspartic acid	<10	2,040	5,640	1,080
D+L glutamic acid	<10	12,000	26,000	7,000
Glycine	278	55,000	52,900	14,100
$\beta$ -alanine	295	4,160	175	2,000
D+L-alanine	81	81,400	72,000	7,130
D+L- $\alpha$ -amino- <i>n</i> -butyric acid	45	20,900	11,500	3,300
$\alpha$ -aminoisobutyric acid	175	56,800	38,600	14,200
D+L- $\beta$ -amino- <i>n</i> -butyric acid	130	6,020	3,310	1,260
$\gamma$ -amino- <i>n</i> -butyric acid	140	2,620	2,940	1,320
D/L ratios				
aspartic acid (D/L)	n.d.	1.01	1.16	1.02
glutamic acid (D/L)	n.d.	0.99	0.85	1.02
alanine (D/L)	1.31	0.97	1.00	1.01

Table 1. Selected amino acid abundances from acid-hydrolyzed samples in a range of CR chondrites. MIL 090657 data are from this study; the remainder are from Glavin et al. 2010 [5].

**Results:** We detected a broad suite of proteinogenic and non-proteinogenic amino acids in MIL 090657 totaling more than 200 parts-per-million (ppm; Table 1). An extraterrestrial origin for most of the amino acids in MIL 090657 is supported by multiple lines of evidence. First, many of the proteinogenic amino acids including aspartic acid, glutamic acid, and alanine are present as racemic mixtures (the D/L ratio is ~1). Because biology has a strong preference for L-amino acids, amino acids arising from terrestrial contamination tend to have D/L ratios of 0.3 or less [6]. A second line of evidence supporting an extraterrestrial origin for amino

acids is the presence of several amino acids that are rare or absent from the terrestrial biosphere, including  $\alpha$ -aminoisobutyric acid (AIB) and  $\beta$ -amino-*n*-butyric acid. Compound-specific stable isotope ratio measurements such as  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  or  $\delta\text{D}$  could be used to unambiguously confirm an extraterrestrial origin; those measurements are underway.

**Discussion:** Consistent with its CR2 classification, the total and amino acid abundances in MIL 090657 are similar to those found in another CR2 chondrite, Elephant Moraine (EET) 92042, and ~4 to 200-fold higher than in CR1 and CR3 chondrites [6]. Considering that Davidson and coworkers [3] reported that MIL 090657 experienced minimal aqueous alteration perhaps more consistent with a type 2.7 petrologic type, it was surprising that amino acid abundances in MIL 090657 more closely resembled the type 2 EET 92042 than the type 3 Queen Alexandria Range (QUE) 99177, as amino acid contents in meteorites of the same group and petrologic type tend to agree within ~25% [4]. However, QUE 99177 may not be representative of CR3 chondrites, as it was found to contain roughly half the amino acid content of the only other CR3 chondrite, Meteorite Hills (MET) 00426, which contains similar abundances of amino acids as EET 92042 [7]. Thus, while it is clear that meteorites that experienced extensive aqueous alteration (i.e., petrologic type 1) have significantly lower amino acid abundances than less altered meteorites, minimal to moderate aqueous alteration appears to have much smaller effects on amino acid abundances.

The amino acids in MIL 090657 are predominantly  $\alpha$ -amino isomers, again consistent with the amino acid distribution of EET 92042 (e.g., Figure 1). The predominance of  $\alpha$ -amino acid isomers over non- $\alpha$ -amino acid isomers suggests that the Strecker-cyanohydrin pathway for amino acid formation was predominant on the MIL 090657 parent body [4, 8]; in the context of the amino acids analyzed here, this synthetic pathway involves the aqueously-mediated reaction of aliphatic aldehydes and ketones with ammonia and hydrogen cyanide, implying that these precursor molecules were abundant in the parent body. Thus, some soluble organics appear to record aqueous alteration that is only minimally reflected in the mineralogy of this meteorite. As was the case with the amino acid abundances, there appear to be only minor changes in amino acid structural distributions between meteorites that experienced minimal and moderate aqueous alteration, while meteorites that experienced extensive aqueous alteration have noticeably different amino acid distributions.

**Conclusion:** The CR2 chondrite MIL 090657 was found to contain abundant amino acids that are almost certainly extraterrestrial in origin. The abundances and distributions of amino acids are most similar to other CR

chondrites that experienced minimal to moderate aqueous alteration. With more than 100 g of sample mass available for study, MIL is among the largest CR2 chondrites that we have in our collection. The combined results of this work and the related abstracts (Cao et al. and Messenger et al.), all performed on the same ~4g sub-sample, represent the initial steps in a consortium characterization of MIL 090657 that is intended to bridge the gap in our knowledge between mineralogy, parent body processing, and soluble and insoluble organic matter. Future work in soluble organics include the analysis of amines and hydroxy acids in MIL 090657, *in situ* L2MS analyses, and extractions of smaller sample masses of MIL 090657 to try to better match the scale between mineralogy and soluble organics measurements.

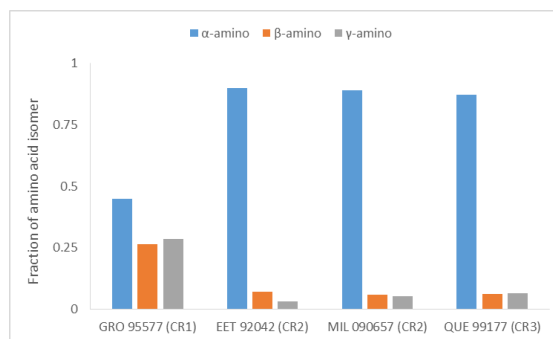


Figure 1. Fraction of four-carbon aliphatic amino acids that are  $\alpha$ -amino (= D+L- $\alpha$ -amino-*n*-butyric and  $\alpha$ -aminoisobutyric acids),  $\beta$ -amino (= D+L- $\beta$ -amino-*n*-butyric acid), or  $\gamma$ -amino (=  $\gamma$ -amino-*n*-butyric acid) isomers. Data are from this work and [6].

**Acknowledgement:** T. Cao thanks financial support from the the LPI Summer Intern Program 2015. A. S. Burton acknowledges support from the NASA Exobiology and Early Career programs.

**References:** [1] Burton, A., et al. (2012) *Chem. Soc. Rev.*, 41: 5459- 5472. [2] Pizzarello S., et al. (2006) *Meteorites and Early Solar System*, 2: 626- 63. [3] Davidson, J. et al., (2015). *LPSC XLVI*, Abstract #1603. [4] Glavin et al. (2006) *Met. Plan. Sci.* 41, 889-902. [5] Burton et al. (2014) *Met. Plan. Sci.* 49, 2074-2086. [6] Glavin et al. (2010) *Met. Plan. Sci.* 45, 1948-1972. [7] Pizzarello et al. (2012) *Proc. Natl. Acad. Sci. USA* 109, 11949-11954. [8] Elsila et al. (2012) *Met. Plan. Sci.* 47, 1517-1536. [9] Pizzarello S. and Holmes W. (2009) *Geochim. Cosmochim. Acta* 73, 2150-2162.