

CORRELATED AMINO ACID AND MINERALOGICAL ANALYSES OF MILLIGRAM AND SUBMILLIGRAM SAMPLES OF CARBONACEOUS CHONDRITE LONEWOLF NUNATAKS 94101. A.

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Introduction: Amino acids, the building blocks of proteins, have been found to be indigenous in the eight carbonaceous chondrite groups [1]. The abundances, structural, enantiomeric and isotopic compositions of amino acids differ significantly among meteorites of different groups and petrologic types [2, 3]. These results suggest parent-body conditions (thermal or aqueous alteration), mineralogy, and the preservation of amino acids are linked. Previously, elucidating specific relationships between amino acids and mineralogy was not possible because the samples analyzed for amino acids were much larger than the scale at which petrologic heterogeneity is observed (sub mm-scale differences corresponding to sub-mg samples); for example, Pizzarello and coworkers [4] measured amino acid abundances and performed X-ray diffraction (XRD) on several samples of the Murchison meteorite, but these analyses were performed on bulk samples that were 500 mg or larger.

Advances in the sensitivity of amino acid measurements by liquid chromatography with fluorescence detection/time-of-flight mass spectrometry (LC-FD/TOF-MS) [5], and application of techniques such as high resolution X-ray diffraction (HR-XRD) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) for mineralogical characterizations have now enabled coordinated analyses on the scale at which mineral heterogeneity is observed. In this work, we have analyzed samples of the Lonewolf Nunataks (LON) 94101 CM2 carbonaceous chondrite. We are investigating the link(s) between parent body processes, mineralogical context, and amino acid compositions in meteorites on bulk samples (~20mg) and mineral separates (≤3mg) from several of spatial locations within our allocated samples. Preliminary results of these analyses are presented here.

Methods: We began with a ~1.4 g chip of LON 94101 for this study. This sample was initially disaggregated into 4 subfragments with masses greater than 200 mg, designated A–D, using a ceramic mortar and pestle. Each subfragment was further divided by additional gentle crushing with a mortar and pestle. Aliquots of powdered meteorite from each subfragment were transferred to a glass slide for hand-picking of grains. For subfragment A, a total of 20 individual samples were selected (≤3 mg) comprising materials identified as either predominantly matrix, or

predominantly non-matrix (such as chondrules); for subfragments B–D, 30 samples were collected for each. After each set of 10 samples were collected, a bulk sample (14 – 26 mg; designated I – XI) was also collected, bringing the total number of samples to 121 (110 samples of ≤3 mg plus 11 bulk samples). All samples were placed into tared glass ampoules, flame-sealed, and extracted in 0.5 mL of ultrapure water (18.2 MΩ·cm, <3 ppb total organic carbon) at 100 °C for 24 hours. Meteorite extracts were collected and transferred to individual glass vials, where they were dried down under vacuum. Samples were redissolved in water, and no further processing occurred prior to analysis. After the supernatant was removed, the ampoules containing the meteorite solids were also dried under vacuum, and the resulting materials were transferred to SEM mounts (for the small samples) or collected and sent off for HR-XRD analyses (bulk samples). All glassware and aluminum foil used for sample preparation and processing were cleaned by heating in air at 500 °C overnight. Other materials and instruments that could not withstand elevated temperatures were cleaned prior to use by sonication in baths of ultrapure water and liquid chromatography-mass spectrometry (LC-MS) grade methanol.

Amino acid analyses of the extracts were performed as described previously (*e.g.*, [3]). Derivatization reactions were quenched with the addition of hexylamine in methanol, followed by the addition of water to bring the final solvent composition of the sample to approximately that of the initial LC-MS buffer conditions. Derivatized samples were injected on three consecutive days, and were stored at -80 °C between injections.

Back-scattered and secondary electron images and EDS analyses were collected on the JEOL 7600 SEM. Operating conditions were 15kV and 850pA.

Results: Analyses of the bulk LON 94101 samples revealed amino acid distributions that were generally comparable to what was found in LON 94102 which is believed to be paired with LON 94101 [3]. This includes broad suites of two-carbon to six-carbon aliphatic amino acids, including complete structural diversity (*i.e.*, all possible enantiomers and isomers) of the two, three, four and five-carbon amino acids. Among the different bulk samples, individual amino acid abundances were typically within 25%. However, bulk sample III was significantly lower in amino acids

than the rest, including bulk samples IV and V, all three of which were from subfragment B (Figure 1). The remaining six bulk samples are currently being analyzed and will be compared similarly; samples have been sent out for HR-XRD analyses, which will provide quantitative data to probe for relationships between meteorite composition and amino acid abundances.

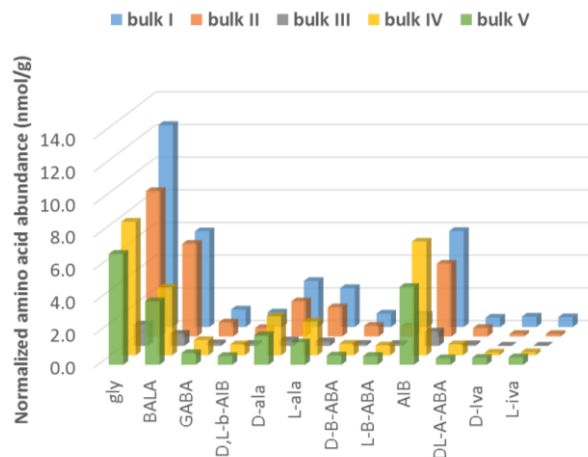


Figure 1. Background-subtracted amino acid abundances in bulk samples of LON 94101. Amino acid abbreviations are (gly=glycine, BALA=β-alanine; GABA=γ-aminobutyric acid; D,L-b-AIB=D,L-β-aminoisobutyric acid; D-ala=D-alanine; L-ala=L-alanine; D-B-ABA=D-β-aminobutyric acid; L-B-ABA=L-β-aminobutyric acid; AIB=α-aminoisobutyric acid; D-Iva=D-isovaline; L-Iva=L-isovaline).

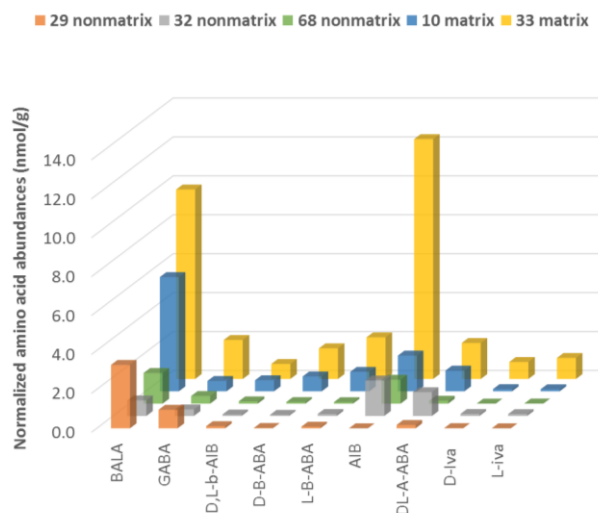


Figure 2. Background-subtracted amino acid abundances in small (<3 mg) LON 94101 samples; abbreviations are the same as in Figure 1.

A subset of the small samples have been analyzed, including two matrix and three non-matrix samples (Figure 2). Greater heterogeneity in amino acid abundances and composition were observed at this scale. Amino acids appear to be more concentrated in the matrix than in non-matrix samples, though each of the samples contained amino acids that were plausibly extraterrestrial in origin. Intriguingly, sample 33 (matrix) contained higher levels of all amino acids surveyed than sample 10 (matrix), in contrast with the results of the bulk samples collected in conjunction with each of these subsamples (III and I, respectively).

The post-extraction meteorite materials were analyzed by SEM:

Sample	Description
29 non-matrix	Ferromagnesian olivine, some patches of Fe-oxide on the grain surface
32 non-matrix	Pyroxene chondrule – darker regions: Ferromagnesian pyroxene with minor Ca, Mn, and Cr (<1 at. %); lighter regions: more Fe-rich ferromagnesian pyroxene with minor Ca, Mn, and Cr (<1 at. %).
68 non-matrix	Ferromagnesian olivine surrounded by Fe-Ni metal (some oxidized).
10 matrix	3 pieces of ferromagnesian phyllosilicates - very similar in composition to 33
33 matrix	6 pieces of ferromagnesian phyllosilicate, accessory minerals include sulfide, oxide, chromite, carbonate, phosphate.

Future Work: We have analyzed all 11 of the bulk amino acid samples to date, but only 5 of the 110 small samples. These analyses are underway, and are expected to be completed in the near future.

References: [1] Elsila J. E. et al. (2016) *ACS Cent. Sci.* 2, 370–379. [2] Elsila J. E. et al. (2012) *Met. Planet. Sci.*, 47, 1517–1536. [3] Glavin D. P. et al. (2011) *Met. Planet. Sci.* 45, 1948–1972. [4] Pizzarello S. et al. (2003) *Geochim. Cosmochim. Acta* 67, 1589–1595. [5] Callahan M. P. et al. (2014) *J. Chrom. A* 1332, 30 – 34.