Correlating Mineralogy and Amino Acid Contents of Milligram-Scale Murchison Carbonaceous Chondrite Samples

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Amino acids, the building blocks of proteins, have been found to be indigenous in most of the carbonaceous chondrite groups [1 and references therein]. The abundances of amino acids, as well as their structural, enantiomeric and isotopic compositions differ significantly among meteorites of different groups and petrologic types [e.g., 2, 3]. This suggests that there is a link between parent-body conditions, mineralogy and the synthesis and preservation of amino acids (and likely other organic molecules). However, elucidating specific causes for the observed differences in amino acid composition has proven extremely challenging because samples analyzed for amino acids are typically much larger (~100 mg powders) than the scale at which meteorite heterogeneity is observed (sub mm-scale differences, ~1-mg or smaller samples). Thus, the effects of differences in mineralogy on amino acid abundances could not be easily discerned. Recent advances in the sensitivity of instrumentation have made possible the analysis of smaller samples for amino acids [4, 5], enabling a new approach to investigate the link between mineralogical con-text and amino acid compositions/abundances in meteorites. Through coordinated mineral separation, mineral characterization and highly sensitive amino acid analyses, we have performed preliminary investigations into the relationship between meteorite mineralogy and amino acid composition. By linking amino acid data to mineralogy, we have started to identify amino acid-bearing mineral phases in different carbonaceous meteorites. The methodology and results of analyses performed on the Murchison meteorite are presented here.

All ceramic, glass and aluminum materials that were used for the study were heated in air at 500 °C for 18-24 hours prior to use to remove organic residue. Tweezers and forceps used for mineral picking were first subjected to sonication in 100% methanol, a 50/50 mixture of methanol and water, and 100% water. The cleaning and chromatography solvents used for this study were all high-performance liquid chromatography grade; ultrapure water (18.2 MΩ, <4 ppb total organic carbon) was obtained from a Millipore Advantage A-10 water purification system. A ~20 mg sample of the Murchison meteorite was used for this study. The sample was gently crushed with a porcelain mortar and pestle, and portions transferred to a glass slide. Material on the slide was observed under a petrographic microscope, and grains were hand-picked by visual appearance (texture, crystal shape, opacity, etc.) to separate "matrix" and "non-matrix" components. We then collected the following samples: 1) bulk, unseparated material (2.8 mg); 2) a single grain containing matrix, non-matrix and sulfide materials (2.5 mg); 3) hand-picked grains containing predominantly matrix (1.2 mg); and 4) hand-picked non-matrix grains (1.0 mg). The samples were hot-water extracted for 24 hr at 100 °C in sealed glass ampoules, and the supernatant containing amino acids was removed and dried down under vacuum. Acid vapor hydrolysis and amino acid analysis were performed as described elsewhere [1, 3], except that liquid chromatography was performed on a Thermo-Dionex UHPLC 3000 Liquid Chromatograph, and amino acids were analyzed

by UV-fluorescence detection (UHPLC-FD) and identified by comparing their retention times with those of known standards, and well previous amino acid analyses of the Murchison meteorite. The extracted meteorite sample residues were analyzed by scanning electron microscopy (SEM). Both back scattered electron images and energy dispersive X-ray data were collected on a JEOL JSM-7600 field emission SEM.

The matrix material of the Murchison meteorite was comprised primarily of fine-grained phyllosilicates, whereas our non-matrix fraction consisted of mostly mafic silicate minerals (Figure 1). Our expectation was that amino acids would be located in the matrix, and that the non-matrix fraction would be devoid of amino acids. This was only partially correct, however. Analysis of the matrix-containing samples (2.8 mg bulk, single grain, and matrix separates; Figure 2) revealed amino acid distributions that were fairly consistent with each other, with glycine as the most abundant amino acid, followed in descending abundance by γ-
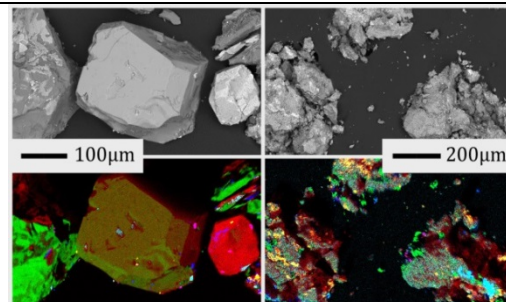

Figure 1. The upper panels of this figure are back-scattered electron (BSE) images of the fractions post- hot water extraction (matrix on the right, non-matrix on the left). Below each BSE is a corresponding x-ray map. (Fe=red, Mg=green, Ca=blue, Al=cyan, Ti=magenta, S=yellow). The non-matrix fraction consists mostly of mafic silicate minerals with iron contents ranging between 2 and 40 wt.%. The matrix portion differs from the non-matrix in shape and chemistry. These post-extraction analyses serve as a quality check on the separation process, and confirm the identities of the amino acid hosts in each fraction.

amino-n-butyric acid, β-alanine, α-aminoisobutyric acid and α-amino-n-butyric acid. Interestingly, the non-matrix material also contained amino acids but with a distinct composition from that of the matrix fractions; the non-matrix contained a large amount of glycine with much lower levels of the other amino acids. In comparison with a typical, relatively large-mass extraction of the Murchison meteorite (>100 mg), the overall amino acid abundances were comparable to the matrix fraction. However, the amino acid distributions were visibly different. In the large sample, α-aminoisobutyric acid was the most abundant amino acid, followed in abundance by glycine, whereas in the small Murchison samples analyzed here, glycine and then γ-amino-n-butyric acid were the two most abundant amino acids of this set. Further studies are needed to understand the cause(s) of these observed differences in amino acid abundances and distributions.

References:

[1] Burton et al. *Met. Plan. Sci.* (in press)
[2] Elsila et al. *Met. Plan. Sci.* 47 (2012) 1517-1536
[3] Glavin et al. *Met. Plan. Sci.* 45 (2010) 1948-1972
[4] Callahan et al. *J. Chrom. A* 1332 (2014) 30 - 34
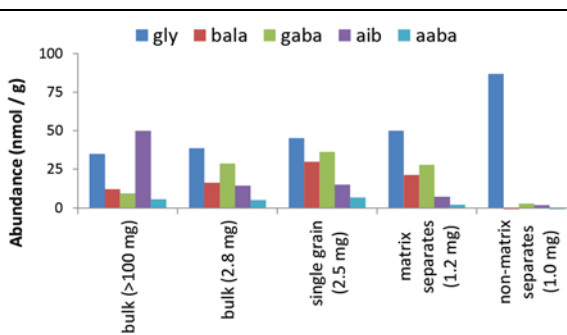[5] Glavin et al. *Met. Plan. Sci* 41 (2006) 889 - 902

Figure 2. Comparison of selected amino acid abundances in samples from the Murchison meteorite. Amino acid abbreviations are: gly = glycine, bala = β-alanine; gaba = γ-amino-n-butyric acid, aib = α-aminoisobutyric acid, aaba = α-amino-n-butyric acid.