

The Diversity of Meteoritic Amino Acids: Variations in Abundance and Enantiomeric Composition and Implications for Exobiology. J. E. Elsila¹, A. S. Burton², J. C. Aponte^{1,3}, D. G. Blackmond⁴, J. P. Dworkin¹, and D. P. Glavin¹, ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, ²Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Mail Code XI3, Houston, TX 77058, ³Catholic University of America, Washington, DC 20064, ⁴Department of Chemistry, The Scripps Research Institute, La Jolla, CA 92037, Email: Jamie.Elsila@nasa.gov

Introduction: The study of meteoritic amino acids is of exobiological interest because they are essential to life on Earth; in addition, amino acids are a structurally diverse group of compounds, many of which are chiral, and their structural distributions and enantiomeric ratios provide clues about their formation and processing histories. The delivery of amino acids to the early Earth's surface by meteorites could have helped to establish the chemical inventory from which life arose. Although the analysis of amino acids in meteorites dates back over 50 years [1], only recently have these analyses expanded beyond a narrow set of meteorite groups into meteorites of other types and classes. An overemphasis on the analysis of a few large and well-studied meteorites (primarily the CM2 carbonaceous chondrites, especially the Murchison meteorite) may have led to biased assumptions about meteoritic amino acid inventories. Here, we summarize recent discoveries of the diversity of meteoritic amino acid contents and discuss the potential of this data for understanding signatures of formation mechanisms and processing histories.

Meteorite types analyzed and methods: Our laboratory has analyzed the amino acid content of over 40 different meteorites, including representatives of all eight carbonaceous chondrite subgroups (CI, CM, CR, CV, CO, CK, CH, and CB) [2-9]. In addition, we have measured amino acids in ungrouped carbonaceous chondrites (e.g., Tagish Lake), ureilites, R chondrites, and a Martian shergottite [2,6,10-12]. Each meteorite was studied using hot water extraction, acid-vapor hydrolysis, derivatization with *o*-phthalaldehyde/N-acetyl-L-cysteine, and analysis via ultrahigh-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry.

Diversity of abundances and structural distributions: Figure 1 shows the amino acid abundances measured in acid-vapor hydrolyzed hot-water extracts from a selection of meteorites of various types (data from [2-12]). Abundances vary by several orders of magnitude. The Murchison meteorite and other CM2 meteorites typically contain part-per-million (ppm) concentrations of amino acids. Abundances in CR2 and CR3 chondrites can be up to an order of magnitude higher than that observed in the CM2 chondrites. Meteorites that have experienced

significant aqueous alteration, such as the CM1, CR1, and CI1 chondrites, contain significantly lower abundances, in the parts-per-billion (ppb) range. Thermally altered meteorites, such as the CV, CO, and CK chondrites, as well as ureilites, are low in amino acid abundances (~100 – 3000 ppb). A combination of aqueous and thermal metamorphism, such as that observed in certain CI chondrites and the CM2 chondrite Sutter's Mill, results in depleted amino acid concentrations. In contrast, the high-metal-containing CH chondrites contain amino acid abundances similar to the CM2 meteorites, while concentrations in the CB chondrites are an order of magnitude lower than this. The amino acid contents of LL5 chondrites, R chondrites, and the Martian shergottite are among the lowest measured.

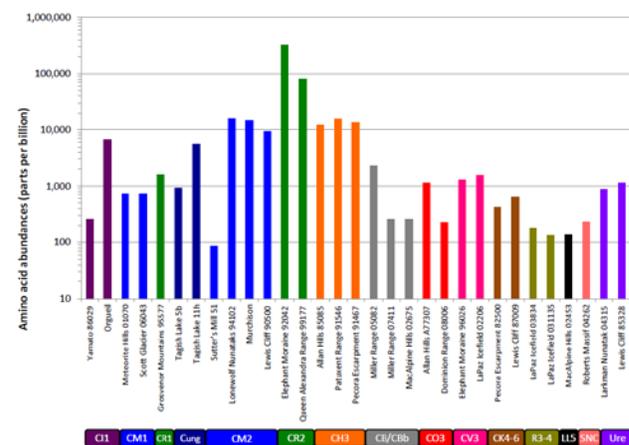


Figure 1. Amino acid abundances from acid-hydrolyzed hot-water extracts of a range of meteorites. Meteorite types are roughly arranged in order from increased aqueous alteration to increased thermal alteration.

We compared not only the abundances of amino acids, but also their structural distributions, with a particular emphasis on the position of the amine group relative to the acid group (α -, β -, γ -, or δ -). Figure 2 shows how the isomeric distribution of the five-carbon amino acids varies across a range of carbonaceous chondrites. The CM2 and CR2 chondrites contain predominantly α -amino acids, similar to those present in terrestrial biological proteins. In contrast, aqueously altered meteorites show a higher percentage of β -, γ -, and δ -isomers, as do the high metal CH and CB chondrites. The thermally altered meteorites contain

primarily straight-chain amino acids in which the amine group is located on the carbon farthest from the carboxylic acid (*n*- ω -amino acids, such as the δ -isomer of the C5 amino acids).

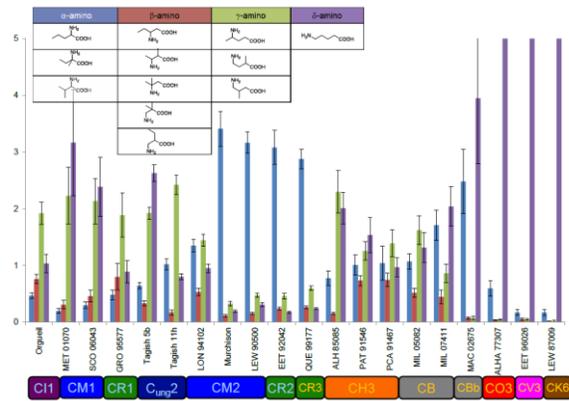


Figure 2. Relative distributions of the α -, β -, γ - and δ -amino isomers of the five-carbon amino acids measured in a variety of carbonaceous chondrites.

The differences in amino acid abundances and structural distributions across the various carbonaceous chondrite classes likely reflect a variety of abiotic amino acid formation mechanisms and processing histories. The high relative abundances of α -amino acids seen in Murchison and other CM2 and CR2 chondrites may result from Strecker-type cyanohydrin synthesis during aqueous alteration on the meteorite parent body [13]. Other isomers must be formed through other mechanisms such as Michael addition for β -amino isomers [14], or possibly Fischer-Tropsch-type reactions for the *n*- ω -amino acids [2,15].

Enantiomeric excesses: Although most chiral meteoritic amino acids are found as racemic mixtures, excesses of the L enantiomer of certain amino acids, particularly the non-protein amino acid isovaline, have been observed. The magnitude of the L-enantiomeric excess varies across meteorite types, as seen in Figure 3. L-isovaline excesses are the highest in the aqueously altered meteorites, as well as in the high-metal CH chondrite Allan Hills 85085; excesses are lowest in the less-altered meteorites. Isovaline was not detected in thermally altered meteorites.

The increase in L-isovaline enantiomeric excesses with increased aqueous alteration could be the result of aqueous processes or crystallization effects that amplify an initial small excess caused by a symmetry-breaking event [16]. The mechanism behind the L-excesses in the metal-rich CH and CB chondrites is currently unknown, although the analyzed chondrites contain a mix of heavily hydrated and anhydrous

material, suggesting that some aqueous alteration occurred on their meteorite parent body.

Large L-excesses (~45 to 60%) of the protein amino acids aspartic and glutamic acid were measured in the Tagish Lake ungrouped C2 chondrite and were confirmed by isotopic measurement to be extraterrestrial and not contamination [12]. It is interesting to note that, thus far, only L-enantiomeric excesses have been found in meteoritic amino acids with a single asymmetric carbon. This may indicate that the origin of life on Earth and possibly elsewhere in our solar system was biased toward L-amino acid homochirality from the beginning.

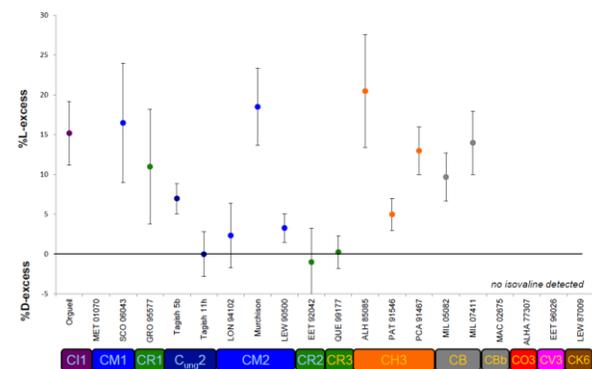


Figure 3. Isovaline enantiomeric excesses measured in a variety of carbonaceous chondrites.

Directions for further study: The expansion of meteoritic amino acid analyses beyond the Murchison meteorite and other CM2 chondrites has revealed a diversity of compositions. Future work combining meteorite analyses with laboratory experiments, as well as samples returned by missions to solar system bodies, will aid in better understanding the formation and alteration of meteoritic organics and their potential contributions to the origin of life on Earth.

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