

Introduction: Understanding the organic content of meteorites and the potential delivery of molecules relevant to the origin of life on Earth is an important area of study in astrobiology. There have been many studies of meteoritic organics, with much focus on amino acids as monomers of proteins and enzymes essential to terrestrial life. The majority of these studies have involved analysis of carbonaceous chondrites, primitive meteorites containing ~3-5 wt% carbon. Amino acids have been observed in varying abundances and distributions in representatives of all eight carbonaceous chondrite groups, as well as in ungrouped carbonaceous chondrites, ordinary and R chondrites, ureilites, and planetary achondrites [1 and references therein].

Beyond carbonaceous chondrites, iron meteorites could also have delivered prebiotic material to the early Earth. These meteorites, which may be the cores of differentiated planetesimals, comprise ~5% of falls to the Earth, but make up ~48% by mass of recorded meteorite falls [2,3]. The IAB iron meteorites contain silicate inclusions, often of primitive chondritic composition, as well as carbon in the form of graphite [4]. However, there have been no previously reported studies of organic content in iron meteorites. This may be due to the difficulties in extracting and analyzing soluble organic compounds from such samples, or due to low expectations of organic compounds forming or surviving in these environments. Here, we report the first analyses of amino acids in iron meteorites, as well as in the iron and silicate portions of a pallasite and in control material.

Methods: We analyzed samples of three iron meteorites and both the iron and silicate components of a pallasite: Campo del Cielo (IAB), Canyon Diablo (IAB), Cape York (IIIAB), and Imilac (pallasite). Sample sizes were 1-2 g for each meteorite, with an additional analysis of a larger 12.3 g sample of Campo del Cielo. Meteorite samples were sonicated in ultrapure water prior to further processing, and the water washes were also analyzed. In addition, we analyzed baked fused silica as a procedural blank and a vacuum-oven baked sample of commercially available iron granules (Alfa Aesar, 99.99% metals basis) as a terrestrial comparison.

The cohesion and malleability of iron meteorites means that the typical method used for preparing stony meteorites (i.e., grinding a sample by hand using a ceramic mortar and pestle to produce fine-grained powders for extraction) is not possible. Instead, we processed iron and fused silica samples for this study in

a N₂(l)-cooled ball mill, which produced flakes and grains from the embrittled metal. The Imilac pallasite was first manually disaggregated in a mortar and pestle to separate iron and silicate fractions; the iron was then processed in the ball mill while the silicate was powdered in a mortar and pestle.

After processing, all crushed samples were extracted for 24 hours in ultrapure water. Some extract portions were subjected to acid-vapor hydrolysis (3 hours at 150°C in the presence of 6N HCl), while others remained unhydrolyzed. Both hydrolyzed and unhydrolyzed portions were desalted on a cation-exchange column, derivatized using *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC), and analyzed via ultraperformance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) [5,6].

Results and Discussion: Amino acids were observed in all meteorite samples, but not in the fused silica procedural blank. Both the iron and silicate portions of the pallasite contained amino acids, although the silicate portion contained lower abundances. Some amino acids appeared to be terrestrial contamination, based on an excess of L-enantiomers resulting from terrestrial biological processes. Analyses of the wash water from the exterior of the meteorite samples showed contamination of proteinogenic amino acids, but amino acid distributions were distinct from those seen in the extracts from the milled samples. In addition, several amino acids that are rare in the terrestrial biosphere were observed, including β -amino-*n*-butyric acid and α -aminoisobutyric acid. The most abundant of the two-to-four-carbon primary aliphatic amino acids detected were glycine, β -alanine, γ -amino-*n*-butyric acid, and α -aminoisobutyric acid.

The most striking feature of the detected amino acids in the iron-rich meteorites was a suite of non-proteinogenic five-carbon (C5) amino acids, which was observed in all of the meteorite samples with similar relative abundance distributions (Fig. 1). The most abundant C5 amino acids in all samples were L-valine (potential terrestrial contaminant), 5-amino-*n*-pentanoic acid (also present at lower levels as a contaminant in procedural blanks), 4-amino-*n*-pentanoic acid, and 3-amino-*n*-pentanoic acid. The observation that the amino acids with a straight-chain carbon backbone (*n*-pentanoic acid variants) were more abundant than the branched chain compounds (e.g., 4-amino-2-methylbutyric acid, also observed in all meteorite

samples) suggests that the formation mechanism leading to these compounds may favor straight chains.

The amounts of the C5 amino acids present in the samples were above the detection limit, but less than or close to the quantitation limit, of the analytical technique. This means that although detection of the compounds is verified, there are uncertainties in absolute quantitation, although it is possible to compare relative abundances of compounds. Extracting larger sample amounts in an attempt to increase compound abundances for analysis leads to additional difficulties with increased interferences from mineral backgrounds and required desalting processing. The total abundance of amino acids varied between the samples, with overall low abundances (typically <100 ppb for all amino acids and <10 ppb for the suite of C5 amino acids). The IAB iron meteorites contained higher abundances of amino acids than the IIIAB and pallasite samples, although sample heterogeneity may prevent the assumption that these differences are fully due to differences in the meteorite groups.

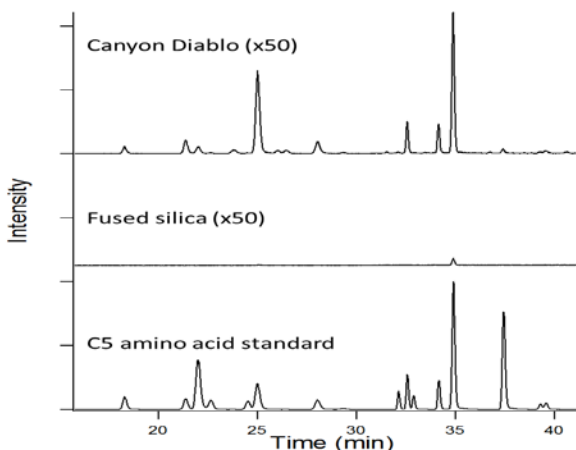


Fig. 1. Representative LC-FD/ToF-MS single ion chromatogram of the mass corresponding to derivatized C5 amino acids for the unhydrolyzed Canyon Diablo (IAB) meteorite extract (top, x50), milled fused silica (middle, x50) and a C5 amino acid standard mix (bottom).

Amino acids were also observed in the terrestrial iron granules that were processed identically to the meteorites. Although the exterior of the sample was cleaned of most amino acids by vacuum oven treatment, analysis of the iron after grinding revealed similar C5 amino acid relative distributions to those seen in the meteorite, although at lower abundances. Baked, unmilled iron granules did not show the same amino acids, suggesting that the observed amino acids were released from the interior of the milled iron. It appears unlikely that these amino acids originate from the processing and analysis, as fused silica carried through

identical procedures did not contain these compounds (see Fig. 1, middle trace). It is possible that the process(es) that led to the formation of the amino acids in the interior of the iron meteorites were active in the environment in which the terrestrial iron originated. The identity of these formation processes remains unknown, but catalytic reaction of amino acid precursors with metallic surfaces may be a possibility.

These results suggest that further study is needed of the organic content of iron meteorites, as well as the potential origin of the amino acids observed within them. Surface-catalyzed reactions of gases have been suggested to form amino acids on metal surfaces [7-9], but it is not yet known if that mechanism could result in the distribution of compounds observed here. It has been suggested that surface-catalyzed reactions such as Fischer Tropsch-type reactions would lead to a predominance of straight-chain backbones, perhaps similar to the predominance of the *n*-pentanoic backbone seen in the C5 compounds. The observation of similar amino acids in the terrestrial iron granules subjected to milling suggests that similar processes may have occurred in terrestrial conditions. The discovery of indigenous amino acids in iron meteorites adds to the potential sources of organic delivery to the early Earth.

References: [1] Elsila J. E. et al. (2016) *ACS Central Science*, 2, 370-379. [2] Korotev, R. (2018). *Meteorite statistics*. [online] Washington University in St. Louis. Available at: http://meteorites.wustl.edu/meteorite_types.htm [Accessed 5 Jan. 2018]. [3] Grossman, J. (2018) *Meteorite Bull. Database*. [online] Lunar and Planetary Institute. Available at <https://www.lpi.usra.edu/meteor/metbull.php> [Accessed 5 Jan. 2018] [4] Chabot, N. L. and Haack, H (2006) Evolution of Asteroidal Cores, in: D.S. Lauretta (Ed.) *Meteorites and the Early Solar System II*, 2006, pp. 747-771. [5] Glavin D. P. and Dworkin J. P. (2009) *Proc. Natl. Acad. Sci. U. S. A.*, 106, 5487-5492. [6] Glavin D. P. et al. (2006) *Meteorit. Planet. Sci.*, 41, 889-902. [7] Burton A. S. et al. (2012) *Meteorit. Planet. Sci.*, 47, 374-386. [8] Pizzarello S. (2012) *Meteorit. Planet. Sci.*, 47, 1291-1296. [9] Yoshino D. et al. (1971) *Geochim. Cosmochim. Acta*, 5, 927-938.