

AMINO ACID ANALYSES OF ENSTATITE CHONDRITES. D. N. Simkus^{1,2}, J. C. Aponte^{2,3}, J. E. Elsila², H. L. McLain^{2,3}, J. P. Dworkin², and D. P. Glavin². ¹NASA Postdoctoral Program, Universities Space Research Association, NASA Goddard Space Flight Center, Greenbelt, MD 20771 (danielle.n.simkus@nasa.gov), ²NASA Goddard Space Flight Center, Greenbelt, MD 20771, ³Dept. of Chemistry, Catholic Univ. of America, Washington, DC 20064

Introduction: Enstatite chondrites have low water contents [1] and are highly chemically reduced [2], suggesting that their asteroid parent bodies may have accreted in the inner protoplanetary disk. Based on their bulk isotopic signatures that closely resemble terrestrial values, enstatite chondrites are believed to represent the building blocks of Earth [3]. Despite the carbon-rich compositions of enstatite chondrites (0.15-0.70 wt%; [4]), very little is known about their organic contents. Previous studies have described the analysis of graphite, insoluble organic matter, and light hydrocarbons in thermally altered enstatites (e.g., [5,6,7]), but soluble organic compounds, such as amino acids, have not yet been reported for enstatite samples. Understanding the origin and distribution of amino acids in meteorites such as enstatite chondrites is of astrobiological interest as these molecules are the chemical building blocks of protein in living organisms.

Though amino acids have not yet been investigated in enstatites, they are commonly detected in carbonaceous chondrite meteorites [8]. Of the eight carbonaceous chondrite classification groups, enstatite chondrites closest resemble CH and CB chondrites, in terms of their high metal contents, low abundances of calcium aluminum inclusions (CAIs) and amoeboid olivine aggregates (AOAs), high abundances of chondrules, and their reduced oxidation states [2]. Recent analyses identified amino acids from CH and CB chondrite samples, with total abundances ranging from 0.2 to 16 parts per million (ppm) [9]. The CH and CB chondrites were found to contain high abundances of β -, γ -, and δ -amino acids relative to α -amino acids, unlike relatively aqueously altered carbonaceous chondrite samples (e.g., CM and CR chondrites). This relatively high abundance of β -, γ -, and δ -amino acids is thought to be an indication of thermal alteration and/or absence of aqueous alteration within an asteroid parent body.

By expanding our amino acid database with the analyses of enstatite chondrites, we can gain further insights into the prebiotic inventory of the early inner solar system, and assess the influence of reduced oxidation state, high metal content, and lack of aqueous alteration during amino acid synthesis. Here, we present our preliminary results from amino acid analyses of three enstatite chondrites.

Materials and Methods: Interior chips of three minimally altered (EH3) enstatite meteorite samples (Dominion Range (DOM) 14021, 2.0 g; Larkman Nunatak (LAR) 12001, 2.2 g; Larkman Nunatak (LAR)

06252, 2.5 g) were provided by the Antarctic Meteorite Collection, NASA Johnson Space Center. The individual meteorite samples were powdered, subdivided into ~ 500 mg aliquots in flame-sealed glass ampules containing 1 mL of ultrapure water, and extracted at 100 °C for 24 hours. For each meteorite, the water extract was divided into two equal portions: one portion for the analysis of “free” amino acids, and one portion carried through an acid-vapor hydrolysis step (6 M HCl, 150 °C for 3 hours [10]) to measure the “total” amino acid content (free plus hydrolysable). Both the unhydrolyzed and hydrolyzed extracts were desalted using cation-exchange resins, then derivatized using *o*-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC) [9,10,11] and analyzed via Ultra-Performance Liquid Chromatography-Fluorescence Detection/Time-of-Flight Mass Spectrometry (LC-MS) using a Waters ACQUITY H Class UPLC with fluorescence detector and Waters Xevo G2 XS. Procedural blanks were carried through the method alongside the enstatite extracts to monitor background levels of amino acids.

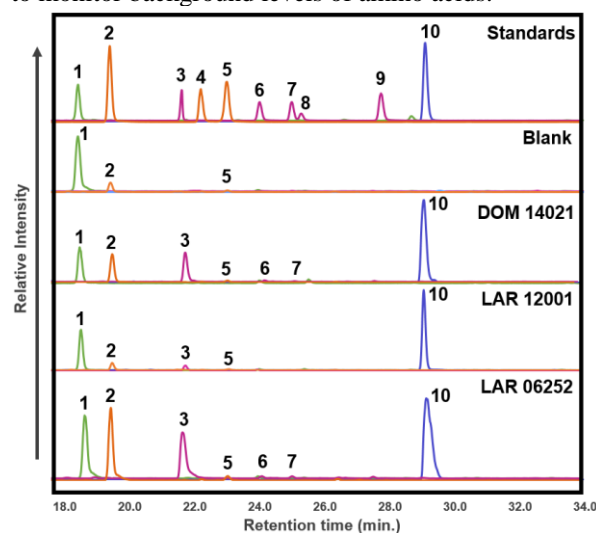


Figure 1. Stacked LC-MS single ion chromatograms for $m/z = 337.09$ (green), 351.11 (orange), 365.12 (purple), and 393.15 (blue) from OPA/NAC analyses of hydrolyzed water extracts of DOM 14021, LAR 12001, LAR 06252, a procedural blank, and amino acid standards. Peak identifications: 1) glycine, 2) β -alanine, 3) γ -amino-n-butyric acid (γ -ABA), 4) D-alanine, 5) L-alanine, 6) D- β -amino-n-butyric acid (D- β -ABA), 7) L- β -amino-n-butyric acid (L- β -ABA), 8) α -aminoisobutyric acid (α -AIB), 9) α -amino-n-butyric acid (α -ABA), 10) ϵ -aminocaproic acid (EACA).

Preliminary Results: Amino acids were detected in low abundances in the hydrolyzed enstatite extracts and included EACA, γ -ABA, glycine, β -alanine, and D,L- β -ABA (Fig. 1). Trace amounts of glycine, L-alanine, and β -alanine were detected in the procedural blanks and subtracted from the enstatite amino acid measurements. With the exception of ~ 0.3 ppb of glycine present above background levels in LAR 06252, no native α -amino acids were detected in the enstatite samples. In contrast to the hydrolyzed extracts, the unhydrolyzed samples did not appear to contain amino acids above background levels, indicating that the amino acids detected are likely present as labile amino acid polymers within the meteorites.

For all three meteorite specimens, EACA was the most abundant amino acid, with concentrations ranging between 4 and 28 ppb (compared to 0.1–5 ppb for the other amino acids identified). Notably, EACA is a known component of nylon sample storage bags used during meteorite collection and may be released from the Nylon-6 polymer via hydrolysis [10]. The relatively high levels of EACA detected in the hydrolyzed extracts may have been released via hydrolysis from Nylon-6 peptides present in the water extracts.

Equal abundances of D- and L- β -ABA detected in LAR 06252 (i.e., a racemic mixture of the two isomers) is indicative of an extraterrestrial origin. The amino acid content of the samples (γ -ABA, glycine, β -alanine, and β -ABA) is consistent with the amino acid compositions previously observed for CH and CB chondrites [9]. However, in contrast, the abundances of these n - ω -amino acids in the present study are much lower overall (ppb vs. ppm levels) and no δ -amino acids were detected. The lack of α -amino acids indicate that Strecker-cyanohydrin synthesis was not a dominant mechanism for amino acid synthesis in the enstatite parent body asteroids, and that other processes (e.g., Michael addition of β -amino acids, or Fischer-Tropsch type reactions) may have played a more significant role [8].

Conclusions: The low levels of amino acids measured for all three enstatite meteorite samples suggests that the conditions within enstatite parent body asteroids are not particularly conducive to the synthesis and preservation of high abundances of amino acids. Nevertheless, the positive detection of amino acids in hydrolyzed enstatite extracts suggests that labile amino acid polymers may be present within enstatite asteroid parent bodies. Similar to previous observations for CH and CB chondrites, the chemical and alteration history of the enstatite samples appear to have favored the prebiotic synthesis of predominantly n - ω -amino acids (e.g., γ -ABA, β -alanine, β -ABA), and/or any α -amino

acids originally present in the asteroids were destroyed through parent body alteration processes.

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