EXTRATERRESTRIAL AMINO ACIDS IN THE ALMAHATA SITTA METEORITE. D. P. Glavin[1], A. D. Aubrey[2], M. P. Callahan[1], J. P. Dworkin[1], J. E. Elsila[1], E. T. Parker[3], and J. L. Bada[3], [1]Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, daniel.p.glavin@nasa.gov, [2]NASA Jet Propulsion Laboratory, Pasadena, CA 91109, [3]Scripps Institution of Oceanography, La Jolla, CA 92093

Introduction: Meteorite fragments from the TC_3 asteroid impact that occurred in northern Sudan on October 7, 2008, collectively named Almahata Sitta, were recovered and revealed a rare, anomalous polymict ureilite containing large carbonaceous grains [1]. The presence of large (up to 0.5 mm in size) aggregates of carbonaceous material and the high porosity of Almahata Sitta is similar to primitive carbonaceous chondrites [1]. Previous studies of ureilites suggest that the carbonaceous precursor materials may be linked to CV type carbonaceous meteorites [2]. Given evidence for high temperature (~1100°C-1300°C) igneous processing on asteroid 2008 TC_3 [3] and carbon aggregates in Almahata Sitta (primarily graphite) that appear to be the most thermally altered of any meteorite [1], it would be surprising if any indigenous organic compounds were detected in this meteorite. Nevertheless, C-H stretching bands from aliphatic hydrocarbons have been measured in Almahata Sitta and several other ureilites [1, 4]. Polycyclic aromatic hydrocarbons have also been reported in Almahata Sitta [5].

Despite strong evidence of a link between ureilites and primitive carbonaceous meteorites, very few studies have reported the presence of organic compounds in ureilites [6]. The investigation of complex organic compounds in primitive chondrites is important since these meteorites provide a record of the chemical processes that occurred in the early solar system and on the meteorite parent body itself. In addition, the delivery of amino acids to the early Earth prior to the emergence of life by carbon-rich asteroids and comets and their fragments could have been an important source of the Earth's prebiotic organic inventory [7]. To date, over 80 amino acids have been identified in the CM meteorites Murchison and Murray, many of which are rare or completely non-existent in the terrestrial biosphere [8]. Extraterrestrial amino acids have also been reported in CI and primitive CR type meteorites [9, 10]. In contrast, only trace quantities of amino acids have been identified in CV meteorites that experienced more extensive thermal alteration [11]. Therefore, if the carbonaceous precursor material of Almahata Sitta and other ureilites was CV chondrite-like, we would expect these meteorites to be highly depleted in amino acids.

Recent optimization of a highly sensitive liquid chromatography with UV fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) technique coupled with OPA/NAC derivatization has made it possible to detect extremely low abundances of amino acids in meteorites [11]. Here we report the first amino acid analysis of the Almahata Sitta meteorite using LC-FD/ToF-MS. Amino acid analyses of any kind have not been previously reported for the ureilites.

Results and Discussion: LC-FD/ToF-MS analyses of hot-water extracts from the Almahata meteorite sample #4 revealed a complex distribution of free and bound two- to six-carbon aliphatic amino acids and one- to three-carbon amines with abundances ranging from 0.5 to 149 parts-per-billion (ppb) (Table 1). Several non-protein amino acids that are rare in the terrestrial biosphere were identified above background levels in the Almahatta Sitta extracts. These include α-aminoiso butyric acid (α-AIB), and the five carbon amino acids 2-amino-2-methylbutanoic acid (isovaline), 4-amino-2-methylbutanoic acid, 4-amino-3-methylbutanoic acid, and 3-, 4-, 5-aminopentanoic acid The total abundances of α-AIB and isovaline in Almahata Sitta are ~1000 times lower than the abundances of these amino acids found in the CM meteorite Murchison. Meteorite enantiomeric ratios of alanine, β-amino-*n*-butyric acid, isovaline, and norvaline were racemic

Amine Compound Detected	Almahata Sitta (2008 TC_3)	
	Free (ppb)	*Total (ppb)*
D-aspartic acid	1.2 ± 0.2	3.0 ± 0.2
L-aspartic acid	1.4 ± 0.3	5.0 ± 1.5
D-glutamic acid	0.5 ± 0.1	3.5 ± 0.4
L-glutamic acid	0.9 ± 0.2	7.7 ± 0.7
Glycine	21 ± 1	69 ± 24
D-alanine	5.0 ± 0.2	11 ± 3
L-alanine	5.1 ± 0.2	11 ± 2
β-alanine	4.2 ± 0.7	17 ± 7
D,L-α-amino-*n*-butyric acid (α-ABA)	1.7 ± 0.1	5.0 ± 0.5
D-β-amino-*n*-butyric acid (D-β-ABA)	1.2 ± 0.2	4.5 ± 1.4
L-β-amino-*n*-butyric acid (L-β-ABA)	1.2 ± 0.8	4.7 ± 1.3
γ-amino-*n*-butyric acid (γ-ABA)	1.8 ± 0.3	12 ± 1
α-aminoisobutyric acid (α-AIB)	3.6 ± 1.0	7.1 ± 5.8
D,L-valine	1.7 ± 0.4	1.8 ± 0.6
D-norvaline	< 0.3	0.7 ± 0.1
L-norvaline	< 0.2	0.7 ± 0.1
D-isovaline	0.6 ± 0.1	1.3 ± 0.1
L-isovaline	0.7 ± 0.1	1.4 ± 0.1
ε-amino-*n*-caproic acid (EACA)	3.6 ± 1.8	< 4
ethanolamine (MEA)	19 ± 1	21 ± 1
methylamine (MA)	11 ± 1	13 ± 1
ethylamine (EA)	76 ± 5	105 ± 8
isopropylamine (IPA)	84 ± 10	149 ± 17

Table 1. Summary of the average blank-corrected amino acid and amine concentrations in the unhydrolyzed (free) and 6M HCl acid-hydrolyzed (total), hot-water extracts of the Almahata Sitta meteorite.

(D/L ~ 1), indicating these amino acids are indigenous to the meteorite and not terrestrial contaminants.

The detection of ppb levels of amino acids in Almahata Sitta is surprising given that mineralogical evidence of the meteorite points to extremely high fractional melting and shock heating temperatures above 1100°C. Amino acids will rapidly decompose when heated to temperatures above 500-600°C. One possibility is that the amino acids and amines were formed directly from their chemical precursors after asteroid 2008 TC_3 cooled to lower temperatures. The formation of amino acids has also been experimentally observed by Fischer-Tropsch Type (FTT) catalytic reactions of CO, H_2, and NH_3 in the gas phase at 200-700°C in the presence of nickel-iron [12]. In contrast, there is chemical evidence that the complex distribution of α-amino acids found in CM and CR meteorites were formed from the reaction of aldehydes, ketones, NH_3, and HCN by Strecker-cyanohydrin synthesis on the parent body during an aqueous alteration phase. The amino acid distribution in Almahata Sitta is unique compared to CM and CR meteorites and is dominated by the five carbon γ-amino acids (Fig. 1) that cannot be produced by the Strecker route. In addition, the formation of amino acids by Strecker requires aqueous activity and there is no mineralogical evidence for aqueous alteration in the Almahata Sitta meteorite [13]. Given the high relative abundance of amines compared to amino acids in Almahata Sitta (Table 1), it is also possible that the amines were produced by thermal decarboxylation of the amino acids on the parent body at elevated temperatures.

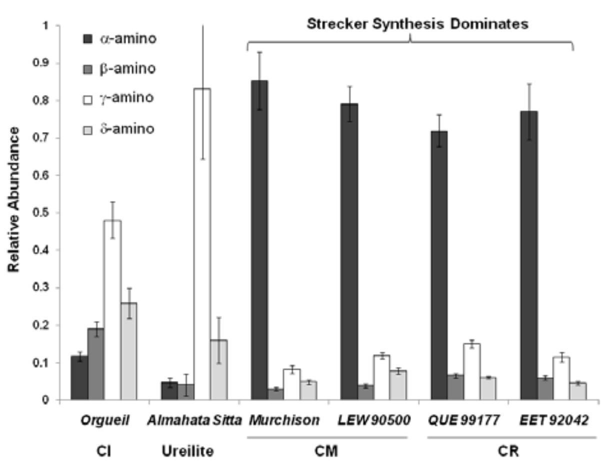

Figure 1. The relative abundances of the five-carbon amino acids in the Almahata Sitta ureilite compared to several other carbonaceous meteorites as a function of amine position (α-, β-, γ-, and δ-).

Conclusion: We were able to identify a total of 19 different amino acids and their enantiomers and 4 amines in Almahata Sitta using LC-FD/ToF-MS. This is the first report of amino acids and amines in any ureilite type meteorite. The high D/L amino acid ratios for alanine, β-ABA, isovaline, and norvaline, as well as the presence of a variety of unusual structural isomers for the C_5 amino acids suggest that most of the amino acids are indigenous to Almahata Sitta and of an abiotic origin. It remains unclear if the amines detected in Almahata Sitta are extraterrestrial in origin. The total amino acid abundance in the Almahata Sitta meteorite is 15 to 900 times lower than previous measurements of the CI, CM, and CR type carbonaceous meteorites using the same techniques. It is possible that these amino acids or their precursors formed by FTT catalytic reactions from CO, H_2, and NH_3 after asteroid 2008 TC_3 cooled to lower temperatures. It has been suggested that the carbonaceous precursor material was incorporated into the daughter asteroid 2008 TC_3 after impact of the parent proto-ureilite. Therefore, some of the re-accreted carbonaceous material may not have been exposed to the high temperatures associated with fractional melting and impact shock heating. Future amino acid analysis of other ureilites, as well as carbon and nitrogen isotopic analysis of amino acids and amines in Almahata Sitta will be necessary to further constrain the origin of these compounds.

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