Heterogeneous distributions of amino acids provide evidence of multiple sources within the Almahata Sitta parent body, asteroid 2008 TC$_3$

Aaron S. BURTON[1][*], Daniel P. GLAVIN[1], Michael P. CALLAHAN[1], Jason P. DWORKIN[1], Peter JENNISKENS[2], and Muawia H. SHADDAD[3]

[1]NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA
[2]Carl Sagan Center, SETI Institute, 515 North Whisman Road, Mountain View, California 94043, USA
[3]Department of Physics, University of Khartoum, P.O. Box 321, Khartoum 11115, Sudan
[*]Corresponding author. E-mail: aaron.s.burton@nasa.gov

Abstract–Two new fragments of the Almahata Sitta meteorite and a sample of sand from the related strewn field in the Nubian Desert, Sudan, were analyzed for two to six carbon aliphatic primary amino acids by ultrahigh performance liquid chromatography with UV-fluorescence detection and time-of-flight mass spectrometry (LC-FT/ToF-MS). The distribution of amino acids in fragment #25, an H5 ordinary chondrite, and fragment #27, a polymict ureilite, were compared with results from the previously analyzed fragment #4, also a polymict ureilite. All three meteorite fragments contain 180–270 parts-per-billion (ppb) of amino acids, roughly 1000-fold lower than the total amino acid abundance of the Murchison carbonaceous chondrite. All of the Almahata Sitta fragments analyzed have amino acid distributions that differ from the Nubian Desert sand, which primarily contains L-α-amino acids. In addition, the meteorites contain several amino acids that were not detected in the sand, indicating that many of the amino acids are extraterrestrial in origin. Despite their petrological differences, meteorite fragments #25 and #27 contain similar amino acid compositions; however, the distribution of amino acids in fragment #27 was distinct from those in fragment #4, even though both are polymict ureilites from the same parent body. Unlike in CM2 and CR2/3 meteorites, there are low relative abundances of α-amino acids in the Almahata Sitta meteorite fragments, which suggest that Strecker-type chemistry was not a significant amino acid formation mechanism. Given the high temperatures that asteroid 2008 TC$_3$ appears to have experienced and lack of evidence for aqueous alteration on the asteroid, it is possible that the extraterrestrial amino acids detected in Almahata Sitta were formed by Fischer-Tropsch/Haber-Bosch type gas-grain reactions at elevated temperatures.

INTRODUCTION

The fall of asteroid 2008 TC$_3$ in the Nubian Desert of northern Sudan provided a rare opportunity for the analysis of meteorite fragments that are directly linked to a specific parent body. More than 600 meteorites, ranging in size from 0.2 to 379 g and totaling 10.7 kg, have been recovered (Shaddad et al. 2010). These pieces have been collectively dubbed "Almahata Sitta." Analysis of the recovered Almahata Sitta meteorites has afforded insights into the evolution of asteroid 2008 TC$_3$, revealing a wealth of information about its composition and history (Jenniskens and Shaddad 2010). A striking feature of asteroid 2008 TC$_3$ is the diversity of petrographic material that it contained. Based on cosmic-ray age determination and a lack of apparent terrestrial weathering, ureilites and chondrites of types EL, EH, H ordinary, and a heretofore undocumented chondrite class, recovered as part of Almahata Sitta, are all believed to have come from asteroid 2008 TC$_3$ (Bischoff et al. 2010; Horstmann et al. 2010). This heterogeneous composition implies a violent history, involving iterations of fragmentation and accretion, resulting in conversion of a ureilite protoplanet to a

family of asteroids that includes 2008 TC$_3$ (Jenniskens et al. 2010). It was during the repeated fragmentation/accretion cycles that chondrite material was incorporated into ureilite asteroids.

In addition to its rich collision history, evidence suggests asteroid 2008 TC$_3$ experienced high-temperature (>1300 °C) thermal processing (Herrin et al. 2010; Zolensky et al. 2010) and there is no mineralogical evidence in the meteorites for any aqueous alteration on the parent asteroid (Zolensky et al. 2010). Polycyclic aromatic hydrocarbons (PAHs) have been detected in several Almahata Sitta meteorite fragments (Sabbah et al. 2010). Almahata Sitta fragment #4 also contains extraterrestrial amino acids, the first such detection in a ureilite (Glavin et al. 2010a). The presence of amino acids is surprising considering that these molecules are not stable at temperatures above 500 °C, even in an inert atmosphere of N$_2$ (Rodante et al. 1992). It was previously suggested that these compounds could have formed from Fischer-Tropsch/Haber-Bosch-like (Fischer-Tropsch Type, or FTT) catalytic reactions of CO, H$_2$, and NH$_3$ in the presence of nickel or iron as asteroid 2008 TC$_3$ cooled (Glavin et al. 2010a). Although most of the amino acids detected in Almahata Sitta fragment #4 were shown to be nonterrestrial in origin (Glavin et al. 2010a), the heterogeneous nature of the meteorite fragments makes it unclear whether these amino acids are indigenous to the ureilite fragment #4 from which they were isolated or diffused into the ureilite from a carbonaceous chondrite fragment which would have been located near fragment #4 in 2008 TC$_3$. To further investigate the source and distribution of amino acids in Almahata Sitta, we analyzed a second Almahata Sitta ureilite fragment (#27), as well as an Almahata Sitta H5 ordinary chondrite (#25) and compared these to a sample of sand from the Nubian Desert collected near where fragment #25 was found. Only very low abundances of some extraterrestrial amino acids were found in four LL5 ordinary chondrites (Botta et al. 2008). Previous amino acid analyses of two L6 chondrites (Shişr 031 and Shişr 035; Martins et al. 2007) and an H4 ordinary chondrite (Forest Vale; Zenobi et al. 1992) found that these meteorites do not contain indigenous amino acids. To our knowledge, this is the first amino acid analysis of an H5 ordinary chondrite.

MATERIALS AND METHODS

Chemicals and Reagents

Sample-handling tools, ceramics, and glassware were all rinsed with Millipore Direct Q3 UV (18.2 MΩ, <3 parts-per-billion [ppb] total organic carbon) ultrapure water, wrapped in aluminum foil, and heated in air at 500 °C for 18–24 h to clean them of organic residue. Ultrapure water was used exclusively. Most of the chemicals used were purchased from Fischer Scientific, Sigma-Aldrich, or Acros Organics. Details on the sources of specific five-carbon (C$_5$) amino acids used as standards are available in Glavin and Dworkin (2009). To prepare standard solutions for liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) analysis, individual compounds were dissolved in water and then combined to enable their measurement in a single chromatographic separation. Solutions of sodium borate were prepared from solid sodium tetraborate (Sigma Ultra 99.5–100% purity) that was pyrolyzed in air at 500 °C for 3 h to remove any organic contaminants prior to dissolution in ultrapure Millipore water. All other solutions were prepared as described by Glavin et al. (2006).

Almahata Sitta Meteorite and Controls

The fragments of Almahata Sitta were recovered from the Nubian Desert in north Sudan 2 months after the fall of asteroid 2008 TC$_3$ (Jenniskens et al. 2009). Portions of the H5 ordinary chondrite fragment #25 (recovered mass 222 g, extracted mass 416 mg), ureilite fragment #27 (recovered mass 284 g, extracted mass 410 mg) and Nubian Desert sand (extracted mass 418 mg) were allocated for this study. Samples were crushed into a powder using a clean mortar and pestle in a Class 100 Labconco laminar flow hood under HEPA-filtered positive pressure. Crushed serpentine (extracted mass 413 mg) that had been heated at 500 °C for 3 h and a procedural reagent blank were processed in parallel to the Almahata Sitta samples as controls.

Extraction Procedures and Analytical Techniques

The samples and controls described above were sealed in glass ampoules with 1 mL of ultrapure water and placed in an oven set at 100 °C for 24 h. After extraction, the tubes were cooled and centrifuged for 5 min. (Labconco Centrivap) to separate solid particulate from water supernatant. Half of the water extract was dried under vacuum and subjected to acid hydrolysis under 6 M HCl vapor at 150 °C for 3 h to liberate amino acids in bound or precursor forms. The remaining water extract (unhydrolyzed extract) and the acid-hydrolyzed extract, containing amino acids with primary amines (free) and both primary amines and those that can be converted to primary amines upon acid hydrolysis (total), respectively, were dried under vacuum (Labconco Centrivap) and redissolved in 1 mL of water. Both hydrolyzed and unhydrolyzed extracts were desalted by

cation exchange chromatography using prepacked columns (BioRad) and the NH₄OH eluates were derivatized with *o*-phthaldialdehyde/*N*-acetyl-ʟ-cysteine (OPA/NAC) fluorescent derivatization as previously described (Glavin et al. 2006).

o-phthaldialdehyde/*N*-acetyl-ʟ-cysteine amino acid derivatives were immediately analyzed by liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) using a Waters Acquity ultrahigh performance LC and a Waters Acquity fluorescence detector connected in series to a Waters LCT Premier ToF-MS. Derivatized samples were separated using a Waters BEH C18 column (2.1 × 50 mm, 1.7 μm particle size) followed by a second Waters BEH phenyl column (2.1 × 150 mm, 1.7 μm particle size). Chromatographic conditions were as follows: column temperature, 30 °C; flow rate, 150 μL min⁻¹; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (0), 35 (55), 45 (100). To better resolve the five-carbon amino acids, chromatographic conditions were: column temperature, 30 °C; flow rate, 150 μL min⁻¹; solvent A (50 mm ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (15), 25 (20), 25.06 (35), 44.5 (40), 45 (100). The electrospray conditions and mass spectrometry settings have been described by Glavin et al. (2006). As in related studies, meteorite and control samples were identified by correlating sample compounds with known standards using the masses of the OPA/NAC amino acid derivatives at the expected chromatographic retention times.

RESULTS AND DISCUSSION

Amino Acid Analyses

Amino acids were extracted from the Nubian Desert sand and meteorites samples with hot water; half of the extracted sample was acid-vapor hydrolyzed to allow a comparison of the amino acids that contain primary amines following hot water extraction ("free amino acids") with the total primary amino acids (free + bound) including those that can be converted to primary amines from bound precursors (e.g., primary amide-containing carboxylic acids or aminonitriles). The free and bound amino acid abundances of the Nubian Desert sand from the fall site and Almahata Sitta fragments #25 (H5 chondrite) and #27 (ureilite) are given in Table 1 along with the previously measured values for Almahata Sitta ureilite fragment #4 (Glavin et al. 2010a). All amino acids in the procedural blanks were present at concentrations of less than 5 ppb except glycine (<15 ppb). Typical mass chromatograms of the OPA/NAC amino acid derivatives of hydrolyzed sample extracts are

given in Fig. 1. To facilitate comparisons of chromatograms, the acid-hydrolyzed extract of fragment #4 was reanalyzed for this study. These chromatograms show clear differences between the meteorite samples and the Sudan sand that are borne out in the amino acid abundances. The meteorite samples contain similar total amino acid levels to fragment #4 (180–270 ppb), but much lower than the sand (nearly 2000 ppb; Table 1).

The available evidence suggests most of the amino acids in fragments #25 and #27 are extraterrestrial in origin. A powerful method for establishing an extraterrestrial origin for organic molecules is by measuring the stable carbon, nitrogen, and hydrogen isotopic ratios of individual amino acids (e.g., Engel et al. 1990; Pizzarello et al. 1991; Pizzarello and Huang 2005). Unfortunately, the low abundance of amino acids in these fragments makes determination of their compound-specific isotopic compositions nontrivial based on current state-of-the-art isotope ratio mass spectrometry measurements. For example, 3–5 g of meteorite sample would be required to measure the stable carbon isotopic composition of glycine (assuming the same limits of detection in Elsila et al. 2009). Performing this measurement would require a significant fraction of fragment #4 (14.5 g recovered), but may be possible on fragments #25 and #27. Even without isotope measurements, however, comparing the amino acid distributions of the meteorite samples to the Nubian Desert sand strongly suggests that many of the amino acids are indigenous to the meteorite. If the meteorites did not contain indigenous amino acids, then the overall distribution of these molecules should closely match the biological signature observed in the sand. Because the abundances and distributions of amino acids differ significantly between the meteorites and the Nubian sand, we conclude that the nonproteinogenic amino acids present in greater abundance in the meteorites than in the sand are indigenous to the meteorites. Several of these compounds, such as isovaline, 4-amino-2-methylbutyric acid, and 4-amino-3-methylbutyric acid, are present in the meteorites but were not detected in the sand or the procedural blank.

Unfortunately, there appears to have been some contamination from the biological amino acids present in the sand, making it impossible to determine how much, if any, of these molecules are extraterrestrial in origin. The predominant chiral amino acids in the sand are proteinogenic: ʟ-aspartic acid, ʟ-glutamic acid, ʟ-alanine, ʟ-serine, and ʟ-valine comprise 60% of the total amino acids (compared with less than 30% of the amino acids in the meteorites; Table 2). Consistent with the observation that fragments #25 and #27 spent more time in the Nubian Desert than did fragment #4 (84 days versus 61 days), the ᴅ/ʟ ratios for the chiral proteinogenic amino acids of fragments #25 and #27 are

Table 1. Summary of the average blank-corrected amino acid concentrations in the unhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot water extracts of Almahata Sitta samples[a]. The aliphatic amino acids are separated and numbered to correspond to the traces in Fig. 1.

Amino acid	Nubian sand This study		H5 chondrite Almahata Sitta #25 This study		Polymict ureilite Almahata Sitta #27 This study		Polymict ureilite Almahata Sitta #4 Glavin et al. 2010a	
	(Free)	(Total)	(Free)	(Total)	(Free)	(Total)	(Free)	(Total)
D-aspartic acid	1.7 ± 0.8	102 ± 31	<1	<3	0.4 ± 0.2	<3	1.2 ± 0.2	3.0 ± 0.2
L-aspartic acid	10 ± 7.4	221 ± 70	<1	<9	2.0 ± 1.8	3.8 ± 1	1.4 ± 0.3	5.0 ± 1.5
L-glutamic acid	33 ± 4	552 ± 110	1.2 ± 0.4	13 ± 3	1.0 ± 0.4	7.8 ± 0.9	0.9 ± 0.1	7.7 ± 0.4
D-glutamic acid	<4	164 ± 20	<0.1	2.3 ± 0.6	n.d.	1.9 ± 0.6	0.5 ± 0.2	3.5 ± 0.7
D-serine	4.1 ± 0.3	44 ± 1	0.7 ± 0.2	2.7 ± 0.3	0.4 ± 0.1	1.3 ± 0.1	<0.5	<1.3
L-serine	16 ± 1	97 ± 3	0.7 ± 0.3	12 ± 1.3	2.7 ± 0.5	6.7 ± 0.8	<1.6	<1.4
D-threonine	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.8	<1.3
L-threonine	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.8	<1.5
C_2-amino acid								
Glycine [1]	39 ± 1	280 ± 40	65 ± 7	83 ± 10	64 ± 3	64 ± 10	21 ± 1	69 ± 24
C_3-amino acids								
β-alanine [2]	27 ± 1	70 ± 3	14 ± 1	23 ± 2	17 ± 2	22 ± 2	4.2 ± 0.7	17 ± 7
D-alanine [3]	13 ± 2	46 ± 3	10 ± 1	13 ± 2	13 ± 1	13 ± 2	5.0 ± 0.2	11 ± 3
L-alanine [4]	39 ± 8	127 ± 42	16 ± 2	20 ± 2	22 ± 8	19 ± 2	5.1 ± 0.2	11 ± 2
C_4-amino acids								
γ-aminobutyric acid (GABA) [5]	8.6 ± 2.0	31 ± 2	0.9 ± 0.7	18 ± 2	5.9 ± 3.6	9.2 ± 1.4	1.8 ± 0.3	12 ± 1.0
D,L-β-aminoisobutyric acid[b] (β-AIB) [6]	~6	~7	~8	~8	~10	~10	<0.1	<0.1
D-β-aminobutyric acid (β-ABA) [7]	<1	0.6 ± 0.3	<1	1.0 ± 0.1	0.5 ± 0.1	1.0 ± 0.2	1.2 ± 0.2	4.5 ± 1.4
L-β-aminobutyric acid [8]	0.4 ± 0.2	0.6 ± 0.2	0.2 ± 0.1	0.8 ± 0.2	0.5 ± 0.1	0.9 ± 0.3	1.2 ± 0.8	4.7 ± 1.3
α-aminoisobutyric acid (α-AIB) [9]	2.6 ± 0.4	<0.1	5.7 ± 0.5	2.9 ± 0.3	4.5 ± 0.7	1.8 ± 0.6	3.6 ± 1.0	7.1 ± 5.8
D,L-α-aminobutyric acid[d] (α-ABA) [10]	0.6 ± 0.5	8.5 ± 1.3	0.8 ± 0.1	1.9 ± 0.4	0.8 ± 0.2	1.1 ± 0.2	1.7 ± 0.1	5.0 ± 0.5
ε-amino caproic acid	3.1 ± 2.6	84 ± 4	2.8 ± 0.9	30 ± 5	6.5 ± 2.7	35 ± 4	3.6 ± 1.8	<4

Table 1. *Continued.* Summary of the average blank-corrected amino acid concentrations in the unhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot water extracts of Almahata Sitta samples[a]. The aliphatic amino acids are separated and numbered to correspond to the traces in Fig. 1.

Amino acid	Nubian sand This study (Free)	(Total)	H5 chondrite Almahata Sitta #25 This study (Free)	(Total)	Polymict ureilite Almahata Sitta #27 This study (Free)	(Total)	Polymict ureilite Almahata Sitta #4 Glavin et al. 2010a (Free)	(Total)
C$_5$-α-amino acids								
D-norvaline (D-2-apa) [23]	<0.1	6.1 ± 0.8	<0.1	<0.8	<0.1	<0.7	<0.3	0.7 ± 0.1
L-norvaline (L-2-apa) [24]	<0.1	4.8 ± 0.7	<0.1	<0.9	<0.1	<0.7	<0.2	0.7 ± 0.1
D-isovaline (D-2-a-2-mba) [18]	<0.1	<0.1	spectrometry 0.4	1.2 ± 0.1	0.5 ± 0.4	0.5 ± 0.2	0.6 ± 0.1	1.3 ± 0.1
L-isovaline (L-2-a-2-mba) [20]	<0.1	<0.1	<0.1	1.5 ± 0.1	1.2 ± 0.7	1.2 ± 0.2	0.7 ± 0.1	1.4 ± 0.1
D-valine (D-2-a-3-mba) [22]	<0.1	12.6 ± 0.5	<0.1	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.2	0.3 ± 0.1	0.5 ± 0.1
L-valine (L-2-a-3-mba) [21]	25 ± 5	190 ± 10	6.3 ± 1.0	12 ± 2	5.7 ± 1.0	11 ± 4	1.4 ± 0.3	1.3 ± 0.5
C$_5$-β-amino acids								
D,L-3-aminopentanoic acid[c] (3-apa) [19]	<0.1	<0.1	<0.1	<0.1	0.5 ± 0.4	0.5 ± 0.2	0.4 ± 0.1	1.1 ± 0.2
D,L- and allo-3-a-2-methylbutyric acid[c] (3-a-2-mba) [14]	<0.1	<0.4	<0.1	0.3 ± 0.1	<0.1	0.2 ± 0.1	<0.1	<0.1
3-a-3-methylbutryic acid[e] (3-a-3-mba) [17]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<3
3-a-2,2-dimethylpropanoic acid (3-a-2,2-dmpa) [11]	<0.1	0.4 ± 0.1	<3	5.0 ± 0.4	<3	3.4 ± 0.2	0.8 ± 0.1	1.8 ± 0.2
D,L-3a-2-ethylpropanoic acid[c] [25]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.8	<2
C$_5$-γ-amino acids								
D,L-4-aminopentanoic acid[c] (4-apa) [12]	<0.1	<0.1	<0.1	<0.6	<0.2	<0.6	0.8 ± 0.1	15 ± 2
D,L-4-a-2-methylbutyric acid[d] (4-a-2-mba) [16]	<0.1	<0.1	<0.1	0.7 ± 0.3	<0.1	1.2 ± 0.6	2.6 ± 0.2	65 ± 8
D,L-4-a-3-methylbutryic acid[d] (4-a-3-mba) [13]	<0.1	<0.1	<0.7	3.1 ± 0.1	<0.7	3.1 ± 0.1	1.5 ± 0.5	18 ± 3
C$_5$-δ-amino acids								
5-aminopentanoic acid (5-apa) [15]	<0.4	9.3 ± 0.1	<0.2	2.1 ± 0.1	<0.2	2.1 ± 0.1	0.9 ± 0.1	6.3 ± 2.1
C$_5$ amino acid totals	26 ± 5	223 ± 11	10 ± 1	25 ± 4	11 ± 2	25 ± 5	10 ± 2	113 ± 17
Total amino acids	225 ± 13	2050 ± 150	127 ± 8	262 ± 12	146 ± 10	215 ± 12	62 ± 9	274 ± 66
Percent of amino acids that are free[f]	11%		48%		68%		23%	

[a]Values are reported in parts-per-billion based on the bulk sample. Meteorite extracts were analyzed by OPA/NAC derivatization (1 and 15 min) and LC-FD/ToF-MS detection. Monoisotopic chromatograms were used for quantification of ToF-MS data and final peak integrations were corrected for background contamination using a procedural blank. Peak areas for sample compounds were compared with pure amino acid standards that were analyzed on the same day. Final values were normalized using desalting and derivatization recoveries based on the D,L-norleucine internal standard (recoveries were typically 70–80% for the meteorite extracts). Uncertainties (δ_x) are calculated from the standard error based on the number of separate measurements (n), $\delta_x = \sigma_x (n-1)^{-1/2}$. For all UV fluorescence data, coeluting peaks and/or compounds with interfering peaks were not included in the average. Upper limits are presented for amino acids that were not present at levels above the procedural blank background levels. Numbers in parentheses are peak assignments in Fig. 1.

[b]b-AIB could not be accurately quantitated due to lack of pure standards. Values reported are estimated based on the γ-ABA standard peak.

[c]Enantiomers could be separated but not identified due to a lack of optically pure standards.

[d]Enantiomers could not be separated under the chromatographic conditions.

[e]3-a-3-mba coelutes with one enantiomer of D,L-4-apa. As a result, upper limits for 3-a-3-mba were estimated by taking the difference in peak areas of the two D,L-4-apa enantiomers.

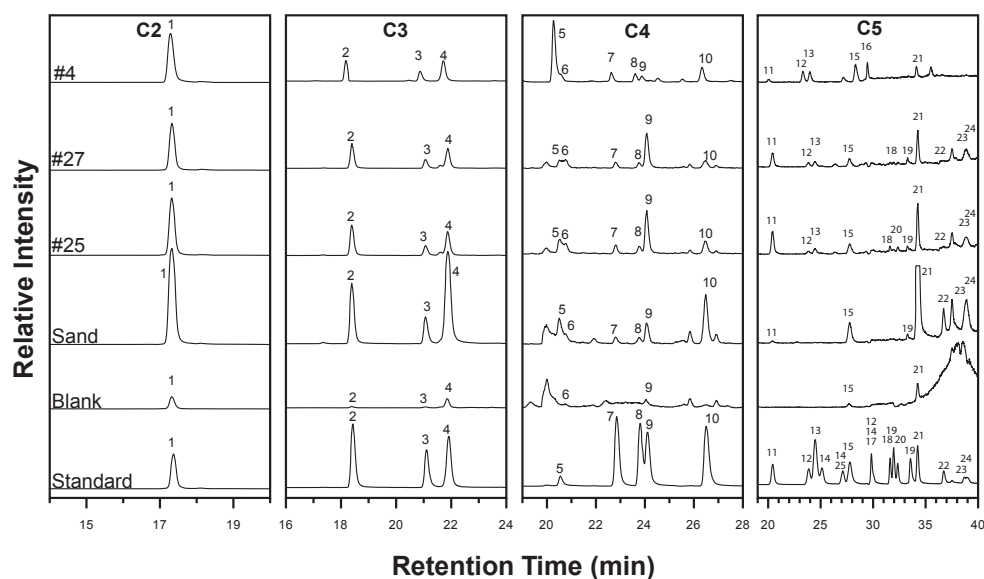[f]Percent of amino acids that are free is defined as (total ppb unhydrolyzed/total ppb hydrolyzed).

Fig. 1. Representative LC-ToF-MS single ion chromatograms of acid-hydrolyzed Almahata Sitta meteorite samples, Nubian Desert sand, partial amino acid standards, and procedural blanks analyzed in this study. Chromatograms shown are for the 2, 3, 4, and 5-carbon primary, aliphatic, acyclic amino acids (derivatized mass-to-charge ratios of 337.0858, 351.1015, 365.1171, and 379.1328, respectively). The masses plotted represent a 0.07 Da window (the peak width at half maximum) centered around the corresponding theoretical monoisotopic masses of the mono-protonated positive ions of C2 to C5 OPA/NAC amino acid derivatives and are all set to the same scale. Peak numbers correspond to amino acid assignments in Table 1. Similar chromatograms were obtained for the nonhydrolyzed fractions.

Table 2. Amino acid enantiomeric ratios[a] of Almahata Sitta samples.

Percentage of total amino acids that are chiral and proteinogenic	Sudan sand		Almahata Sitta fragment #25		Almahata Sitta fragment #27		Almahata Sitta fragment #4	
	(Free) 55%	(Bound) 60%	(Free) 19%	(Bound) 28%	(Free) 23%	(Bound) 27%	(Free) 16%	(Bound) 8%
D/L ratios[a]								
Aspartic acid	0.16	0.46	1.44	0.38	0.22	0.79	0.86	0.60
Glutamic acid	0.13	0.30	0.04	0.18	0.05	0.24	0.56	0.45
Serine	0.25	0.45	1.04	0.24	0.16	0.19	0.31	0.93
Alanine	0.33	0.36	1.63	0.67	0.56	0.66	0.98	1.00
Valine	0.00	0.07	0.00	0.03	0.03	0.03	0.21	0.38
Isovaline	n/a	n/a	n/a	0.80	0.40	0.43	0.85	0.93
β-aminobutyric acid	1.22	1.06	1.88	1.34	0.96	1.16	1.06	0.96

The "n/a" signifies that the L-enantiomer was below detection limits, making D/L ratio calculation impossible.
[a]D/L ratios were calculated from the amino acid abundances in Table 1. Fractional errors were calculated using the standard errors in Table 1 and ranged from 0.03 to 0.7.

appreciably lower than those for fragment 4, indicative of biological contamination. In addition, the total contributions of the proteinogenic L-amino acids are noticeably higher in fragments #25 and #27 than in #4 (Table 2). The indigenous inventory of achiral amino acids that are frequently observed in meteorites but are also found in biology, such as glycine, β-alanine, and γ-aminobutyric acid, also cannot be determined because they are more abundant in the sand than in the meteorite fragments. Because of these factors, our focus for this study was on the nonproteinogenic amino acids that we

can reasonably conclude are extraterrestrial in origin. Thus, we report the first analysis of extraterrestrial amino acids from meteorite stones of different petrologic types that were part of the same parent body.

Comparing Amino Acid Compositions across Almahata Sitta Petrographic Classes

We have determined that two different meteorite classes and three fragments of Almahata Sitta contain extraterrestrial amino acids, allowing a comparison

Table 3. Summary of selected properties of the Almahata Sitta meteorite fragments.

Trait	Fragment #25	Fragment #27	Fragment #4
Meteorite type	H5 chondrite	Ureilite	Ureilite
Location in ureilite parent body (from Rumble et al. 2010)	n/a	Distant from #4	Distant from #25
Relative recovery location (from Shaddad et al. 2010)	~2 km from #27	~2 km from #25	~20 km from #25 and #27
Free amino acids	48%	68%	23%
Predominant amine position of C5 amino acids	β and γ	β and γ	γ
Most similar as inferred by PAHs in common (from Sabbah et al. 2010)	#25 and #27	#25 and #27	#4 and #25

between the three fragments based on several properties (summarized in Table 3). Although the two meteorite classes contain similar amino acid totals, the isomeric compositions show some differences. Comparing the isomeric compositions of the five-carbon (C_5) amino acids (based on the position of their amine group relative to their carboxylic acid group) provides insights into the synthesis of amino acids in meteorites and allows comparison across meteorite petrologies. For example, among several type 2 and type 3 CM and CR carbonaceous chondrites that did not experience extensive aqueous alteration, the C_5 amino acids are enriched in α-amino acid isomers (Glavin and Dworkin 2009; Glavin et al. 2010b), strongly suggesting that Strecker-type chemistry was active on the parent bodies of these meteorites. Performing the same comparison on the Almahata Sitta meteorites yielded a much different result (Fig. 2). Fragments #25 and #27, an H5 chondrite and ureilite respectively, both shared a similar distribution of C_5 amino acids, with β- and γ-amino isomers more prevalent than α- and δ-amino acids, despite the fragments having different petrologies. In contrast to fragments #25 and #27, the C_5 amino acids of ureilite fragment #4 were almost exclusively γ-amino acids. The low abundance of α-amino acids was not unexpected because there is no mineralogical evidence for aqueous alteration in asteroid 2008 TC_3 (Zolensky et al. 2010), therefore Strecker-cyanohydrin amino acid synthesis would not have taken place. However, it is surprising that fragments #25 (H5) and #27 (polymict ureilite) have an amino acid distribution that is far more similar to each other than to fragment #4 (polymict ureilite). Fragments #25 and #27 also have greater fractions of their amino acids in water extractable forms (approximately 50% and 70%, respectively) than does fragment #4 (approximately 25%; Table 3). The amino acid distributions of these three meteorite fragments are consistent with their distributions of a suite of PAHs (Sabbah et al. 2010)—fragments #25 and #27 have 14 molecular species in common, #4 and #25 have 10 in common, and #4 and #27 have eight in common, corroborating the similarities observed in the amino acid data.

Multiple Sources of Amino Acids in Almahata Sitta

The discovery of amino acids in fragment #4 of Almahata Sitta (Glavin et al. 2010a) was unexpected; the high temperatures experienced by the ureilites were more than sufficient to destroy any amino acids that were present. Although fragment #25 likely experienced a cooler peak metamorphic temperature (approximately 750 °C for H5 chondrites; Bennet and McSween 1996) than the ureilites, it has been shown that temperatures greater than 500 °C cause rapid decomposition of amino acids (Rodante et al. 1992) and, based on previous heating experiments with the Murchison meteorite, all indigenous amino acids are destroyed after heating to 1200 °C for only 10 s (Glavin and Bada 2001). Therefore, any evidence of amino acid syntheses that occurred on the proto-ureilite parent body should have been erased during the subsequent high temperature (>1300 °C) period asteroid 2008 TC_3 experienced. It remains unclear, then, when and how the amino acids detected in Almahata Sitta formed. Because asteroid 2008 TC_3 was petrologically heterogeneous, one possible explanation for the observed amino acids was that they diffused from carbonaceous chondrite material incorporated after the asteroid was exposed to high temperatures. While each meteorite fragment contained comparable abundances of amino acids, the isomeric compositions of the C5 amino acids argue against simple diffusion from a single common source. Were the distributions similar for the ureilites and different for the H5 chondrite, one could make a case for differences in porosity of the meteorite types or diffusion rates; however, this relationship is not observed. Diffusion of amino acids between fragments #25 and #27 is plausible; however, the most straightforward explanation is that the amino acids in fragment #4 are from a different source than the amino acids in fragments #25 and #27. This correlates with the observation that fragments #4 and #27 have distinct oxygen isotope compositions, meaning that they were in different locations within the ureilite parent body (Rumble et al. 2010). The observation that the H4 ordinary chondrite Forest Vale
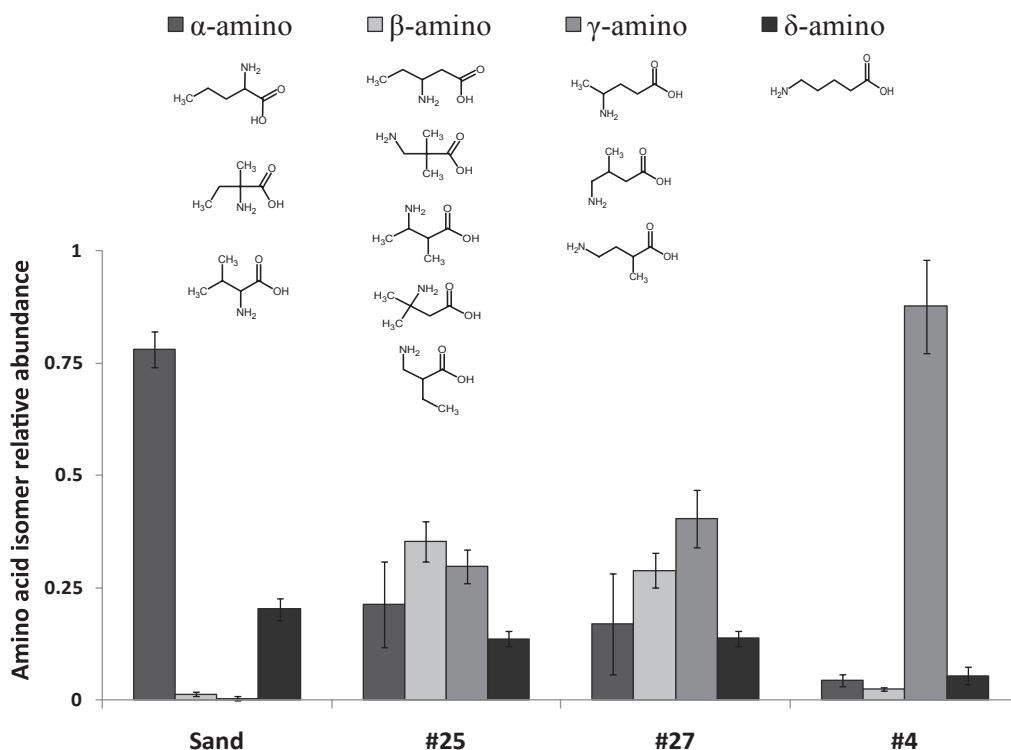
Fig. 2. Comparison between Almahata Sitta meteorites of the C_5 amino acids by amine position (α-, β-, γ-, or δ-amino). Relative abundances were obtained by dividing the fraction of amino acids of each group by the total C_5 amino acids, except that the total valine contribution was counted as twice the abundance of D-valine to approximate extraterrestrial valine.

(Zenobi et al. 1992) did not contain indigenous amino acids supports diffusion from #27 (polymict ureilite) to #25 (H5); however, one should be cautious in this interpretation as the amino acid analysis of the H4 Forest Vale was performed by HPLC with fluorescence detection without the chromatographic resolution, sensitivity, and specificity of modern instruments such as those employed in this study.

The amino acids in asteroid 2008 TC_3 most likely were formed after it cooled to lower temperatures, perhaps from material trapped between accreting fragments or from Fischer-Tropsch/Haber-Bosch type (FTT) catalytic reactions of CO, H_2, and NH_3 gases on iron or nickel surfaces inside the asteroid (see Hayatsu et al. 1972). The relevance of FTT reactions for amino acid formation in aqueously altered meteorites such as Murchison has been disputed (Cronin and Pizzarello 1990; Kerridge 1999). However, the observed lack of aqueous alteration occurring on asteroid 2008 TC_3 makes it unlikely that the chemistry leading to the amino acids observed in Almahata Sitta was the same as the chemistry that occurred in aqueously altered meteorites. Analysis of the amino acid isomeric distributions and isotopic fractionations produced by laboratory FTT reaction products catalyzed on asteroid analog material

using modern analytical tools will be necessary to evaluate the potential contributions of these reactions to amino acids in thermally altered meteorites; some preliminary work has been performed (Johnson et al. 2011). The different amino acid distributions we observe between Almahata Sitta fragments could be explained by the presence of different catalytic surfaces present at the interfaces of newly accreted material. For example, amino acids in fragments #25 and #27 may have formed near an interface between ureilite and H5 chondrite material, while fragment #4 was in a strictly ureilite interface. Alternatively, the amino acids in fragment #4 may have been synthesized on asteroid 2008 TC_3, while those in fragments #25 and #27 were imported during the collision with the H5 chondrite parent body. The diversity of catalytic surfaces available to such a heterogeneous asteroid provided a range of microenvironments in which amino acid chemistry could have taken place.

CONCLUSION

Asteroid 2008 TC_3 was a complex mixture of chondrite and ureilite materials. These clasts appear to have been heterogeneously dispersed despite evidence for

high-temperature processing of the ureilite and H5 chondrite materials. Amino acids have been identified in several Almahata Sitta meteorites, fragments of asteroid 2008 TC₃. The amino acid compositions of Almahata Sitta meteorites are not homogeneous, but rather reflect the global heteropetrology of asteroid TC₃, further accentuating its uniqueness. Further work is needed to elucidate the synthetic mechanisms leading to amino acid formation in "hot" meteorites. Analysis of other ureilites will lend insight as to whether the amino acids in Almahata Sitta are a rare consequence of the conglomerate nature of asteroid 2008 TC₃, or if amino acid-forming reactions are commonplace in the protosolar nebula, even in places where aqueous alteration is insignificant. Stable isotopic composition measurements would allow a comparison between the amino acids present in Almahata Sitta fragments to those in other meteorites, perhaps providing a signature indicative of their synthetic route. The discovery of amino acids in several Almahata Sitta meteorite fragments expands the range of meteorite types that could have contributed to the prebiotic organic inventory of the early Earth.

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