Extraterrestrial amino acids in the Almahata Sitta meteorite

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Abstract–Amino acid analysis of a meteorite fragment of asteroid 2008 TC_3 called Almahata Sitta was carried out using reverse-phase liquid chromatography coupled with UV fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) as part of a sample analysis consortium. LC-FD/ToF-MS analyses of hot-water extracts from the meteorite revealed a complex distribution of two- to seven-carbon aliphatic amino acids and one- to three-carbon amines with abundances ranging from 0.5 to 149 parts-per-billion (ppb). The enantiomeric ratios of the amino acids alanine, β-amino-*n*-butyric acid, 2-amino-2-methylbutanoic acid (isovaline), and 2-aminopentanoic acid (norvaline) in the meteorite were racemic (D/L ~ 1), indicating that these amino acids are indigenous to the meteorite and not terrestrial contaminants. Several other nonprotein amino acids were also identified in the meteorite above background levels including α-aminoisobutyric acid (α-AIB), 4-amino-2-methylbutanoic acid, 4-amino-3-methylbutanoic acid, and 3-, 4-, and 5-aminopentanoic acid. The total abundances of isovaline and α-AIB in Almahata Sitta are approximately 1000 times lower than the abundances of these amino acids found in the CM carbonaceous chondrite Murchison. The extremely low abundances and unusual distribution of five-carbon amino acids in Almahata Sitta compared to CI, CM, and CR carbonaceous chondrites may reflect extensive thermal alteration of amino acids on the parent asteroid by partial melting during formation or subsequent impact shock heating. It is also possible that amino acids were synthesized by catalytic reactions on the parent body after asteroid 2008 TC_3 cooled to lower temperatures, or introduced as a contaminant from unrelated meteorite clasts and chemically altered by α-decarboxylation.

INTRODUCTION

The recovery of meteorite fragments from the 2008 TC_3 asteroid impact that occurred in northern Sudan on October 7, 2008, collectively named Almahata Sitta, revealed a rare, anomalous polymict ureilite containing large carbonaceous grains (Jenniskens et al. 2009). The reflectance spectrum of this dark carbon-rich meteorite closely matches that of an F-class asteroid (Tholen 1989; Jenniskens et al. 2009) and is unlike any of the ureilites currently found in meteorite collections. The presence of large (up to 0.5 mm in size) aggregates of carbonaceous material and the high porosity (25–37%) of Almahata Sitta is similar to primitive carbonaceous chondrites (Jenniskens et al. 2009). An even larger carbonaceous vein (~4.7 mm × 0.3 mm) was previously reported in the Antarctic ureilite Yamato-74130 and provides additional evidence for a genetic link between ureilites and carbonaceous chondrites (Tomeoka and Takeda 1990). Oxygen isotopic analyses of Almahata

Sitta indicates that this meteorite falls on a carbonaceous chondrite anhydrous mineral slope (Rumble et al. 2010), and previous oxygen isotope studies of ureilites suggest that the carbonaceous precursor materials may be linked to CV carbonaceous chondrites (Clayton and Mayeda 1988). The ureilites are believed to represent the mantle material of a partially melted, carbon-rich asteroid (Mittlefehldt et al. 1998; Goodrich et al. 2004), possibly derived from impact shock heating or partial melting of a CV chondrite-like material (Higuchi et al. 1976; Rubin 1988).

Most of the fine-grained carbon aggregates found in Almahata Sitta and other ureilites consist primarily of graphite (Tomeoka and Takeda 1990; Jenniskens et al. 2009). However, spectroscopic measurements of the Almahata Sitta carbon aggregates indicate the presence of nanodiamonds, and the carbon appears to be the most thermally altered of any meteorite. Despite evidence for high temperature ($\sim$1100–1300 °C) igneous processing on the parent body of Almahata Sitta and other ureilites (Sinha et al. 1997; Goodrich et al. 2007; Herrin et al. 2009), C–H stretching bands from aliphatic hydrocarbons have been reported in Almahata Sitta (Jenniskens et al. 2009) and several Antarctic ureilites (Sandford 1993). Polycyclic aromatic hydrocarbons including phenanthrene (178 amu) and pyrene (202 amu) have also been detected in several different samples of the Almahata Sitta meteorite by two-step laser desorption laser ionization mass spectrometry (Morrow et al. 2009; Sabbah et al. 2009). The presence of aliphatic and aromatic hydrocarbons in Almahata Sitta is surprising given that many complex organic compounds are highly unstable at high temperatures. For example, amino acids are completely decomposed when heated to temperatures above 500–600 °C (Rodante 1992).

Organic solvent extracts of the ureilites Novo Urei, Dyalpur, and Goalpara revealed the presence of between 0.02 and 0.07 wt% of soluble organic material (Vdovykin 1970). Investigation of this organic material by infrared spectrophotometry revealed vibrational absorption bands corresponding to –CH$_3$ and $=$CH$_2$ groups and their chains (Vdovykin 1970). Vdovykin (1970) concluded that soluble organic compounds in ureilites make up 2–5% of all carbon, while the remaining carbon is represented predominantly by graphite and diamond. Some ureilites have been found to contain up to 6 wt% carbon (Grady et al. 1983) with bulk $\delta^{13}C$ values falling between −11‰ and 0‰ (Vdovykin 1970; Grady et al. 1985), similar to primitive carbonaceous chondrites. A much wider range of nitrogen isotope ($\delta^{15}N$) values ranging from −120‰ to +160‰ has been reported in ureilites (Grady and Pillinger 1988; Yamamoto et al. 1998), and the carrier phase of the heavier nitrogen in polymict ureilites is believed to be related to organic materials, similar to the heavy nitrogen in organics found in carbonaceous chondrites (Krishnamurthy et al. 1992; Pizzarello et al. 1994). The nature, distribution, isotopic composition, and origin of aliphatic and aromatic hydrocarbons and possibly other organic compounds in ureilites remain unclear.

Despite evidence of a link between ureilites and primitive carbonaceous chondrites, it is surprising that so few studies of organic compounds present in ureilites have been reported (Vdovykin 1970). The investigation of complex organic compounds, including amino acids in primitive carbonaceous chondrites, is important as these meteorites provide a record of the chemical processes that occurred in the early solar system and on the meteorite parent bodies. In addition, the delivery of amino acids to early Earth by carbon-rich asteroids and comets and their fragments prior to the emergence of life could have been an important source of Earth's prebiotic organic inventory (Chyba and Sagan 1992).

Carbonaceous chondrites continue to be the primary targets for amino acid analyses as it was reported nearly 40 yr ago that the Murchison CM chondrite contained 12 nonprotein amino acids of extraterrestrial origin (Kvenvolden et al. 1970, 1971). To date, over 80 different amino acids have now been identified in the CM chondrites Murchison and Murray, many of which are rare or completely nonexistent in the terrestrial biosphere (Cronin and Pizzarello 1983; Cronin and Chang 1993; Botta and Bada 2002; Glavin and Dworkin 2009). In contrast to the CMs, a much simpler distribution of amino acids was found in the CI chondrites Orgueil and Ivuna, indicating that these meteorites formed on a chemically distinct parent body, possibly an extinct comet (Ehrenfreund et al. 2001). Several primitive Antarctic CR carbonaceous chondrites were recently reported to have extremely high amino acid abundances, greatly exceeding the concentrations found in CM and CI meteorites (Martins et al. 2007; Pizzarello et al. 2008; Glavin and Dworkin 2009). In contrast, only trace quantities of amino acids have been identified in the CV carbonaceous chondrites Allende and Mokoia that have experienced more extensive thermal alteration (Cronin and Moore 1971, 1976). 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 has made it possible to detect extremely low abundances of amino acids in meteorites (Glavin and

Dworkin 2009). Here, we report the first amino acid analyses of the Almahata Sitta meteorite carried out independently at the Scripps Institution of Oceanography (SIO) and at the NASA Goddard Space Flight Center (GSFC). Amino acid analyses of any kind have not been previously reported for the ureilites.

MATERIALS AND METHODS

Almahata Sitta Meteorite and Controls

Fragments of the Almahata Sitta meteorite were found in the Nubian Desert of northern Sudan 2 months after asteroid 2008 TC$_3$ impacted Earth and individual meteorite samples were collected in aluminum foil (Jenniskens et al. 2009). A small interior chip weighing approximately 1.2 g from one of the 47 meteorite fragments recovered in 2008 (sample no. 4, total mass = 14 g) was allocated by P. Jenniskens for this research as part of the asteroid 2008 TC$_3$ sample consortium study. The detection of carbonaceous grains and aliphatic carbon reported by Jenniskens et al. (2009) was from a different fragment (sample no. 7) of the Almahata Sitta meteorite than the one reported here (sample no. 4). There was no fusion crust observed on the meteorite fragment analyzed in this study. The sample was crushed into a fine powder and homogenized by using a mortar and pestle in a positive pressure HEPA filtered laminar flow bench (Labconco, Kansas City, MO) at GSFC. A single smaller chip ($\sim$5 mm × 10 mm) that had broken from the larger fragment was sent to the NASA Johnson Space Center for mineralogical analyses (see Zolensky et al. 2010). As controls, a procedural reagent blank, a sample of crushed serpentine (a hydrated magnesium silicate) that had been heated at 500 °C for 3 h, and the standard mix of amino acids and amines were carried through the identical extraction procedure as the meteorite sample. Desert soil samples collected from the meteorite fall site in northern Sudan were requested, but were not available at the time of this study.

Extraction Procedures and Analytical Techniques

A portion of the powdered Almahata Sitta meteorite (404.3 mg) and serpentine blank (192.3 mg) were weighed and sealed in glass ampoules with 1 mL of Millipore Direct Q3 UV (18.2 MΩ, <5 parts-per-billion [ppb] total organic carbon) ultrapure water and placed in a heating block at 100 °C for 24 h at GSFC. Half of the water supernatants were then subjected to a 6 M HCl acid vapor hydrolysis procedure at 150 °C for 3 h to determine total hydrolyzable amino acid content (Glavin et al. 2006).

The remaining water supernatants were not acid hydrolyzed to determine the concentration of dissolved free amino acids and free amines in the extracts. Another portion of the same powdered Almahata Sitta sample (160.5 mg) was allocated to SIO and carried through identical extraction procedures. Both the unhydrolyzed (free) and acid-hydrolyzed (total = free + bound) extracts were redissolved in Millipore water and passed through equilibrated cation-exchange resin (AG50W-X8, 100–200 mesh, hydrogen form; BIO-RAD) columns to remove salts, and the amino acids recovered by elution with 2 M NH$_4$OH. During column loading at GSFC, a D,L-norleucine internal standard was added to each sample to estimate the amino acid and amine recoveries from desalting and derivatization. Norleucine was selected as an internal standard as this amino acid had a very late LC retention time and it did not interfere with the targeted meteoritic amino acids.

After desalting, the NH$_4$OH eluates were dried in 0.1 M sodium borate buffer (pH 9) under vacuum to remove excess NH$_3$, resuspended in 20 µL Millipore water and derivatized with 5 µL o-phthaldialdehyde/ N-acetyl-L-cysteine (OPA/NAC) (Zhao and Bada 1995). Separate 1 and 15 min derivatization reactions were then quenched at room temperature with 75 µL of 50 mM sodium acetate buffer, pH 5.5 (SIO analyses) or 75 µL of 0.1 M aqueous hydrazine (GSFC analyses), and immediately analyzed by reverse-phase high performance liquid chromatography with UV fluorescence detection (HPLC-FD) at SIO and LC-FD/ToF-MS analysis at GSFC. For each HPLC-FD analysis at SIO, 50 µL of the derivatized sample was injected onto a Phenomenex Luna C-18(II) 250 × 4.6 mm column (5 µm particle size). Fluorescence was monitored at 450 nm after excitation at 340 nm using a Shimadzu RF-535 variable wavelength fluorescence detector (chromatographic conditions specified in Fig. 3). Amine and amino acid abundances and their enantiomeric ratios in the meteorite extracts were determined by comparison of the peak areas generated from the UV fluorescence chromatograms of their OPA/NAC derivatives to the corresponding peak areas of standards under the same chromatographic conditions, and the GSFC analyses included peak identification confirmation by exact mass enumerations (ToF-MS). The instrument used at GSFC was an ACQUITY ultra performance LC with the fluorescence detector coupled in series to a Waters LCT Premier ToF-MS. Detailed description of the liquid chromatographic techniques and quantification methods used is provided elsewhere (Glavin et al. 2006). In addition to identifying the major fluorescent peaks present in the LC-FD/ToF-MS chromatograms by retention time, we also searched for the masses of various amines corresponding to C$_2$–C$_6$ amino acids

and C_1–C_6 amines by plotting the mass of each primary amine derivative over the elution time.

Chemicals and Reagents

All glassware and sample handling tools used at NASA GSFC and at SIO were rinsed with water, wrapped in aluminum foil, and then heated in air at 500 °C overnight. The water used for the analyses at SIO was double distilled. Most of the chemicals used in this study were purchased from Sigma-Aldrich and Fisher Scientific. For specific details on the sources of the synthetic C_5 amino acid standards used in this study, see Glavin and Dworkin (2009). A stock solution of amino acids and amines ($\sim$$10^{-5}$–$10^{-6}$ M) was prepared by mixing individual standards (97–99% purity) in water. These individual standards were combined to enable a single HPLC-FD or LC-FD/ToF-MS measurement. The OPA/NAC reagent used as a chemical tag for enantiomeric separation and UV fluorescence and mass identification of primary amine compounds was prepared by dissolving 4 mg OPA in 300 μL methanol (Fisher Optima), and then adding 685 μL 0.1 M sodium borate buffer (pH 9) and 15 μL 1 M NAC. The sodium tetraborate decahydrate powder (Sigma Ultra, 99.5–100% purity) was heated in air at 500 °C for 3 h to reduce amine contamination in the reagent. For the analyses at GSFC, a 0.1 M hydrazine (NH_2NH_2) solution used to remove excess OPA after derivatization was prepared by double vacuum distillation of concentrated anhydrous NH_2NH_2 (98% purity) and subsequent dilution in H_2O. The 6 M HCl was double distilled, 2 M ammonium hydroxide was prepared in vacuo from Millipore water and anhydrous ammonia gas (AirProducts), and the ammonium formate buffer used in the LC-FD/ToF-MS analyses was prepared by NH_4OH titration of a 50 mM formic acid solution to pH 8. A 1 μM phenolphthalein solution in acetonitrile with 0.1% formic acid was used for internal mass calibration of the ToF-MS instrument. For the HPLC-FD analyses at SIO, a 50 mM sodium acetate buffer (8% methanol, pH $\sim$9) was used for the mobile phase and 50 mM sodium acetate (pH adjusted to 5.5 with acetic acid) was used to quench the OPA/NAC reaction.

Isotope Measurements

Bulk meteorite carbon and nitrogen abundance and isotopic data were measured at GSFC using a Costech ECS 4010 combustion elemental analyzer (EA) connected through a Thermo Conflo III interface to a Thermo MAT 253 isotope ratio mass spectrometer (IRMS). Three separate aliquots of the powdered Almahata Sitta meteorite sample were weighed in separate tin cups (16.0, 16.2, and 23.4 mg), folded into small sealed packets, and then loaded into the Costech zero-blank autosampler of the EA, which was purged with ultrapure helium for 5 min. The tin cups were then dropped into the EA oven set at 1000 °C, flash combusted and then subsequently oxidized and reduced to CO_2 and N_2. These gases were separated on a GC column before passing into the IRMS for isotopic measurement. An L-alanine standard of known isotopic composition ($\delta^{13}C = -23.33‰$, $\delta^{15}N = -5.56‰$; Iso-Analytical) was used to calibrate the bulk isotopic values measured for the meteorite sample. Carbon and nitrogen abundances were calculated by comparison of peak areas from the meteorite data with calibration curves of peak areas from known quantities of acetanilide. The total nitrogen abundance in this Almahata Sitta sample was low (<0.01 wt%) and a reproducible $\delta^{15}N$ value could not be obtained. The average abundance of carbon was 3.1 ± 0.3 wt% with a bulk $\delta^{13}C$ value of $-5.1 \pm 0.1‰$. The carbon values measured for Almahata Sitta fall within the range measured for several other ureilites (Grady et al. 1985; Smith et al. 2001). Carbon and nitrogen isotopic measurements of the organic fraction of the meteorite could not be determined due to the low levels of organic material present and the limited mass of meteorite sample available for this study.

RESULTS AND DISCUSSION

The data from this study presented in Figs. 1–4 and in Tables 1–3 are based on the HPLC-FD and LC-FD/ToF-MS analytical techniques described above. Amino acid and amine peak designations are given in Table 1. The amino acid and amine concentrations for the meteorite extracts in Tables 2 and 3 are reported in ppb on a bulk sample basis and represent the average value of three to four separate measurements. The amino acid data reported in Tables 2–4 are from the GSFC analyses only. The average concentrations for the amines reported in Table 2 were calculated from the SIO measurements. Each peak in the chromatograms was identified by comparison of its UV fluorescence retention time and exact molecular mass with amino acid and amine reference standards.

Amino Acid Analyses of the Almahata Sitta Meteorite

Typical HPLC-FD and LC-ToF-MS chromatograms of the hot-water extracts from the GSFC and SIO analyses of the Almahata meteorite and procedural blank are shown in Figs. 1–3. The peaks labeled with an "X" in the chromatograms are desalting artifacts and
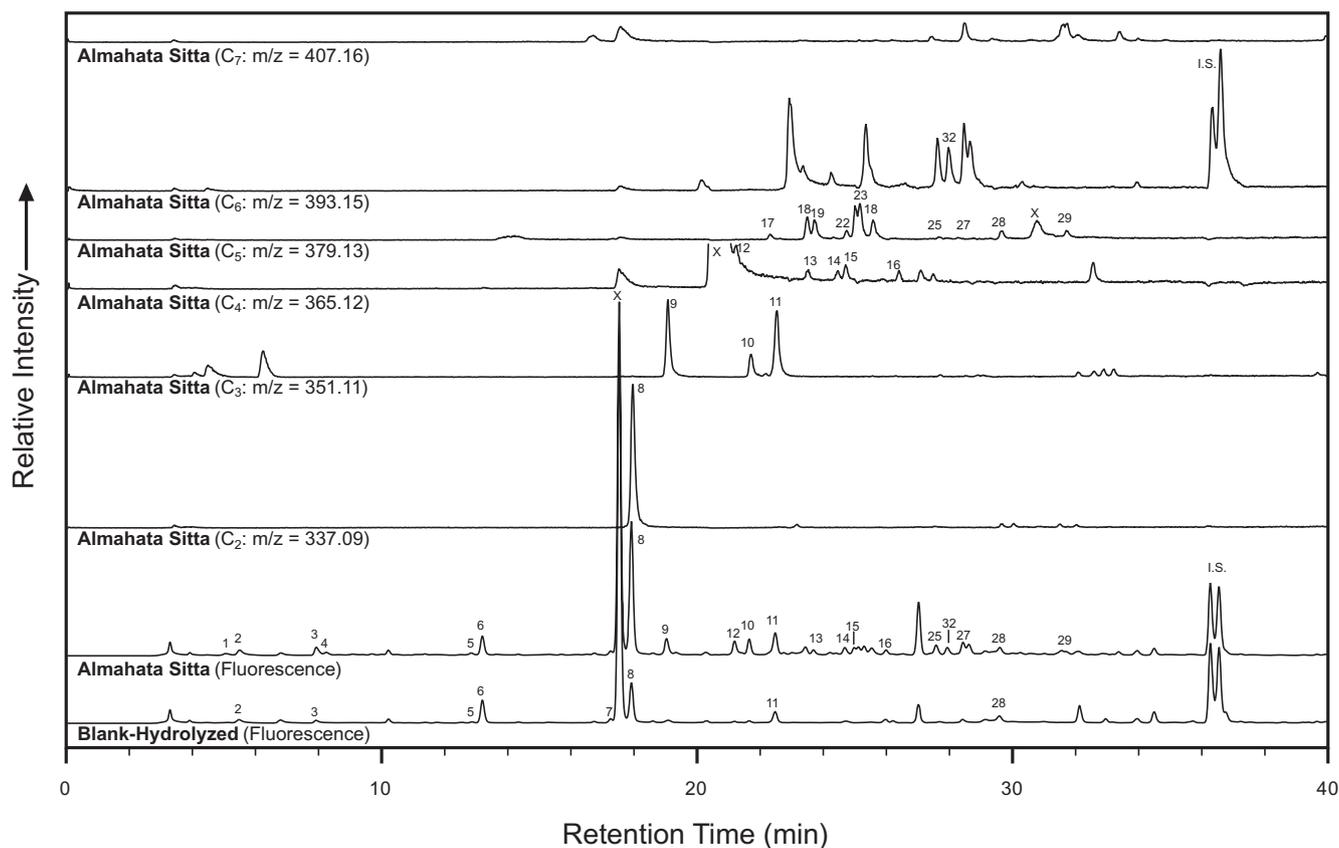
Fig. 1. The 0–40 min region of the LC-FD and ToF-MS chromatograms of the procedural blank and Almahata Sitta meteorite acid-hydrolyzed, hot-water extracts from the GSFC analyses. Similar LC-FD and ToF-MS chromatograms were obtained for the nonhydrolyzed extracts and are available upon request. The traces corresponding to the masses of the C_2–C_6 amino acids were plotted as the sum over a given mass range (peak width at half maximum of $\sim$200 ppm) for the Almahata Sitta meteorite sample only. Separation was achieved using a Waters BEH C18 column (2.1 × 50 mm, 1.7 μm bead) followed by a second Waters BEH phenyl column (2.1 × 150 mm, 1.7 μm bead). The conditions for separation of the OPA/NAC (15 min derivatization) amino acid derivatives at 30 °C were as follows: 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). The peaks were identified by comparison of the retention time and exact molecular mass to those in the amino acid standard run on the same day. Peaks in the chromatograms that did not correspond to the same UV fluorescence and mass retention times of the standard amino acids tested were not identified. (See Table 1 for the identities of the numbered peaks.)

non-UV fluorescent mass peaks that did not interfere with the ability to identify the amino acids and amines in the extracts. The most abundant primary amines detected in the Almahata Sitta acid-hydrolyzed extracts were isopropylamine (149 ppb), ethylamine (104 ppb), glycine (69 ppb), and 4-amino-2-methylbutanoic acid (65 ppb). Trace to low levels ($\sim$1–21 ppb) of aspartic and glutamic acids, alanine, β-alanine (BALA), α-, β-, and γ-amino-n-butyric acid (ABA), α-aminoisobutyric acid (α-AIB), ethanolamine, methylamine, and the five-carbon (C_5) amino acids valine, norvaline, isovaline, 3-, 4-, and 5-aminopentanoic acid, 3-amino-2,2-dimethyl-propanoic acid, and 4-amino-3-methylbutanoic acid were also identified (Tables 2 and 3). As an interfering mass peak ($m/z = 379.13$) was detected in both the nonhydrolyzed and acid-hydrolyzed procedural reagent

blank at the same retention time as L-valine (Fig. 2), accurate quantification of this amino acid was problematic and the values reported for L-valine in Table 3 should be considered to be upper limits.

Several unidentified peaks in the $m/z = 393.15$ and $m/z = 407.16$ mass traces corresponding to the C_6 and C_7 aliphatic amino acid isomers, respectively, were also detected in the Almahata Sitta extracts (Fig. 1). However, we were only able to confirm the identity of two of the C_6 amino acid peaks: ε-amino-n-caproic acid (EACA) and the norleucine internal standard (IS) used to estimate amino acid desalting recoveries. Analyses of Antarctic meteorites have previously shown that EACA in bound form is derived from contamination from the Nylon-6 storage bags used in sample collection and curation (Glavin et al. 2006).
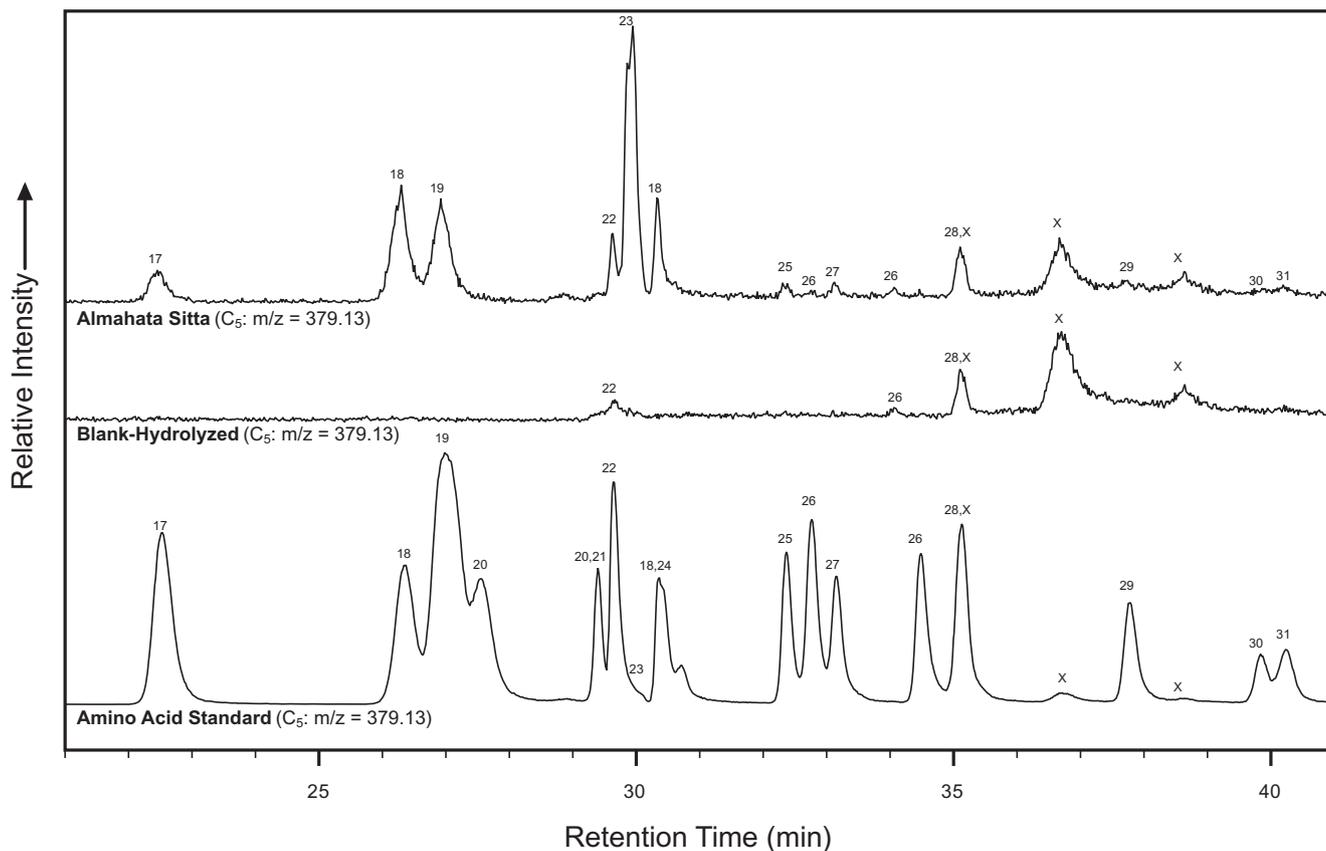
Fig. 2. The 21–41 min region of the LC-ToF-MS single ion chromatograms (m/z = 379.13) in positive electrospray ionization mode from the GSFC analyses. OPA/NAC derivatization (15 min) of the five-carbon (C_5) amino acids in the standard mix and the acid-hydrolyzed, hot-water extracts from the procedural blank and the Almahata Sitta meteorite. Similar LC-ToF-MS single ion chromatograms were obtained for the nonhydrolyzed extracts and are available upon request. To separate all possible C_5 α-, β-, γ-, and δ-amino alkanoic acid isomers the same Waters columns discussed in Fig. 1 caption with the following chromatographic conditions for the mobile phase at 30 °C were used: 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 peaks were identified by comparison of the retention time and exact molecular mass to those in the C_5 amino acid standard run on the same day. Peak identifications are given in Table 1.

However, Almahata Sitta was collected with clean aluminum foil (Jenniskens, personal communication), and as EACA is present entirely in free and not bound form in Almahata Sitta (Table 2), this amino acid cannot be derived from nylon. Additional analyses of amino acid standards will be required to identify the remaining C_6 and C_7 amino acid isomers in Almahata Sitta. No peaks in the chromatograms corresponding to the α-, β-, γ-, and δ-amino alkanoic acids containing more than seven carbons were detected in this meteorite. Many of the C_6 and C_7 acyclic primary α-amino alkanoic acids have previously been found in the Murchison meteorite (Cronin et al. 1981; Cronin and Pizzarello 1986), and primary aliphatic amino acids with as many as 10 carbons (C_{10}) have been detected in Murchison meteorite extracts using our LC-FD/ToF-MS technique.

A similar distribution of free amino acids and amines was also detected in the nonhydrolyzed water extracts of Almahata Sitta (Fig. 3). Most of the amino acids detected by HPLC-FD from the SIO analyses are near background levels except for glycine, the most abundant amino acid detected both at SIO and GSFC. Although the HPLC-FD instrument used at SIO does not have the enhanced sensitivity and mass identification capability as the LC-ToF-MS needed to quantify accurately trace levels of amino acids, several volatile amines (eethanolamine, methylamine, ethylamine, and isopropylamine) present at concentrations ranging from ~10 to 150 ppb were identified and quantified by HPLC-FD at SIO (Fig. 3; Table 2). Mass peaks corresponding to these four volatile amines were confirmed by LC-ToF-MS in the Almahata Sitta extracts analyzed at GSFC. However,
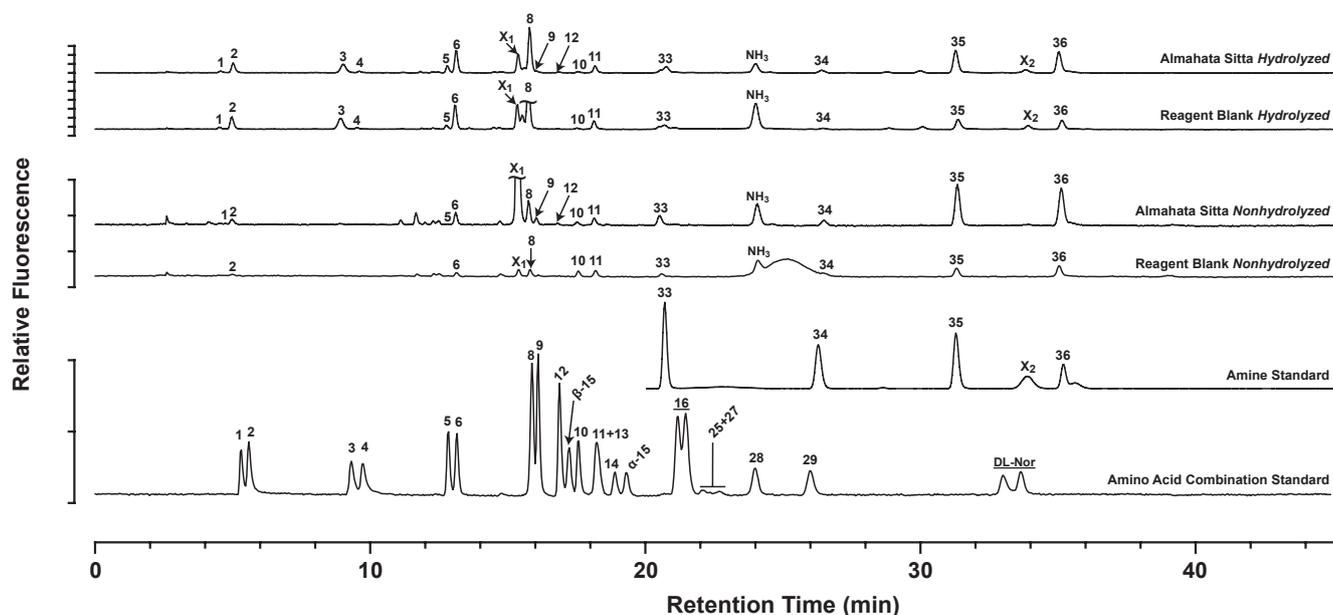
Fig. 3. The 0–45 min region of representative HPLC-FD chromatograms from the SIO analyses showing amino acid and amine peak identifications in the procedural reagent blanks and Almahata Sitta acid-hydrolyzed (total) and nonhydrolyzed (free) water extracts, and the primary amine standards after precolumn derivatization with OPA/NAC for 1 min. Chromatogram attenuations relative to the acid-hydrolyzed extracts are 4× for the nonhydrolyzed and 8× for the standards, represented by scale bar graduations. Chromatograms from the 15 min derivatizations showed similar results and are available upon request. The conditions for separation of the OPA/NAC (1 min derivatization) amino acid derivatives at ambient temperature (21 °C) were as follows: flow rate, 1 mL min⁻¹; solvent A (50 mM sodium acetate, 8% methanol, pH 9.0); solvent B (methanol); gradient 0–5 min, 100% A; 5–15 min, 0–37% B; 15–25 min, 37–42% B; 25–30 min, 42–60% B; 30–35 min, 60% B; 35–45 min, 60–0% B; 45–55 min, 100% A. The peaks were identified by the retention times of the amino acids in the standards and quantified based on relative area (Table 1). NH_3 = residual ammonia from NH_4OH carried through the desalting process; X_N = unidentified primary amines.

these volatile amine peaks were too small to quantify and may have been partially lost during the extraction and processing procedure used at GSFC. Ammonia was also identified in both the Almahata Sitta and procedural reagent blank extracts from SIO (Fig. 3); however, the most likely source of the ammonia is incomplete evaporation of the NH_4OH after desalting.

From the data in Tables 2 and 3, we calculate that the ratio of free amino acids to total (free + bound) amino acids identified in Almahata Sitta is 0.23 ± 0.06. This ratio is lower than the ratio of approximately 0.4 measured in the CM carbonaceous chondrites Murchison and Lewis Cliffs 90500 (Glavin et al. 2006). The parent body of Murchison and other CM carbonaceous chondrites experienced much lower temperatures compared to asteroid 2008 TC_3 (Clayton and Mayeda 1984). Therefore, one possible explanation for the difference between the ratio of free to total amino acids is that free amino acids in the presence of iron or other metal cations are less stable to thermal decomposition and more readily oxidized at elevated temperatures than amino acids in bound form. In

contrast to the CM chondrites, we observed a much higher abundance of amines in Almahata Sitta compared to amino acids with a total amine to total amino acid ratio of 1.1 ± 0.3 (Table 2) compared to a ratio of 0.1–0.5 for the Murchison meteorite (Botta and Bada 2002). This result may indicate a higher rate of thermal decomposition of amino acids to amines at elevated temperatures on the Almahata Sitta parent body. The total amino acid abundance measured in Almahata Sitta (~275 ppb) is 15–900 times lower than reported in the CI chondrites Orgueil and Ivuna, CMs Murchison and Murray, and Antarctic CRs Elephant Moraine (EET) 92042 and Graves Nunataks 95229 (Ehrenfreund et al. 2001; Glavin et al. 2006; Martins et al. 2007). The low amino acid abundances and relatively high concentration of amines in Almahata Sitta compared to other carbonaceous chondrites is not surprising given that the Almahata Sitta meteorite was subjected to much higher temperatures (as inferred from its mineralogy) than these CI, CM, and CR chondrites, which experienced only the relatively low temperatures of 0–150 °C during aqueous alteration (Zolensky et al. 1993; Clayton and Mayeda 1999).
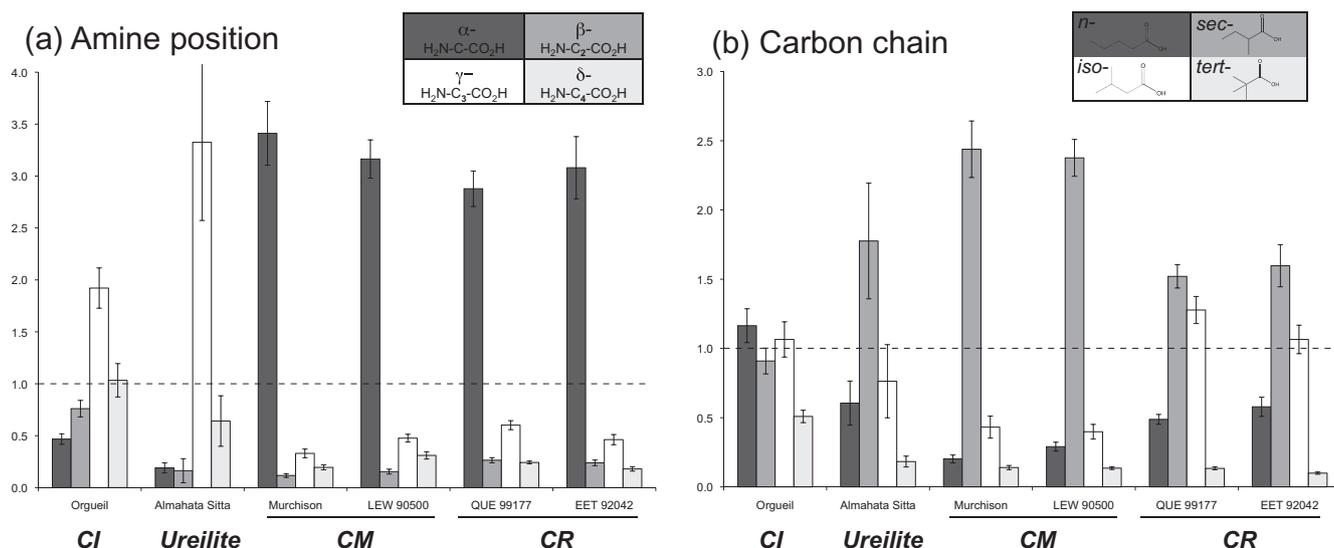
(a) Amine position

(b) Carbon chain

Fig. 4. The relative molar abundances of the C_5 amino acids in Almahata Sitta ureilite (data from Table 3) compared to several other carbonaceous chondrites as a function of (a) amine position (α-, β-, γ-, and δ-) and (b) valeric acid carbon chain structure (n-, sec-, iso-, and tert-) normalized to the total number of possible structures. The dashed line corresponds to the expected relative abundance if the amino acids were formed by a completely random synthetic process. The data for the CI, CM, and CR chondrites were taken from Glavin and Dworkin (2009). It is apparent from the data that there is structural similarity in C_5 amino acid abundances within a carbonaceous chondrite group, and differences between groups. For the purpose of this manuscript, these plots illustrate that Almahata Sitta has a unique distribution of C_5 amino acids based on both carbon chain structure and amine position compared to other CI, CM, and CR carbonaceous chondrites.

Table 1. Peak identifications and abbreviations for amino acids and amines detected in the chromatograms of the standards, procedural control samples, and meteorite extracts.

Peak	Amine compound	Peak	Amine compound
1	D-aspartic acid	19	D,L-4-amino-3-methylbutanoic acid
2	L-aspartic acid	20	D,L-3-amino-2-methylbutanoic acid
3	L-glutamic acid	21	D,L-3-amino-2-ethylpropanoic acid
4	D-glutamic acid	22	5-aminopentanoic acid
5	D-serine	23	D,L-4-amino-2-methylbutanoic acid
6	L-serine	24	3-amino-3-methylbutanoic acid
7	L-threonine	25	D-2-amino-2-methylbutanoic acid (D-isovaline)
8	Glycine	26	D,L-3-aminopentanoic acid
9	β-alanine (BALA)	27	L-2-amino-2-methylbutanoic acid (L-isovaline)
10	D-alanine	28	L-2-amino-3-methylbutanoic acid (L-valine)
11	L-alanine	29	D-2-amino-3-methylbutanoic acid (D-valine)
12	γ-amino-n-butyric acid (GABA)	30	D-2-aminopentanoic acid (D-norvaline)
13	D-β-amino-n-butyric acid (D-β-ABA)	31	L-2-aminopentanoic acid (L-norvaline)
14	L-β-amino-n-butyric acid (L-β-ABA)	32	ε-amino-n-caproic acid (EACA)
15	α- or β-aminoisobutyric acid (AIB)	33	Ethanolamine
16	D,L-α-amino-n-butyric acid (D,L-α-ABA)	34	Methylamine
17	3-amino-2,2-dimethylpropanoic acid	35	Ethylamine
18	D,L-4-aminopentanoic acid	36	Isopropylamine
X	Desalting or nonfluorescent artifact	IS	D,L-norleucine internal standard

Unusual Amino Acids and D/L Enantiomeric Ratios

The nonprotein amino acids α-AIB and isovaline detected in Almahata Sitta are not common amino acids on Earth, and are thus characteristic of amino acids of apparent extraterrestrial origin. Biological α-AIB and isovaline have been detected in acid-hydrolyzed extracts of a variety of fungal peptides (Brückner et al.

Table 2. Summary of the average blank-corrected amino acid and amine concentrations in the nonhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot-water extracts of the Almahata Sitta meteorite[a].

| | Almahata Sitta | |
Amine compound	Free (ppb)	Total (ppb)
Amino acids		
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
D-serine	< 0.5	< 1.3
L-serine	< 1.6	< 1.4
D-threonine	< 0.8	< 1.3
L-threonine	< 0.8	< 1.5
Glycine	21 ± 1	69 ± 24
BALA	4.2 ± 0.7	17 ± 7
GABA	1.8 ± 0.3	12 ± 1
D-alanine	5.0 ± 0.2	11 ± 3
L-alanine	5.1 ± 0.2	11 ± 2
D-β-ABA	1.2 ± 0.2	4.5 ± 1.4
L-β-ABA	1.2 ± 0.8	4.7 ± 1.3
α-AIB	3.6 ± 1.0	7.1 ± 5.8
D,L-α-ABA[b]	1.7 ± 0.1	5.0 ± 0.5
EACA	3.6 ± 1.8	< 4
C_5 amino acids (from Table 3)	10 ± 2	113 ± 17
Total amino acids	62 ± 9	274 ± 66
Amines		
Ethanolamine	19 ± 1	21 ± 1
Methylamine	11 ± 1	13 ± 1
Ethylamine	76 ± 5	105 ± 8
Isopropylamine	84 ± 10	149 ± 17
Total amines	190 ± 17	288 ± 27

[a]All values are reported in parts-per-billion (ppb) on a bulk sample basis. The amino acid data are from the GSFC analyses and the amine data were taken from the SIO analyses. Extracts were analyzed by OPA/NAC derivatization (1 and 15 min) and HPLC separation with UV fluorescence and time-of-flight mass spectrometry (ToF-MS) detection. For the ToF-MS data, the mono-isotopic masses of each protonated OPA/NAC amino acid derivative $(M + H^+)$ was used for quantification and final peak integrations included background level correction using the procedural blank and a comparison of the peak areas with those of the pure standard run on the same day. The final values were normalized using the desalting and derivatization recoveries of an internal D,L-norleucine standard (recoveries ranged from 70% to 80% for the meteorite extracts). The uncertainties (δ_x) are based on the standard deviation of the average value of three to four separate measurements (n) with a standard error, $\delta_x = \sigma_x (n - 1)^{-1/2}$. For all UV fluorescence data, coeluting peaks and/or compounds with interfering peaks were not included in the average. The total amino acid values shown do not include several C_6 amino acid isomers that were detected, but not identified. Upper limits are shown for amino acids that were not detected above procedural blank background levels.
[b]Enantiomers could not be separated under the chromatographic conditions.

Table 3. Summary of the average abundances of the C_5 α-, β-, γ-, and δ-amino acids in the water extracts of the Almahata Sitta meteorite[a].

| | Almahata Sitta | |
C_5 amino acid detected	Free (ppb)	Total (ppb)
α		
D-norvaline (D-2-apa)	< 0.3	0.7 ± 0.1
L-norvaline (L-2-apa)	< 0.2	0.7 ± 0.1
D-isovaline (D-2-a-2-mba)	0.6 ± 0.1	1.3 ± 0.1
L-isovaline (L-2-a-2-mba)	0.7 ± 0.1	1.4 ± 0.1
D-valine (D-2-a-3-mba)	0.3 ± 0.1	0.5 ± 0.1
L-valine (L-2-a-3-mba)	1.4 ± 0.3	1.3 ± 0.5
β		
D,L-3-apa[b]	0.4 ± 0.1	1.1 ± 0.2
D,L- and allo-3-a-2-mba[b]	< 0.1	< 0.1
3-a-3-mba[c]	< 0.4	< 3
3-a-2,2-dmpa	0.8 ± 0.1	1.8 ± 0.2
D,L-3-a-2-epa[d]	< 0.8	< 2
γ		
D,L-4-apa[b]	0.8 ± 0.1	15 ± 2
D,L-4-a-2-mba[d]	2.6 ± 0.2	65 ± 8
D,L-4-a-3-mba[d]	1.5 ± 0.5	18 ± 3
δ		
5-apa	0.9 ± 0.1	6.3 ± 2.1
Total C_5 amino acids	10 ± 2	113 ± 17

[a]All values are reported in ppb on a bulk sample basis from the GSFC analyses. Extracts were analyzed by OPA/NAC derivatization (15 min) and HPLC-FD/ToF-MS. For the ToF-MS data, the mono-isotopic masses ($m/z = 379.13$) of each protonated OPA/NAC amino acid derivative $(M + H^+)$ was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. Upper limits are shown for amino acids that were not detected at GSFC above procedural blank background levels.
[b]Enantiomers were separated but could not be identified due to the lack of optically pure standards.
[c]3-Amino-3-methylbutanoic acid (3-a-3-mba) coelutes with one of the enantiomers of D,L-4-apa, therefore upper limits for 3-a-3-mba were estimated by taking the difference in peak areas of the two D,L-4-apa enantiomers.
[d]Enantiomers could not be separated under the chromatographic conditions.

2009). However, terrestrial contamination as the sole source of α-AIB and isovaline detected in Almahata Sitta is not consistent with the high relative abundance of free α-AIB and isovaline (∼50% in free form; Tables 2 and 3) measured in this meteorite as fungal derived α-AIB and isovaline would be entirely in the peptide bound form (Brückner et al. 2009), and not the free form as observed in Almahata Sitta. Moreover, the presence of several unusual five-carbon β-, γ-, and δ-amino acids that are not found in fungal peptides (Table 3), and racemic D/L ratios of the amino acids alanine, β-amino-n-butyric acid (β-ABA), 2-amino-2-methylbutanoic acid (isovaline), and 2-aminopentanoic acid (norvaline) in the Almahata Sitta meteorite (Table 4), provide additional evidence that

Table 4. Summary of the amino acid enantiomeric ratios in the water extracts of the Almahata Sitta meteorite[a].

	Enantiomeric ratio (D/L)	
Amino acid	Free	Total
Aspartic acid	0.86	0.60
Glutamic acid	0.56	0.45
Alanine	0.98	1.00
Valine	> 0.21	> 0.38
β-ABA[b]	1.00	0.96
Isovaline[b]	0.86	0.93
Norvaline[b]	b.d.	1.00

Note: b.d. = below detection.
[a]D/L ratios from the GSFC analyses calculated from the amino acid concentrations reported in Tables 2 and 3. The fractional uncertainties ranged from 0.05 to 0.4 and are based on the errors in the absolute values of the individual D- and L-amino acids.
[b]Nonprotein amino acid.

these amino acids have an abiotic origin and are indigenous to the meteorite.

Large L-enantiomeric excesses (ee) of isovaline exceeding 15% have been measured in the CM chondrite Murchison (Cronin and Pizzarello 1997; Pizzarello et al. 2003; Glavin and Dworkin 2009) and similar L-isovaline ee were recently reported for the first time in the CI Orgueil (Glavin and Dworkin 2009). The large L-isovaline excesses observed in CI and CM chondrites is inconsistent with UV circularly polarized light as the primary mechanism, as UV CPL has only been shown to produce amino acid excesses of a few percent (Flores et al. 1977; Takano et al. 2007). As L-isovaline ee have only been observed in the more aqueous altered CM and CI chondrites and not in the most pristine, unaltered carbonaceous chondrites (such as the Antarctic CRs Queen Alexandra Range 99177 and EET 92042), amplification of a slight initial L-isovaline imbalance may have occurred during aqueous alteration on the meteorite parent bodies (Glavin and Dworkin 2009). Based on the total abundance data for isovaline in Table 3, we calculated an L-isovaline enantiomeric excess ($L_{ee} = L\% - D\%$) in Almahata Sitta of 3.7 ± 5.1%. A similar L_{ee} was obtained for the free isovaline (Table 3). The L_{ee} for isovaline in Almahata Sitta is indistinguishable from zero within measurement error and is consistent with the lack of any mineralogical evidence for aqueous activity on the Almahata Sitta meteorite parent body (Zolensky et al. 2009), but does not rule out UV CPL as a possible source of a small amount of L-isovaline asymmetry in Almahata Sitta that is within our analytical error of a few percent.

Only trace amounts (< 1–10 ppb) of L-aspartic acid, L-serine, glycine, β-alanine, L-alanine, and L-valine in the

procedural and serpentine blank could be detected by standard RP-HPLC-FD and LC-ToF-MS (Figs. 2 and 3), which indicates that minimal amino acid contamination of the samples occurred during the processing procedure. Nevertheless, given the extremely low abundances of amino acids in Almahata Sitta and low enantiomeric ratios of the protein amino acids aspartic and glutamic acids (D/L ∼ 0.5–0.6) in the hydrolyzed extracts (Table 4), we cannot rule out the possibility that some terrestrial protein amino acid contamination of Almahata Sitta occurred after its fall. A similarly low D/L glutamic acid ratio of approximately 0.6 previously measured in the Antarctic CR chondrite EET 92042 was attributed to terrestrial amino acid contamination from exposure to the Antarctic ice or during sample curation (Martins et al. 2007). Although the D- and L-enantiomers of valine were separated using the LC conditions employed, there was a relatively large unidentified coeluting mass peak in the $m/z = 379.13$ mass trace at the same retention time as L-valine in the procedural reagent blank (Fig. 2), which may have led to artificially high L-valine abundances, and hence lower D/L valine ratios (∼0.2–0.4) in the extracts (Table 4). Biologically derived L-amino acid contamination of Almahata Sitta, possibly from exposure to soil at the landing site during the approximately 2 month residence time in the Nubian Desert prior to collection, may have lowered the initial D/L ratios of these protein amino acids to the D/L ratios presently observed. Amino acid analyses of the Martian meteorites Allan Hills 84001 and Nakhla have shown that terrestrial amino acid contaminants can be rapidly absorbed by meteorites from the landing site environment (Bada et al. 1998; Glavin et al. 1999). Future analysis of amino acids in soil collected from the meteorite fall site as well as compound-specific stable isotopic analyses (CSIA) would help constrain the origin of these protein amino acids. Isotopic measurements of the amino acids and amines in Almahata Sitta were not possible given their very low abundances and the limited mass of sample available for this study. Based upon a detection limit of 1 nmol for carbon CSIA using our gas chromatography-isotope ratio mass spectrometry instrument at GSFC (Elsila et al. 2009), we would require a minimum of several grams of meteorite for carbon isotope measurements of the most abundant amino acid glycine.

The Origin and Survival of Amino Acids on Asteroid 2008 TC₃

The detection of even part-per-billion levels of amino acids and amines in Almahata Sitta is surprising given that mineralogical evidence of the meteorite

points to fractional melting and shock heating temperatures of approximately 1100–1300 °C on asteroid 2008 TC$_3$ (Herrin et al. 2009). Amino acids will rapidly decompose when heated to temperatures above 500–600 °C, even for very short durations (Rodante 1992). For example, heating experiments of the Murchison meteorite showed that only 3% of the amino acids inside the meteorite survived heating to a temperature of 550 °C for approximately 30 s, and all of the amino acids were destroyed after the meteorite fragments were melted using a CO$_2$ laser at a temperature of approximately 1200 °C for 10 s (Glavin and Bada 2001). Based on these experimental results, it seems very unlikely that any indigenous amino acids would be present in the Almahata Sitta meteorite if these organic compounds formed (or were incorporated into the asteroid from carbonaceous precursor materials) prior to or during the shock heating and partial melting experienced by asteroid 2008 TC$_3$.

One possibility is that the amino acids and amines detected in Almahata Sitta were synthesized directly from their chemical precursors (e.g., HCN, H$_2$, CO$_2$, NH$_3$, and CH$_4$) after asteroid 2008 TC$_3$ cooled to lower temperatures. The formation of amino acids has been experimentally observed by Fischer-Tropsch type catalytic reactions of CO, H$_2$, and NH$_3$ in the gas phase at 200–500 °C in the presence of nickel-iron (Hayatsu et al. 1971; Yoshino et al. 1971). Aliphatic amines have also been produced in similar fast Fourier transformation experiments (Kölbel and Trapper 1966). Therefore, it is possible that the amino acids and amines detected in the Almahata Sitta meteorite formed by similar catalytic reactions at elevated temperatures on 2008 TC$_3$. In contrast, there is chemical evidence that the complex distribution of α-amino acids observed in Murchison and other CM chondrites formed from the reaction of aldehydes, ketones, NH$_3$, and HCN by Strecker-cyanohydrin synthesis on its asteroidal parent body during a low temperature aqueous alteration phase (Peltzer and Bada 1978; Ehrenfreund et al. 2001; Lerner and Cooper 2005). Alternative sources for the amino acids in carbonaceous chondrites (e.g., from interstellar ices) that do not require aqueous activity have also been proposed (Bernstein et al. 2002). The high relative abundance of the five-carbon α-amino acids over β-, γ-, and δ-amino acids in the CM and CR chondrites studied provides additional evidence that Strecker synthesis was active on the parent bodies of these meteorites (Fig. 4).

In contrast to the CM and CR chondrites, the Almahata Sitta amino acid distribution is unique and is dominated by the five-carbon γ-amino acids (Fig. 4), which cannot be produced by the Strecker route. In addition, the formation of amino acids by the Strecker

mechanism requires aqueous activity on the meteorite parent body, and there is no mineralogical evidence for aqueous alteration in the Almahata Sitta meteorite (Zolensky et al. 2009). Several α-amino acids and one β-amino acid (β-alanine) have been synthesized by Fischer-Tropsch; however, no γ-amino acids were reported (Yoshino et al. 1971). Additional studies of the Fischer-Tropsch based synthesis of amino acids are clearly needed using modern analytical methods to ascertain the distribution of amino acids produced by this process. It has been suggested that some meteoritic γ-amino acids could be produced from the hydrolysis of lactams that have been found in Murchison (Cooper and Cronin 1995; Pizzarello et al. 2006). It is possible that the γ-amino acids detected in Almahata Sitta could have formed from lactams by a similar process; however, lactams contain secondary (and not primary) amines and are therefore not detectable using our OPA/NAC derivatization and LC-FD/ToF-MS analytical method.

It has been suggested that polymict ureilites such as Almahata Sitta represent regolith that subsequently formed on the surface of a daughter asteroid from the remnants of the proto-ureilite asteroid and other carbon-rich asteroid impactors that reaccreted in a rubble pile (Downes et al. 2008). This could have introduced meteorites of unrelated origin, which carried amino acids. Subsequent collisions could have spread this material throughout the asteroid. Another possible explanation for the presence of amino acids and amines in Almahata Sitta is that the carbonaceous chondrite precursor material of asteroid 2008 TC$_3$ contained a very high initial abundance of amino acids or their precursors prior to impact of the parent asteroid and the subsequent heating of this material during reaccretion did not reach high enough temperatures to destroy completely all the amino acids and amines. If this formation model for asteroid 2008 TC$_3$ is correct, it seems unlikely that any of the carbonaceous precursor material found in Almahata Sitta was originally CV chondrite-like given that the CV chondrites Allende and Mokoia have been found to be essentially devoid of amino acids with total abundances of <1 nmol g^{-1} (Cronin and Moore 1971, 1976). Based on amino acid evidence alone, it is possible that the carbonaceous precursor material for asteroid 2008 TC$_3$ originally contained a higher abundance of amino acids, similar to the range of abundances reported for CI, CM, and CR carbonaceous chondrites. However, future analyses of CVs and other ureilites using modern high sensitivity analytical techniques may reveal that these meteorites contain similar levels of indigenous amino acids to Almahata Sitta. Although we are currently unable to

rule out either one of these possible explanations for the presence of amino acids and amines in Almahata Sitta, formation of these compounds after asteroid 2008 TC_3 cooled to lower temperatures is the more likely explanation given the high fractional melting and shock heating temperatures on 2008 TC_3.

Given the higher abundance of amines compared to amino acids in Almahata Sitta (Table 2), it is reasonable to conclude that the amines could have been produced by thermal decomposition of amino acids on the parent body at elevated temperatures (Simmonds et al. 1972). We did not observe any evidence for thermal decomposition of amino acids into amines in a pure amino acid standard carried through the identical extraction procedure as the meteorite samples, therefore the amines observed in Almahata Sitta were not produced by our extraction method. As several simple amines have been detected in soil samples collected from the Atacama Desert in Chile (Skelley et al. 2007), we cannot rule out the Nubian Desert soil in Sudan as a possible terrestrial source of these amines in Almahata Sitta. However, if the amines in Almahata Sitta are extraterrestrial in origin and thermal decomposition by α-decarboxylation of the amino acids glycine, alanine, and α-AIB was the primary source of methylamine, ethylamine, and isopropylamine, respectively, then the relative abundances of these amines should be consistent with the decarboxylation rates measured for the corresponding amino acids.

From the total abundance data reported for the hydrolyzed Almahata Sitta extracts in Table 2, we calculate the following molar ratios from the molecular weights: methylamine/glycine = 0.44, ethylamine/alanine = 9.4, and isopropylamine/α-AIB = 37. Assuming that these three amines are produced entirely by α-decarboxylation of the corresponding amino acids, we would conclude from the molar ratios that α-amino acid stability follows the order of glycine > alanine > α-AIB. However, direct measurement of the decarboxylation rates of these α-amino acids in aqueous solution at 310–330 °C and 275 bar follow the exact opposite order of stability of α-AIB > alanine > glycine (Li and Brill 2003). Although the amine to amino acid ratios observed in Almahata Sitta do not follow the expected trend for thermal decarboxylation, it should be emphasized that the amino acid decarboxylation rates reported by Li and Brill (2003) were measured in solution and the relative rates could be very different in the solid state in the absence of any aqueous activity on asteroid 2008 TC_3. In addition, we cannot rule out the possibility that the amine to amino acid molar ratio trend observed in Almahata Sitta is related to evaporative loss of amines during the extraction procedure and the relative volatility of these

compounds. In any case, if the amines detected in Almahata Sitta are indigenous to the meteorite and derived directly from interstellar precursors or amino acid decarboxylation as has been previously suggested for the Murchison meteorite (Pizzarello et al. 1994), these amines could not have been exposed to the high temperatures associated with thermal alteration of the parent body.

In contrast to Almahata Sitta, a much more complex distribution and higher abundances of C_1–C_5 aliphatic amines have been identified in Murchison (Jungclaus et al. 1976; Pizzarello et al. 1994), and 16 of the 20 amines identified could be produced from the corresponding amino acids present in Murchison by α-decarboxylation (Simmonds et al. 1972). Based on published Murchison data from Pizzarello and coworkers (Cronin and Pizzarello 1983; Pizzarello et al. 1994), we calculate the following amine to amino acid molar ratios in Murchison: methylamine/glycine = 0.72, ethylamine/alanine = 0.40, and isopropylamine/α-AIB = 0.07. These ratios are consistent with α-decarboxylation as the primary source of amines based on the amino acid decarboxylation rates discussed above. In addition, nitrogen isotopic measurements of amino acids and volatile bases (including ammonia and amines) in Murchison show that these compounds are enriched in ^{15}N and fall in a narrow range ($\delta^{15}N = + 94 \pm 8‰$), consistent with their formation from similar precursors (Pizzarello et al. 1994). Future nitrogen isotopic measurements of both amines and amino acids in Almahata Sitta will be necessary to help constrain their origins.

CONCLUSIONS

As part of this consortium study, we investigated the abundances and enantiomeric compositions of primary amino acids and amines in the Almahata Sitta meteorite using HPLC-FD and LC-ToF-MS. We were able to identify a total of 19 different amino acids and their enantiomers and four amines in Almahata Sitta using these techniques. This is the first report of amino acids and amines in any ureilite. Many more C_6 primary amino acids were observed in Almahata Sitta, but were not identified. 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 are of an abiotic origin. However, it remains unclear whether or not the amines detected in Almahata Sitta are extraterrestrial in origin. The total amino acid abundance in the Almahata Sitta meteorite (~275 ppb) is 15–900 times lower than previous measurements of

the CI, CM, and CR carbonaceous chondrites using the same analytical techniques. Given the mineralogical evidence for high temperatures in excess of 1100 °C on asteroid 2008 TC$_3$ and the fact that amino acids are unstable at temperatures above 500 °C, it is surprising that any extraterrestrial amino acids were found in Almahata Sitta. It is likely that these amino acids and/or their precursors were formed by Fischer–Tropsch-like catalytic reactions from CO, H$_2$, and NH$_3$ after asteroid 2008 TC$_3$ cooled to lower temperatures. However, we cannot rule out the possibility that the carbonaceous precursor material was incorporated into the daughter asteroid 2008 TC$_3$ after impact of the parent proto-ureilite with a carbonaceous chondrite-like asteroid and some of the accreted carbonaceous material was not exposed to the extremely 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 organic compounds. Comparison of our amino acid data with additional organic, bulk chemistry, petrographic, and isotopic data that will be reported on this and other fragments of the Almahata Sitta meteorite will reveal important insights into parent body processes on asteroid 2008 TC$_3$.

Editorial Handling—Dr. Scott Sandford

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