

Extraterrestrial Amino Acids in the Almahata Sitta Meteorite

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ABSTRACT

Amino acid analysis of a meteorite fragment of asteroid 2008 TC₃ called Almahata Sitta was carried out using reverse-phase high-performance liquid chromatography coupled with UV fluorescence detection and time-of-flight mass spectrometry (HPLC-FD/ToF-MS) as part of a sample analysis consortium. HPLC analyses of hot-water extracts from the meteorite revealed a complex distribution of 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). The enantiomeric 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 meteorite were racemic (D/L \sim 1), indicating that these amino acids are indigenous to the meteorite and not terrestrial contaminants. Several other non-protein 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 AIB in Almahata Sitta are \sim 1000 times lower than the abundances of these amino acids found in the CM carbonaceous meteorite Murchison. The extremely low abundances and unusual distribution of five carbon amino acids in Almahata Sitta compared to CI, CM, and CR carbonaceous meteorites and may be due to extensive thermal alteration of amino acids on the parent asteroid by partial melting during formation or impact shock heating.

Keywords: Almahata Sitta meteorite, amines, amino acids, α -aminoisobutyric acid, asteroid 2008 TC₃, isovaline, liquid chromatography time-of-flight mass spectrometry, Nubian Desert, polymict ureilites, racemic, Sudan, thermal decarboxylation

INTRODUCTION

The recovery of meteorite fragments from the 2008 TC₃ 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 (Jenniskens et al., 2009; Tholen, 1989) 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 x 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., this issue), and previous oxygen isotope studies of ureilites suggest that the carbonaceous precursor materials may be linked to CV type carbonaceous meteorites (Clayton and Mayeda, 1988). The ureilites are believed to represent the mantle material of a partially melted, carbon-rich asteroid (Goodrich et al., 2004; Mittlefehldt et al., 1998), possibly derived from impact shock heating of CV chondrite-like material (Rubin, 1988).

Most of the fine grained carbon aggregates found in Almahata Sitta and other ureilites consists primarily of graphite (Jenniskens et al., 2009; Tomeoka and Takeda, 1990), however spectroscopic measurements of these carbon aggregates indicate the presence of nano-diamonds, and the carbon in Almahata Sitta appears to be the most thermally altered of any meteorite. Despite evidence for high temperature (~1100-1300°C) igneous processing on the parent body of Almahata Sitta and other ureilites (Goodrich et al., 2007; Herrin et al., 2009; Sinha et al., 1997), 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 (PAHs) 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 complex organic compounds in Almahata Sitta and other ureilites is surprising given that most organic compounds are not stable at high temperatures, and amino acids will completely decompose 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% 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 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% of carbon (Grady et al., 1983) with bulk $\delta^{13}\text{C}$ values falling between -11‰ and 0‰ (Grady et al., 1985; Vdovykin, 1970), similar to primitive carbonaceous chondrites. A much wider range of nitrogen isotope ($\delta^{15}\text{N}$) 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 heavy nitrogen in organics found in primitive chondrites. The nature, distribution, isotopic composition, and origin of aliphatic hydrocarbons and possibly other organic compounds in ureilites remain unclear.

Despite strong evidence of a link between ureilites and primitive carbonaceous meteorites, it is surprising that only a few studies on the analysis of organics in ureilites have been reported (Vdovykin, 1970), and to our knowledge there have been no amino acid analyses carried out for any ureilite. The investigation of complex organic compounds, including amino acids in primitive carbonaceous 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 (Chyba and Sagan, 1992).

Carbonaceous meteorites continue to be the primary targets for amino acid analyses since it was reported nearly 40 years ago that the Murchison CM type carbonaceous meteorite contained twelve non-protein amino acids of extraterrestrial origin (Kvenvolden et al., 1970; Kvenvolden et al., 1971). To date, over 80 different amino acids have now been identified in the CM meteorites Murchison and Murray, many of which are rare or completely non-existent in the terrestrial biosphere (Botta and Bada, 2002; Cronin and Chang, 1993; Cronin and Pizzarello, 1983; Glavin and Dworkin, 2009). In contrast to the CMs, a much simpler distribution of amino acids was found in the CI meteorites Orgueil and Ivuna, indicating that these meteorites formed on a chemically distinct parent body, possibly an extinct comet (Ehrenfreund et al., 2001). The most primitive unaltered CR type carbonaceous meteorites were recently reported to have extremely high amino acid abundances, greatly exceeding the concentrations found in CM and CI meteorites (Glavin and Dworkin, 2009; Martins et al., 2007; Pizzarello et al., 2008). In contrast, only trace quantities of amino acids have been identified in the CV type carbonaceous meteorites 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 high-performance liquid chromatography with UV fluorescence detection and time-of-flight mass spectrometry (HPLC-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 analysis of the Almahata Sitta meteorite using HPLC-FD/ToF-MS. Amino acid analyses of any kind have not been previously reported for the ureilites.

MATERIALS AND METHODS

Chemicals and Reagents

All glassware and sample handling tools were rinsed with Millipore Direct Q3 UV (18.2 M Ω , < 5 ppb total organic carbon) ultrapure water, wrapped in aluminum foil, and then heated in air at 500°C overnight. 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 C₅ amino acid standards used in this study, see (Glavin and Dworkin, 2009). A stock solution of amino acids and amines ($\sim 10^{-5}$ to 10^{-6} M) was prepared by mixing individual standards (97-99% purity) in Millipore Direct Q3 UV (18.2 M Ω , < 5 ppb total organic carbon) ultrapure water. The *o*-phthaldialdehyde / *N*-acetyl-L-cysteine (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 μ l methanol (Fisher Optima), and then adding 685 μ l 0.1 M sodium borate buffer (pH 9) and 15 μ l 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 NASA Goddard Space Flight Center (GSFC), a 0.1 M hydrazine (NH₂NH₂) solution used to remove excess OPA after derivatization was prepared by double vacuum distillation of concentrated anhydrous hydrazine (98% purity) and subsequent dilution in H₂O. The 6M HCl was double-distilled, and the ammonium formate buffer used in the HPLC-FD/ToF-MS analyses was prepared by NH₄OH titration of a 50 mM formic acid solution to pH 8. A 1 mM 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 the Scripps Institution of Oceanography (SIO), a 50 mM sodium acetate buffer (pH 5.5) was used to quench the OPA/NAC reaction and for the mobile phase.

Almahata Sitta Meteorite and Controls

Fragments of the Almahata Sitta meteorite were collected in the Nubian Desert of northern Sudan two months after asteroid 2008 TC₃ impact and the samples were individually wrapped in aluminum foil (Jenniskens et al., 2009). A small interior chip of 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 TC₃ sample consortium study. There was no fusion crust observed on this meteorite fragment. We received one meteorite fragment from sample no. 4 which was weighed (mass ~1.2 g), crushed into a fine powder, and homogenized by using a mortar and pestle in a positive pressure HEPA filtered laminar flow bench at GSFC. A single smaller chip (~5 mm x 10 mm) that had broken from the larger fragment was sent to M. Zolensky for mineralogical analyses. For more details on the mineralogy of fragment no. 4 see Zolensky et al., this issue. 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 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 6M HCl acid vapor hydrolysis procedure at 150°C for 3 hours to determine total hydrolyzable amino acid content (Glavin et al., 2006). The remaining water supernatants were not acid hydrolyzed in order 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 the same extraction procedure. Both the non-hydrolyzed (free) and acid hydrolyzed (total = free + bound) extracts were re-dissolved in Millipore water and passed through a cation-exchange resin (AG50W-X8, 100-200 mesh, hydrogen form, BIO-RAD) to remove salts, and the amino acids recovered by elution with 2 M NH₄OH (prepared *in vacuo* from NH₃ gas, AirProducts). 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 since this amino acid had a very late HPLC retention time and it did not interfere with the targeted meteoritic amino acids.

After desalting, the NH_4OH eluates were dried in 0.1 M sodium borate buffer (pH 9) under vacuum to remove excess NH_3 , re-suspended in 20 μl Millipore water and derivatized with 5 μl OPA/NAC (Zhao and Bada, 1995). The derivatization reaction was then quenched after 1 or 15 minutes at room temperature with 75 μl of 50 mM sodium acetate buffer (SIO analyses) or 75 μl of 0.1 M aqueous hydrazine (GSFC analyses), and the solution was briefly stored at 4°C prior to HPLC-FD at SIO and HPLC-FD/ToF-MS analysis at GSFC. Amine and amino acid abundances and their enantiomeric ratios in the meteorite extracts were then determined by comparison of the peak areas generated from both the exact mass and UV fluorescence chromatograms of their OPA/NAC derivatives to the corresponding peak areas of authentic standards under the same chromatographic conditions. A 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 HPLC-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 nominal mass of each compound over the elution time.

Isotope Measurements

Bulk 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 mg, 16.2 mg, 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 ultra-pure 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 ($\delta^{13}\text{C} = -23.33\text{‰}$, $\delta^{15}\text{N} = -5.56\text{‰}$, 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 (we didn't do any of the peak area stuff in the MAPS paper, so there's no reference for this). The total nitrogen abundance in this Almahata Sitta sample was low ($< 0.01\%$) and a reproducible $\delta^{15}\text{N}$ value could not be obtained. The average abundance of carbon was $3.1 \pm 0.3 \text{ wt\%}$ with a bulk $\delta^{13}\text{C}$ value of $-5.1 \pm 0.1\text{‰}$. 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. 1-5 and in Tables 1-3 are based on the reverse phase HPLC-FD and HPLC-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 parts-per-billion (ppb) on a bulk sample basis and represent the average value of three to four independent analyses at GSFC and at SIO. Each peak in the chromatograms was identified by comparison of its UV fluorescence retention time and exact molecular mass with those of authentic amino acid and amine reference standards.

Amino acid analyses of the Almahata Sitta Meteorite

Typical HPLC-FD and ToF-MS chromatograms of the hot-water extracts from the GSFC and SIO analyses of the Almahata meteorite and procedural blank are shown in Figures 1-3. The peaks labeled with an 'X' in the chromatograms are desalting artifacts and 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 (1 to 21 ppb) of aspartic and glutamic acids, alanine, β -alanine (BALA), α -, β -, and γ -amino-*n*-butyric acid (ABA), α -aminoisobutyric acid (AIB), ethanolamine (ETA), methylamine (MA), and the five-carbon (C_5) amino acids valine, norvaline, isovaline, 3-, 4-, and 5-aminopentanoic acid, 3-amino-2,2-dimethylpropanoic acid, and 4-amino-3-methylbutanoic acid were also identified (Tables 2 and 3). Since an interfering mass peak (m/z 379.13) was detected in both the non-hydrolyzed and acid-hydrolyzed procedural reagent blank at the same retention time as L-valine (Figure 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 mass trace corresponding to the six-carbon (C_6) aliphatic amino acid isomers were also detected in the Almahata Sitta extracts (Figure 1); however, we were only able to confirm the identity of two of these peaks: ϵ -amino-*n*-caproic acid (EACA) and the norleucine internal standard (I.S.) 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). However, Almahata Sitta was collected with clean aluminum foil (Jenniskens et al., 2009), and since 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 authentic amino acid standards will be required to identify the remaining C_6 amino acid isomers in Almahata Sitta. No peaks in the chromatograms corresponding to the α -, β -, γ -, and δ -amino alkanolic acids containing more than six carbons were identified in this meteorite. Many of the C_6 and C_7 acyclic primary α -amino alkanolic 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 ten carbons (C_{10}) have been detected in Murchison meteorite extracts using our HPLC-FD/ToF-MS technique.

A similar distribution of free amino acids and amines was also detected in the unhydrolyzed 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 at SIO and at GSFC (Table 2). 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 accurately quantify trace levels of amino acids, several volatile amines (ETA, MA, EA, and IPA) present at concentrations ranging from ~10 to 150 ppb were identified by HPLC-FD at SIO (Fig. 3). Mass peaks corresponding to these four amines were also detected by LC-ToF-MS in the Almahata Sitta extracts analyzed at GSFC. These volatile amine peaks were too small to quantify and may have been lost during the extraction and processing procedure. 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 ~ 0.4 measured in the CM carbonaceous meteorites Murchison and LEW 90500 (Glavin et al., 2006). In contrast to the CM meteorites, there is a much higher abundance of amines in Almahata Sitta compared to amino acids with a free to total amine ratio of 0.66 ± 0.09 (Table 2). The total amino acid abundance measured in Almahata Sitta (~ 275 ppb) is 15 to 900 times lower than reported in the CI meteorites Orgueil and Ivuna, CM meteorites Murchison and Murray, and Antarctic CR meteorites EET 92042 and GRA 95229 (Ehrenfreund et al., 2001; Glavin et al., 2006; Martins et al., 2007). This finding is not surprising given that the Almahata Sitta meteorite was subjected to much higher temperatures than these CI, CM, and CR meteorites which experienced only relatively low temperatures of 0 to 150°C during aqueous alteration (Clayton and Mayeda, 1999; Zolensky et al., 1993).

Unusual Amino Acids and D/L Enantiomeric Ratios

The non-protein amino acids 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 AIB and isovaline have been detected in acid-hydrolyzed extracts of a variety of fungal peptides (Brückner et al., 2009). However, terrestrial contamination as the sole source of AIB and isovaline detected in Almahata Sitta is not consistent with the high relative abundance of free AIB and isovaline (~50% in free form, Tables 2 and 3) measured in this meteorite since fungal derived 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 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 meteorite Murchison (Cronin and Pizzarello, 1997; Glavin and Dworkin, 2009; Pizzarello et al., 2003) and for the first time in the CI meteorite Orgueil (Glavin and Dworkin, 2009). The large L-isovaline excesses observed in CI and CM meteorites is inconsistent with UV circularly polarized light as the primary mechanism for molecular asymmetry of amino acids as previously suggested (Flores et al., 1977; Takano et al., 2007). Since L-isovaline ee's have only been observed in the more aqueous altered CM and CI type meteorites and not in the most pristine, unaltered meteorites (such as the Antarctic CR meteorites QUE 99177 and EET 92042), amplification of an slight initial L-isovaline imbalance may have occurred during aqueous alteration on the meteorite parent body (Glavin and Dworkin, 2009). Based on the total abundance data for isovaline in Table 3, we calculate an L-isovaline enantiomeric excess ($L_{ee} = L\% - D\%$) in Almahata Sitta of $3.7 \pm 5.1\%$. 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, but does not rule out UV CPL as a possible source of a small L-isovaline asymmetry in Almahata Sitta.

Only trace amounts ($< 1\text{-}10$ 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 HPLC-FD and LC-ToF-MS (Fig. 2 and Fig. 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 ($D/L \sim 0.5$ to 0.6) in the hydrolyzed extracts (Table 4), we cannot rule out the possibility that some terrestrial protein amino acid contamination of this meteorite occurred. Although the D- and L-enantiomers of valine were separated using the HPLC conditions employed, there was a relative large unidentified co-eluting 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 to 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 ~ 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 ALH 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 (GC-IRMS) instrument (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 ~1100-1300°C on asteroid 2008 TC₃ (Zolensky et al., this issue). 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 ~ 30 seconds, and all of the amino acids were destroyed after the meteorite grains were melted using a CO₂ laser at a temperature of ~1200°C for 10 sec (Glavin and Bada, 2001). Based on these experimental results, it seems very unlikely that any indigenous amino acids would be found in the Almahata Sitta meteorite assuming that these organic compounds were formed (or incorporated into the asteroid from carbonaceous precursor materials) prior to or during the shock heating and melting events of asteroid 2008 TC₃.

One possibility is that the amino acids and amines detected in Almahata Sitta were synthesized in the asteroid directly from their chemical precursors (e.g. HCN, CO₂, NH₃, CH₄) after the asteroid cooled to temperatures well below 500-600°C. For example, the complex distribution of α -amino acids observed in the Murchison meteorite and other CM and CR type meteorites are believed to have formed from the reaction of aldehydes, ketones, ammonia, and HCN by Strecker-cyanohydrin synthesis on the asteroid parent body during an aqueous alteration phase (Ehrenfreund et al., 2001; Lerner and Cooper, 2005; Peltzer and Bada, 1978). Alternative sources for the amino acids in carbonaceous meteorites (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 meteorites provides additional

evidence that Strecker synthesis was active on the parent bodies of these meteorites (Fig. 4). However, the Almahata Sitta amino acid distribution is unique and is dominated by the 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). 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 HPLC-FD/ToF-MS analytical method.

Another possible explanation for the presence of amino acids and amines is that the carbonaceous meteorite precursor material of asteroid 2008 TC₃ 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 re-accretion did not reach high enough temperatures to completely destroy the amino acids and amines. 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 re-accreted in a rubble pile (Downes et al., 2008). If this formation model for asteroid 2008 TC₃ 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 meteorites Allende and Mokoia have been found to be essentially devoid of amino acids with total abundances of < 1 nmol per gram (Cronin and Moore, 1971, 1976). Based on amino acid evidence alone, it is more likely that the carbonaceous precursor material for asteroid 2008 TC₃ originally contained a higher abundance of amino acids, similar to the range of abundances reported for CI, CM, and CR type carbonaceous meteorites. However, future analyses of CV and other ureilite type meteorites using current

analytical techniques may reveal that these meteorites contain similar levels of indigenous amino acids as Almahata Sitta. We are currently unable to rule out either one of these possible explanations for the presence of amino acids and amines in Almahata Sitta.

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. Since 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 at this time. However, if the amines in Almahata Sitta are extraterrestrial in origin and thermal decomposition by α -decarboxylation of the amino acids glycine, alanine, and AIB was the primary source of methylamine (MA), ethylamine (EA), and isopropylamine (IPA), 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: MA/glycine = 0.44, EA/alanine = 9.4, and IPA/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 the stability of glycine > alanine > 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 AIB > alanine > glycine (Li and Brill, 2003). Based on these results we believe that the primary source of these amines in Almahata Sitta is not thermal decarboxylation, although we cannot rule out the possibility that the amine to amino acid molar ratio trend observed in Almahata Sitta is related to evaporation 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 from interstellar precursors or thermal decarboxylation as has been previously suggested for the Murchison meteorite (Pizzarello et al., 1994), these amines must not have seen 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 C₁ to C₅ aliphatic amines has been identified in Murchison (Jungclauss 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 co-workers (Cronin and Pizzarello, 1983; Pizzarello et al., 1994), we calculate the following molar ratios in Murchison: MA/glycine = 0.72, EA/alanine = 0.40, and IPA/AIB = 0.07. In contrast to Almahata Sitta, these ratios are consistent with α -decarboxylation as the primary source of these amines based on the amino acid stabilities 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 ¹⁵N and fall in a narrow range ($\delta^{15}\text{N} = +94 \pm 8\%$), 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 composition of primary amines in the Almahata Sitta meteorite using HPLC-FD and ToF-MS. We were able to identify a total of 19 different amino acids and their enantiomers and 4 amines in Almahata Sitta using these techniques. This is the first report of amino acids and amines in any ureilite type meteorite. Many more C₆ 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 C₅ amino acids suggest that most of the amino acids are indigenous to Almahata Sitta and of an abiotic origin. It remains unclear whether or not the 4 amines detected in Almahata Sitta are extraterrestrial in origin. The total amino acid abundance in Almahata Sitta (~ 275 ppb) is 15 to 900 times lower than previous measurements of the CI, CM, and CR type carbonaceous meteorites using similar techniques. Given the mineralogical evidence for high temperatures in excess of 1100°C on asteroid 2008 TC₃, and the fact that amino acids are not stable at temperatures above 500°C, it is surprising that any extraterrestrial amino acids were found in Almahata Sitta. It is possible that these amino acids or their precursors formed after asteroid 2008 TC₃ cooled to temperatures below 500°C. It is also possible that the carbonaceous precursor material was incorporated into the daughter asteroid 2008 TC₃ after impact of the parent proto-ureilite and re-accretion 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.

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FIGURES 1-5

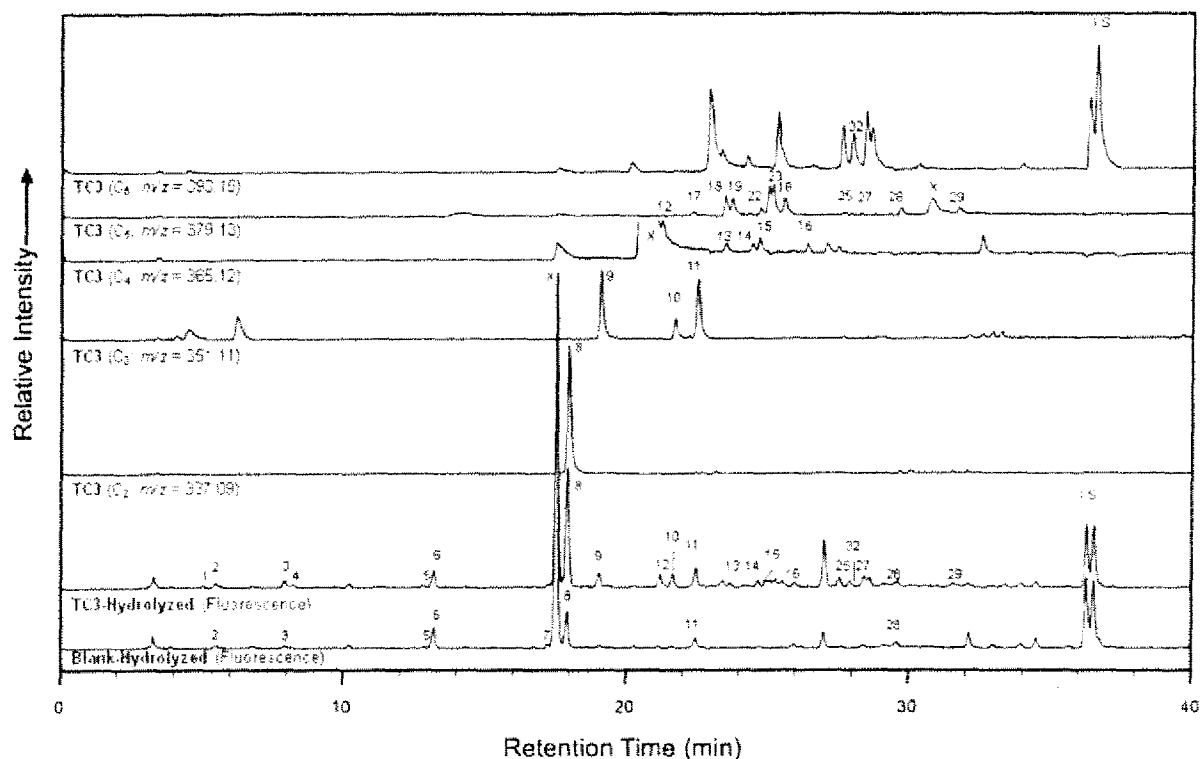


Fig. 1. The 0- to 40-min. region of the HPLC-FD and ToF-MS chromatograms of the procedural blank and Almahata Sitta (TC₃) meteorite acid-hydrolyzed, hot-water extracts from the GSFC analyses. Similar HPLC-FD and ToF-MS chromatograms were obtained for the non-hydrolyzed extracts and are available upon request. The mass traces corresponding to C₂ to C₆ amino acids are plotted for the Almahata Sitta (TC₃) meteorite sample only. Separation was achieved using a Waters BEH C18 column (2.1 x 50 mm, 1.7- μ m bead) followed by a second Waters BEH phenyl column (2.1 x 150 mm, 1.7- μ m bead). The conditions for separation of the OPA/NAC (15 min derivatization) amino acid derivatives at 30°C were as follows: flow rate, 150 μ l/min; solvent A (water); solvent B (methanol); solvent C (50 mM ammonium formate, 8% methanol, pH 8.0); gradient 0 to 5 min, 100% C; 5 to 15 min, 0 to 83% A and 0 to 12% B; 15 to 22 min, 83 to 75% A and 12 to 20% B; 22 to 35 min, 75 to 35% A and 20 to 60% B. 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 exact mass retention times of the standard amino acids tested were not identified. See Table 1 for the identities of the numbered peaks.

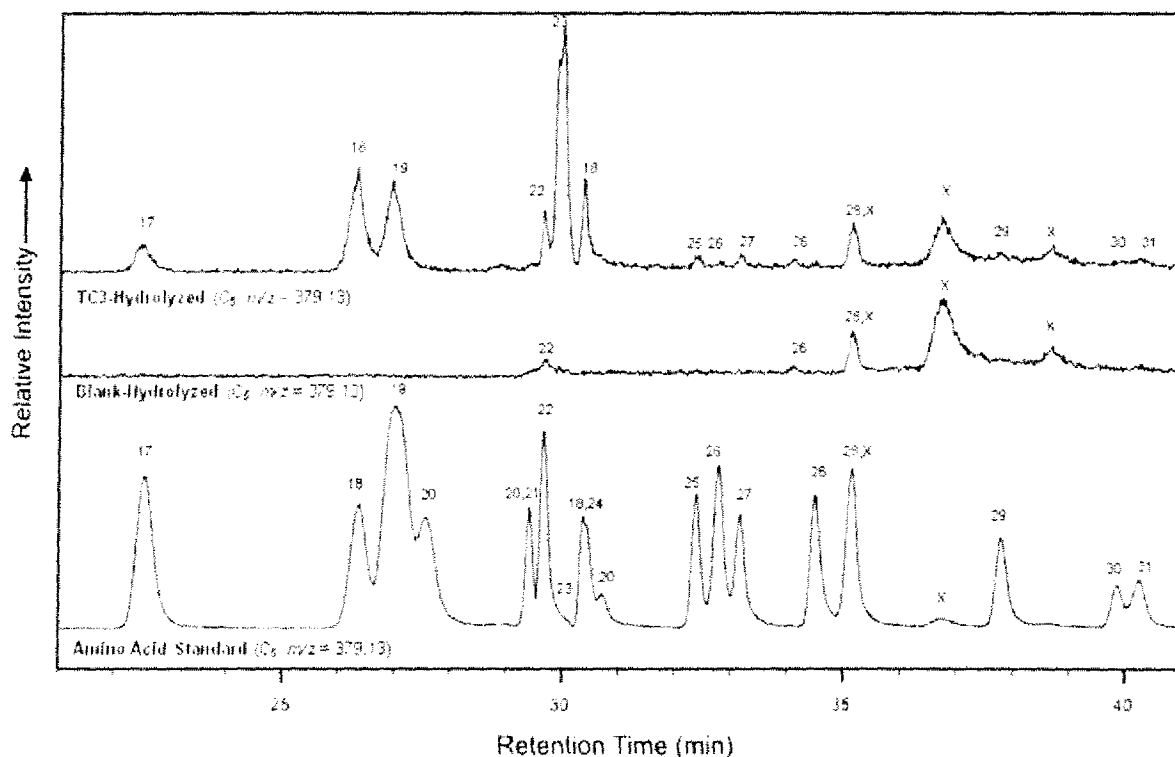


Fig. 2. The 21- to 41-min. region of the HPLC-FD/ToF-MS single ion chromatograms ($m/z = 379.13 \pm 0.02$) in positive electrospray ionization mode from the GSFC analyses. OPA/NAC derivatization (15 min) of the five carbon (C_5) amino acids in the standard mix and the acid-hydrolyzed, hot-water extracts from the procedural blank and the Almahata Sitta (TC_3) meteorite. Similar HPLC-FD/ToF-MS single ion chromatograms were obtained for the non-hydrolyzed extracts and are available upon request. In order to separate all possible C_5 α -, β -, γ -, and δ -amino alkanolic 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, $150 \mu\text{L}/\text{min}$; 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 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.

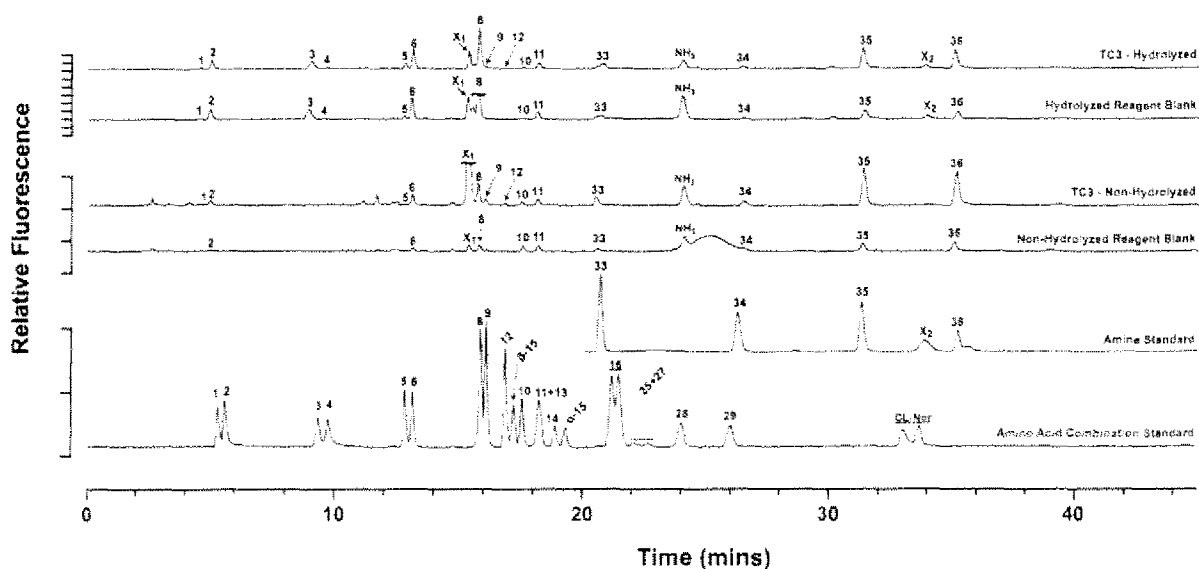


Fig. 3. The 0- to 45-min. region of representative HPLC-FD chromatograms from the SIO analyses showing amino acid and amine peak identifications in the procedural reagent blanks and Almahata Sitta (TC₃) acid hydrolyzed (total) and non-hydrolyzed (free) water extracts, and the authentic standards after pre-column derivatization with OPA/NAC for 1-minute. Chromatogram attenuations relative to the acid hydrolyzed extracts are 4x for the non-hydrolyzed and 8x for the standards, represented by scale bar graduations. Chromatograms from the 15-minute derivatizations showed similar results and are available upon request. (ANDREW and ERIC: please complete the details for the HPLC-FD separation conditions used at SIO, similar to caption in Figs. 1 and 2). Primary amines are labeled according to the designations in Table 1. NH₃ = residual ammonia from NH₄OH carried through the desalting process; X_N = unidentified primary amines.

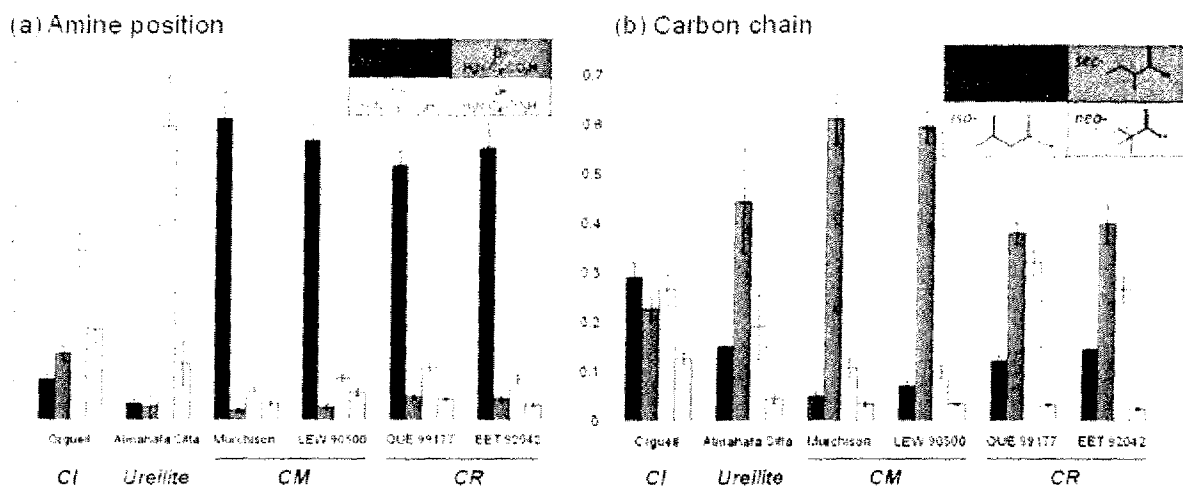


Fig. 4. The relative molar abundances of the 5-carbon amino acids in Almahata Sitta compared to several other carbonaceous meteorites as a function of (a) amine position (α -, β -, γ -, and δ -) and (b) valeric acid carbon chain structure (*n*-, *sec*-, *iso*-, and *neo*-) normalized to the total number of possible structures. It is apparent from the data that there is structural similarity in C_5 amino acid abundances within a meteorite class and between classes. 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 meteorites.

TABLES 1-4

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- <i>n</i> -butyric acid (GABA)	30	D-2-aminopentanoic acid (D-norvaline)
13	D- β -amino- <i>n</i> -butyric acid (D- β -ABA)	31	L-2-aminopentanoic acid (L-norvaline)
14	L- β -amino- <i>n</i> -butyric acid (L- β -ABA)	32	ϵ -amino- <i>n</i> -caproic acid (EACA)
15	α - or β -aminoisobutyric acid (AIB)	33	ethanolamine (ETA)
16	D,L- α -amino- <i>n</i> -butyric acid (D,L- α -ABA)	34	methylamine (MA)
17	3-amino-2,2-dimethylpropanoic acid	35	ethylamine (EA)
18	D,L-4-aminopentanoic acid	36	isopropylamine (IPA)
X	Desalting or non-fluorescent artifact	I.S.	D,L-norleucine internal standard

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

	Amine Compound	Almahata Sitta	
		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*	1.7 ± 0.1	5.0 ± 0.5
	EACA	3.6 ± 1.8	< 4
	Total Amino Acids	52 ± 7	161 ± 49
Amines	ETA	19 ± 1	21 ± 1
	MA	11 ± 1	13 ± 1
	EA	76 ± 5	105 ± 8
	IPA	84 ± 10	149 ± 17
	Total Amines	190 ± 17	288 ± 27

^aAll values are reported in parts-per-billion (ppb) on a bulk sample basis. 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 70-80% for the meteorite extracts). The uncertainties (δx) are based on the standard deviation of the average value of three to four separate measurements (n) with a standard error, $\delta x = \sigma_x \cdot (n-1)^{-1/2}$. For all UV fluorescence data, co-eluting peaks and/or compounds with interfering peaks were not included in the average. Upper limits are shown for amino acids that were not detected above procedural blank background levels.

*Enantiomers could not be separated under the chromatographic conditions.

Table 3. Summary of the average abundances of the 5-carbon α -, β -, γ -, and δ -amino acids in the non-hydrolyzed (free) and 6M HCl acid-hydrolyzed (total), hot-water extracts of the Almahata Sitta meteorite^a.

C ₅ Amino Acid Detected	Almahata Sitta
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		Free (ppb)	Total (ppb)
α	D-norvaline (D-2-apa)	< 0.3	0.7 \pm 0.1
	L-norvaline (L-2-apa)	< 0.2	0.7 \pm 0.1
	D-isovaline (D-2-a-2-mba)	0.6 \pm 0.1	1.3 \pm 0.1
	L-isovaline (L-2-a-2-mba)	0.7 \pm 0.1	1.4 \pm 0.1
	D-valine (D-2-a-3-mba)	0.3 \pm 0.1	0.5 \pm 0.1
	L-valine (L-2-a-3-mba)	1.4 \pm 0.3	1.3 \pm 0.5
β	D,L-3-apa [†]	0.4 \pm 0.1	1.1 \pm 0.2
	D,L- and allo-3-a-2-mba [‡]	< 0.1	< 0.1
	3-a-3-mba [‡]	< 0.4	< 3
	3-a-2,2-dmpa	0.8 \pm 0.1	1.8 \pm 0.2
	D,L-3-a-2-epa [†]	< 0.8	< 2
γ	D,L-4-apa [†]	0.8 \pm 0.1	15 \pm 2
	D,L-4-a-2-mba [†]	2.6 \pm 0.2	65 \pm 8
	D,L-4-a-3-mba [†]	1.5 \pm 0.5	18 \pm 3
δ	5-apa	0.9 \pm 0.1	6.3 \pm 2.1
Total C₅ Amino Acids		10 \pm 2	113 \pm 17

^aAll values are reported in parts-per-billion (ppb) on a bulk sample basis. 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 \pm 0.02) 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 above procedural blank background levels.

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

[‡]Enantiomers were separated but could not be identified due to the lack of optically pure standards.

[‡]3-amino-3-methylbutanoic acid (3-a-3-mba) co-elutes 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.

Table 4. Summary of the amino acid enantiomeric ratios in the hot-water extracts of the Almahata Sitta meteorite^a.

Amino Acid	Enantiomeric ratio (D/L)	
	DFAA	THAA
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. ^c	1.00

^aD/L ratios calculated from the amino acid concentrations reported in Table 2 and Table 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.

^bNonprotein amino acid

^cb.d. = below detection.

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