The amino acid composition of the Sutter's Mill CM2 carbonaceous chondrite

Aaron S. BURTON[1]*, Daniel P. GLAVIN[2], Jamie E. ELSILA[2], Jason P. DWORKIN[2],
Peter JENNISKENS[3,4], and Qing-Zhu YIN[5]

[1]NASA Johnson Space Center, 2101 Space Center Parkway, Houston, Texas 77058, USA
[2]NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, Maryland 20771, USA
[3]SETI Institute, 189 Bernardo Avenue, Mountain View, California 94043, USA
[4]NASA Ames Research Center, Moffett Field, California 94035, USA
[5]Department of Earth and Planetary Sciences, University of California at Davis, Davis, California 95616, USA
*Corresponding author. E-mail: aaron.s.burton@nasa.gov

Abstract–We determined the abundances and enantiomeric compositions of amino acids in Sutter's Mill fragment #2 (designated SM2) recovered prior to heavy rains that fell April 25–26, 2012, and two other meteorite fragments, SM12 and SM51, that were recovered postrain. We also determined the abundance, enantiomeric, and isotopic compositions of amino acids in soil from the recovery site of fragment SM51. The three meteorite stones experienced terrestrial amino acid contamination, as evidenced by the low D/L ratios of several proteinogenic amino acids. The D/L ratios were higher in SM2 than in SM12 and SM51, consistent with rain introducing additional L-amino acid contaminants to SM12 and SM51. Higher percentages of glycine, β-alanine, and γ-amino-*n*-butyric acid were observed in free form in SM2 and SM51 compared with the soil, suggesting that these free amino acids may be indigenous. Trace levels of D+L-β-aminoisobutyric acid (β-AIB) observed in all three meteorites are not easily explained as terrestrial contamination, as β-AIB is rare on Earth and was not detected in the soil. Bulk carbon and nitrogen and isotopic ratios of the SM samples and the soil also indicate terrestrial contamination, as does compound-specific isotopic analysis of the amino acids in the soil. The amino acid abundances in SM2, the most pristine SM meteorite analyzed here, are approximately 20-fold lower than in the Murchison CM2 carbonaceous chondrite. This may be due to thermal metamorphism in the Sutter's Mill parent body at temperatures greater than observed for other aqueously altered CM2 meteorites.

INTRODUCTION

The fall of the Sutter's Mill (SM) meteorites was observed on April 22nd, 2012 (Jenniskens et al. 2012). Detection of the falling meteorites by Doppler weather radar enabled a quick recovery of three stones prior to an impending rainstorm (SM1–SM3). Over the course of the next few months, 74 additional stones were collected (SM4–SM78; one stone recovered and originally designated SM5 was not a meteorite), totaling nearly 1 kg of recovered mass. On the basis of petrography, whole-rock chemistry, O, Os, and Cr isotopic compositions, and evidence of varying degrees of aqueous and thermal metamorphism, the SM meteorites were classified as CM2 carbonaceous chondrites (Jenniskens et al. 2012). In general, CM2 carbonaceous chondrites are very rich in soluble organics, and have been found to contain a diverse suite of soluble organic compounds, including hydrocarbons (Kvenvolden et al. 1970; Cronin and Pizzarello 1990); alcohols (Jungclaus et al. 1976), carboxylic acids (Yuen and Kvenvolden 1973; Cronin et al. 1993), amino acids (Kvenvolden et al. 1970; Cronin and Moore 1971), hydroxy acids (Peltzer and Bada 1978; Pizzarello et al. 2010), and sugar acids (Cooper et al. 2001); and nucleobases (Vandervelden and Schwartz 1977; Martins et al. 2008; Callahan et al. 2011).

The amino acid compositions of a variety of carbonaceous chondrites, in particular the CMs, have been studied extensively because these prebiotic

molecules are essential components of life as the monomers of proteins. Measurements of the abundances and enantiomeric and isotopic compositions of amino acids in meteorites have yielded valuable insights into the parent body chemistry that produces these compounds, as well as informing us about the degree of terrestrial contamination that a meteorite has experienced (Burton et al. [2012b] and references therein).

With the extensive catalog of amino acid research on CM2 carbonaceous chondrites in mind, we determined the amino acid contents of three Sutter's Mill meteorites, SM2, SM12, and SM51, for comparison with similar data we previously obtained on a variety of CM carbonaceous chondrites, as well as CR, CI, CV, CO, CH, and CB carbonaceous chondrites that span alteration types 1–3 and the C2 (ungrouped) Tagish Lake meteorite (Glavin et al. 2010b, 2012; Herd et al. 2011; Burton et al. 2012a, 2013; Elsila et al. 2012a). The amino acid abundance and enantiomeric composition measurements were made by ultrahigh-performance liquid chromatography with UV-fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS). In addition, we performed similar analyses on a sample of terrestrial soil collected near the recovery site of SM51. The high abundances of several amino acids in the soil sample also permitted us to measure their compound-specific $\delta^{13}C$ and $\delta^{15}N$ values by gas chromatography with mass spectrometry and isotope ratio mass spectrometry (GC-MS/IRMS). Finally, we performed bulk carbon and nitrogen analyses of the three SM samples and the recovered soil using elemental analysis-isotope ratio mass spectrometry (EA-IRMS). The results are presented herein.

MATERIALS AND METHODS

Chemicals and Reagents

To remove organic residue, sample-handling tools, porcelain mortars and pestles (CoorsTek), and glassware were all rinsed with Millipore Milli-Q Integral 10 (18.2 MΩ, <3 parts-per-billion [ppb] total organic carbon) ultrapure water (hereafter "water"), wrapped in aluminum foil, and heated in air at 500 °C for 18–24 h (hereafter "clean"). Chemicals used in this study were purchased from Fisher Scientific, Sigma-Aldrich, or Acros Organics. Details on the sources of specific acyclic aliphatic five-carbon (C_5) mono-amino mono-acids used as standards were published previously (Glavin and Dworkin 2009). To prepare standard solutions for LC-FD/ToF-MS analysis, individual compounds were dissolved in water and then combined to enable their measurement in a single chromatographic separation. Solutions of sodium borate

were prepared from solid sodium tetraborate powder (Sigma Ultra 99.5–100% purity) that had been pyrolyzed in air at 500 °C for 3 h to remove any organic contaminants prior to dissolution in water. All other solutions were prepared as described by Glavin et al. (2006).

Meteorite Samples and Controls

For this study, we analyzed three fragments of the Sutter's Mill meteorite, SM2 (146.1 mg), SM12 (167.1 mg), and SM51 (106.7 mg), as well as a soil sample (189.1 mg) collected at the recovery site of SM51 in Coloma, California. For comparison, we also extracted a sample of the Murchison meteorite (126.8 mg, USNM5453). Prerain SM2 fell on an asphalt surface at a parking lot and experienced postfall fracturing. It was collected with unsterilized aluminum foil. Postrain SM12 (fully crusted) was recovered stuck with its narrow side a few mm in muddy soil in a horse pasture. After brief handling, this sample was also collected in unsterilized aluminum foil. Both SM2 and SM12 were stored in a freezer, wrapped in foil, in a clean jar with inorganic desiccant. SM51 was handled by the finder.

Meteorite fragments were crushed into a powder using a clean mortar and pestle in a Class 100 laminar flow hood (AirClean Systems) under HEPA-filtered positive pressure. Procedural blanks and serpentine control samples (170.0 mg, processed with SM2; and 126.7 mg, processed with SM12 and SM51) that had been heated in air at 500 °C for 3 h prior to extraction were processed in parallel with the meteorite samples.

Extraction Procedures and Analytical Techniques

The powdered meteorite samples and controls were flame-sealed in clean glass ampoules with 1 mL of water and the sealed ampoules placed inside an oven set at 100 °C. After the 24 h extraction, the tubes were cooled and centrifuged at approximately 1700 RPM under ambient pressure for 5 min (Labconco Centrivap) to separate solid particulate matter from the water supernatant. Half of the water extract was dried under vacuum and subjected to acid-vapor hydrolysis (6 M HCl) at 150 °C for 3 h to liberate amino acids in bound or precursor forms. The remaining unhydrolyzed water extract (containing free amino acids only) and the HCl-hydrolyzed extract (containing free and acid labile amino acids) were dried separately under vacuum (Labconco Centrivap) and redissolved in 1 mL of water. Both HCl-hydrolyzed and unhydrolyzed extracts were desalted by cation exchange chromatography using prepacked columns from BioRad (AG-50W X8 resin,
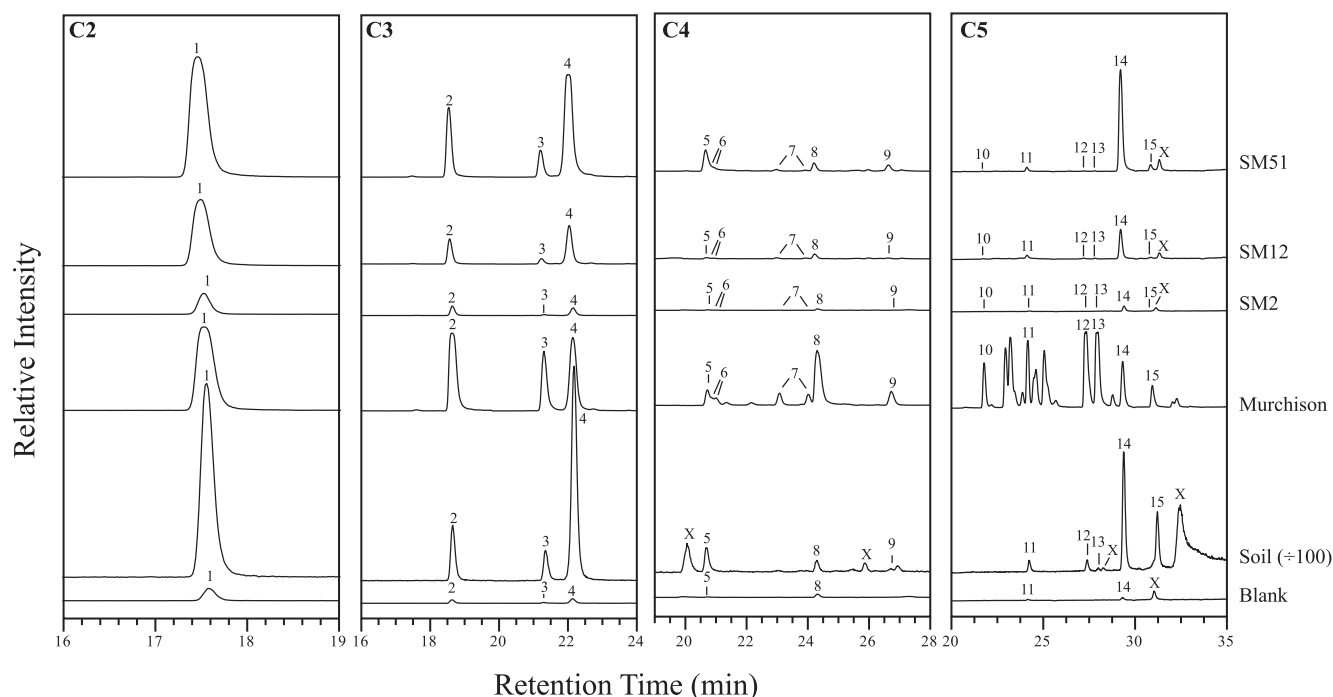
Fig. 1. Representative liquid chromatography-mass spectrometry chromatograms for the acid-hydrolyzed meteorite and soil samples analyzed in this study. Single-ion chromatograms are shown for the C2, C3, C4, and C5 primary, aliphatic, acyclic amino acids (derivatized positive ionization mass-to-charge ratios of 337.0859, 351.1015, 365.1171, and 379.1328, respectively). The masses plotted represent an approximately 0.07 Da window (the peak width at half maximum) centered around the corresponding theoretical mono-isotopic masses of the mono-protonated positive ions of C2–C5 OPA/NAC amino acid derivatives and are all set to the same scale; in the C4 and C5 traces, peaks have been scaled by the factors given after each sample name. Chromatograms of Murchison, an aqueously altered CM2 carbonaceous chondrite, have been included for comparison. Peak numbers correspond to amino acid assignments in Table 1; the "X" denotes a nonfluorescent (nonamino acid) contaminant. Similar chromatograms were obtained for the nonhydrolyzed fractions. The chromatographic conditions were column temperature, 30 °C; flow rate, 150 μL min^{-1}; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol). The following gradient was used: gradient, time in minutes (%B): 0 (0), 35 (55), 45 (100).

100–200 mesh), and their NH$_4$OH eluates derivatized with o-phthaldialdehyde/N-acetyl-L-cysteine (OPA/NAC) prior to LC-FD/ToF-MS analysis as previously described (Glavin et al. 2006). An internal standard (D,L-norleucine) was added to each sample immediately prior to desalting to estimate the desalting and derivatization recovery of amino acids in each sample. These values were used to correct for the reported amino acid abundances in Table 1.

OPA/NAC amino acid derivatives were analyzed by LC-FD/ToF-MS using a Waters ACQUITY ultrahigh-performance liquid chromatograph and a Waters ACQUITY fluorescence detector connected in series to a Waters LCT Premier ToF-MS. OPA/NAC derivatives were separated using a Waters BEH C18 column (2.1 × 50 mm, 1.7 μm particle size) followed by a Waters BEH phenyl column (2.1 × 150 mm, 1.7 μm particle size) with gradients optimized for C2–C4 amino acid analysis (Glavin et al. 2010b) or focusing on separation of the C5 amino acids and enantiomers only (Glavin and Dworkin 2009) as previously described.

The electrospray and mass spectrometer conditions have been described by (Glavin et al. 2006). As in related studies, amino acids in the meteorite and control samples were identified by correlating sample compounds with known amino acid standards using the masses of the OPA/NAC amino acid derivatives and chromatographic retention times using both mass and fluorescence detection, as shown in Fig. 1.

Terrestrial Amino Acid Carbon and Nitrogen Isotopic Measurements by GC-MS/IRMS

Several amino acids in the soil were sufficiently abundant to permit determination of their compound-specific $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios. Compound-specific isotopic analyses of amino acids in the SM meteorite samples were not possible due to low abundances. Roughly 10% of the SM51 recovery site soil extract was used for LC-FD/ToF-MS analysis and the remaining 90% was used for GC-MS/IRMS. Due to differences in sensitivity for nitrogen and carbon as well as the lower

Table 1. Summary of the average abundances (in nmol g^{-1}) of identified two- to six-carbon amino acids in the nonhydrolyzed (free) and 6 M HCl-hydrolyzed (total = free + bound) hot water extracts of three different fragments of the Sutter's Mill meteorite, a terrestrial soil sample from the recovery site of SM51, and the Murchison meteorite measured by LC-FD/TOF-MS[a]. Numbers in parentheses following compound abbreviations correspond to labeled peaks in Fig. 1.

Amino acid[b]	SM2		SM12		SM51		Soil		Murchison	
	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total
D-Aspartic acid (D-Asp)	0.10 ± 0.08	0.20 ± 0.04	0.02 ± 0.01	0.24 ± 0.05	0.31 ± 0.09	2.27 ± 0.14	8.6 ± 4.6	133 ± 22	0.20 ± 0.03	1.1 ± 0.2
L-Aspartic acid (L-Asp)	0.12 ± 0.01	0.44 ± 0.04	0.02 ± 0.01	0.92 ± 0.11	4.27 ± 0.40	8.48 ± 1.08	55.2 ± 15.9	420 ± 42	0.35 ± 0.05	2.5 ± 0.3
D-Glutamic acid (D-Glu)	<0.01	0.20 ± 0.05	0.01 ± 0.01	0.46 ± 0.03	0.57 ± 0.05	3.18 ± 0.49	11.8 ± 2.7	100 ± 12	0.21 ± 0.02	3.6 ± 0.5
L-Glutamic acid (L-Glu)	0.03 ± 0.01	0.76 ± 0.02	0.05 ± 0.01	2.78 ± 0.16	2.70 ± 0.16	16.5 ± 5.7	54.1 ± 9.8	360 ± 58	0.40 ± 0.12	4.7 ± 0.7
D-Serine (D-Ser)	<0.03	0.05 ± 0.01	0.02 ± 0.02	0.04 ± 0.01	0.27 ± 0.04	0.44 ± 0.05	3.9 ± 1.4	35.9 ± 5.0	0.20 ± 0.04	0.60 ± 0.12
L-Serine (L-Ser)	<0.03	1.06 ± 0.11	0.08 ± 0.03	1.57 ± 0.02	1.71 ± 0.07	8.73 ± 1.67	72.3 ± 32.6	213 ± 22	0.29 ± 0.12	1.2 ± 0.2
Glycine (Gly; 1)	0.96 ± 0.19	2.26 ± 0.27	0.04 ± 0.01	2.96 ± 0.76	3.72 ± 0.39	12.8 ± 3.1	111 ± 20	624 ± 189	13.2 ± 2.7	30.1 ± 6.3
D-Threonine (D-Thr)	<0.03	<0.07	<0.03	<0.03	<0.04	0.07 ± 0.00	<0.01	0.22 ± 0.20	nd	nd
L-Threonine (L-Thr)	<0.03	<0.07	<0.03	0.66 ± 0.08	1.20 ± 0.11	5.83 ± 0.81	27.2 ± 10.1	246 ± 93	nd	nd
β-Alanine (β-Ala; 2)	0.21 ± 0.12	0.51 ± 0.18	0.03 ± 0.01	0.53 ± 0.04	1.22 ± 0.08	2.04 ± 0.33	28.6 ± 3.9	140 ± 27	6.12 ± 1.29	15.5 ± 3.3
γ-amino-n-butyric acid (γ-ABA; 5)	0.03 ± 0.01	0.06 ± 0.03	0.02 ± 0.01	0.38 ± 0.30	5.70 ± 1.27	5.98 ± 1.74	22.2 ± 3.9	65.8 ± 10.9	2.42 ± 0.62	9.5 ± 1.7
D-Alanine (D-Ala; 3)	<0.02	0.21 ± 0.18	0.03 ± 0.03	0.19 ± 0.03	0.42 ± 0.11	1.13 ± 0.12	12.6 ± 1.1	121 ± 20	4.74 ± 1.02	9.4 ± 1.7
L-Alanine (L-Ala; 4)	<0.02	0.39 ± 0.08	0.07 ± 0.01	1.20 ± 0.15	4.44 ± 0.34	8.00 ± 1.74	100 ± 21	671 ± 173	4.89 ± 1.34	10.5 ± 2.1
D-β-amino-n-butyric acid (D-β-ABA; 7)	<0.02	<0.05	<0.02	0.02 ± 0.01	0.04 ± 0.02	0.03 ± 0.01	0.82 ± 0.34	1.1 ± 0.06	0.76 ± 0.10	2.2 ± 0.2
L-β-amino-n-butyric acid (L-β-ABA; 7)	<0.02	<0.05	<0.02	0.02 ± 0.01	0.03 ± 0.02	0.03 ± 0.01	0.95 ± 0.51	1.1 ± 0.64	2.42 ± 0.62	9.5 ± 1.7
α-aminoisobutyric acid (α-AIB; 8)	<0.02	<0.05	<0.02	<0.02	0.11 ± 0.03	<0.03	0.89 ± 0.54	8.7 ± 6.7	51.1 ± 13.9	56.4 ± 2.4

Table 1. *Continued.* Summary of the average abundances (in nmol g^{-1}) of identified two- to six-carbon amino acids in the nonhydrolyzed (free) and 6 M HCl-hydrolyzed (total = free + bound) hot water extracts of three different fragments of the Sutter's Mill meteorite, a terrestrial soil sample from the recovery site of SM51, and the Murchison meteorite measured by LC-FD/TOF-MSa. Numbers in parentheses following compound abbreviations correspond to labeled peaks in Fig. 1.

Amino acid[b]	SM2		SM12		SM51		Soil		Murchison	
	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total
DL-β-aminoisobutyric acid[c] (D,L-β-AIB; 6)	<0.02	~0.02[d]	<0.04	~0.02[d]	<0.04	~0.04[d]	<0.01	<0.01	nd	nd
DL-α-amino-*n*-butyric acid[c] (α-ABA; 9)	<0.02	<0.03	<0.02	0.01 ± 0.01	0.05 ± 0.02	0.21 ± 0.16	<0.01	5.4 ± 4.0	1.95 ± 0.64	7.2 ± 0.6
D-isovaline (D-Iva; 12)	<0.02	<0.07	<0.03	<0.03	<0.03	<0.03	1.2 ± 0.8	9.4 ± 3.9	27.2 ± 6.2	30.8 ± 4.1
L-isovaline (L-Iva; 13)	<0.02	<0.05	<0.03	<0.03	<0.04	<0.04	0.2 ± 0.1	1.9 ± 1.0	33.2 ± 6.8	35.6 ± 5.3
3-amino-2,2-dimethylpropanoic acid (3-A-2,2-DMPA; 10)	<0.01	<0.02	<0.03	<0.02	<0.04	<0.03	0.05 ± 0.04	0.04 ± 0.03	nd	1.7 ± 0.1[e]
δ-amino-*n*-valeric acid (δ-AVA; 11)	<0.02	~0.06[c]	<0.03	0.06 ± 0.03	0.05 ± 0.01	0.13 ± 0.05	3.0 ± 0.64	13.5 ± 1.8	nd	2.9 ± 0.5[e]
ε-amino-*n*-caproic acid (ε-ACA)	0.02 ± 0.01	0.74 ± 0.20	0.03 ± 0.03	1.50 ± 0.65	0.11 ± 0.02	1.65 ± 0.55	3.0 ± 1.9	5.2 ± 1.0	0.83 ± 0.19	5.0 ± 1.7
D-Valine (D-Val; 15)	<0.03	<0.10	<0.03	0.14 ± 0.08	0.33 ± 0.19	0.38 ± 0.08	4.4 ± 4.1	11.4 ± 0.4	0.71 ± 0.17	2.0 ± 0.6
L-Valine (L-Val; 14)	<0.03	0.32 ± 0.09	<0.04	0.90 ± 0.05	1.88 ± 0.30	7.10 ± 1.43	29.1 ± 2.4	304 ± 104	1.17 ± 0.24	3.9 ± 0.7
Total amino acids	1.9 ± 0.2	7.8 ± 0.5	0.7 ± 0.1	14.7 ± 1.1	29.3 ± 1.5	85.1 ± 7.4	570 ± 50	3,550 ± 300	152 ± 17	241 ± 11
% free	24%		5%		34%		16%		63%	

[a]Sutter's Mill meteorite fragments and terrestrial soil from the fall location of SM51 were analyzed by OPA/NAC derivatization (15 min) and UPLC separation with UV fluorescence and time-of-flight mass spectrometry (TOF-MS) detection. For the LC-FD/TOF-MS data, the fluorescence peaks and the mono-isotopic masses of each protonated OPA/NAC amino acid derivative (M + H^{+}) were 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. The final values were normalized using the desalting and derivatization recoveries of an internal D,L-norleucine standard (recoveries ranged from 60 to 100% for the meteorite extracts). The uncertainties (δx) are based on the standard deviation of the average value of three separate measurements (n) with a standard error, $\delta x = \sigma_x \cdot (n-1)^{-1/2}$. nd = not determined.

[b]Abbreviations used in the text are given in parentheses.

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

[d]Tentatively detected above blank levels.

[e]Values from Glavin et al. (2010b).

relative abundance of nitrogen to carbon in amino acids, approximately 80% of the fraction allocated for GC-MS/IRMS analysis was used for the $^{15}N/^{14}N$ measurements, and the balance used for $^{13}C/^{12}C$ measurements. The extract was dried under vacuum (Labconco CentriVap), esterified with isopropanol, and the isopropyl esters reacted with trifluoroacetic anhydride (TFAA) using established methods (Elsila et al. 2009). The TFAA/IPA amino acid derivatives were dissolved in 5 μL of ethyl acetate (Fisher Chemical, Optima Grade).

The $\delta^{13}C$ values of the TFAA/isopropanol-derivatized samples were measured by GC-MS/IRMS, with triplicate injections of 1 μL aliquots of derivatized extracts into a Thermo Trace GC outfitted with a 5 m base-deactivated fused silica guard column (Restek, 0.25 mm ID) and four 25 m Chirasil L-Val columns (Varian, 0.25 mm ID) connected using Press-Tight connectors (Restek). The GC conditions are previously described (Elsila et al. 2011). The GC output is split, with approximately 10% directed into a Thermo DSQII electron-impact quadrupole mass spectrometer that provides mass and structural information for each eluting peak. The remaining approximately 90% passes through a Thermo GC-C III interface, where eluting compounds are oxidized and reduced to carbon dioxide and nitrogen gas, which then pass into a Thermo MAT 253 isotope ratio mass spectrometer (IRMS) for $\delta^{13}C$ or $\delta^{15}N$ measurement. For $\delta^{15}N$ analysis, a liquid nitrogen trap is used to remove CO_2 from the gas stream prior to entry into the IRMS.

Standard solutions of amino acids were used to verify compound identification. Isotopic values were calibrated with working standards of L-alanine, CO_2, and N_2 as described previously (Elsila et al. 2012a). The $\delta^{13}C$ values of the underivatized amino acid standards were measured on a Costech ECS 4010 combustion elemental analyzer (EA) connected through a Thermo Conflo III interface to the IRMS to allow correction of the carbon added by the derivatization process; the final $\delta^{13}C$ values of the amino acids in the samples and their precision were calculated as described elsewhere (Elsila et al. 2012a). Isotopic values are reported only for those peaks in which no coelutions were detected, as indicated by the absence of additional mass fragments in the sample compared with the standard (Fig. 2).

Bulk Material Isotopic Measurements

We measured bulk $\delta^{13}C$ and $\delta^{15}N$ values for the three SM samples and the SM51 recovery site soil sample by EA-IRMS. For the soil, three aliquots (7–8.5 mg) were weighed in separate tin cups and analyzed on the EA-IRMS as described previously for the SM samples (Jenniskens et al. 2012). 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. Errors are standard deviations for triplicate measurements. 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.

RESULTS AND DISCUSSION

Amino Acid Analyses

We searched for a suite of several proteinogenic amino acids and simple, two- to five-carbon acyclic mono-amino alkanoic and alkanedioic acids (their names, abbreviations, and abundances are given in Table 1). For chiral (handed) amino acids, we have reported the abundances of individual enantiomers where sufficient chromatographic separation was achieved; representative chromatograms for these analyses are given in Fig. 1. In general, the presence of a relatively high abundance (>40%) of free amino acids compared with the total abundance is common for indigenous amino acids in CM and CR chondrites (Glavin et al. 2006; Botta et al. 2007; Pizzarello et al. 2008), in contrast with amino acids from terrestrial sources that are typically bound as proteins and therefore have a much lower ratio of free to total amino acids. The SM meteorites contained a much lower percentage of free amino acids than the Murchison meteorite, a CM2 chondrite known to contain indigenous amino acids. Free amino acids ranged from 5% to 34% of the total amino acids in the SM samples compared to 63% for the Murchison sample and 16% for the soil sample. This implies that terrestrial contamination of the Sutter's Mill meteorites has occurred, particularly for SM12, which has just 5% of its amino acids present as free compounds. However, elevated free abundances of the individual amino acids Gly and β-Ala in SM2 and SM51 are more similar to the relative free amino acid abundances observed in Murchison than to the abundances in the local soil (Table 2), suggesting that there could be an extraterrestrial contribution. Confirmation of the indigenous nature of these amino acids might be achieved through compound-specific isotope ratio measurements; however, these measurements generally require relatively large amounts of sample that are not currently feasible. For example, current technology requires approximately 1 nmol of a given amino acid for $\delta^{13}C$ measurements, approximately
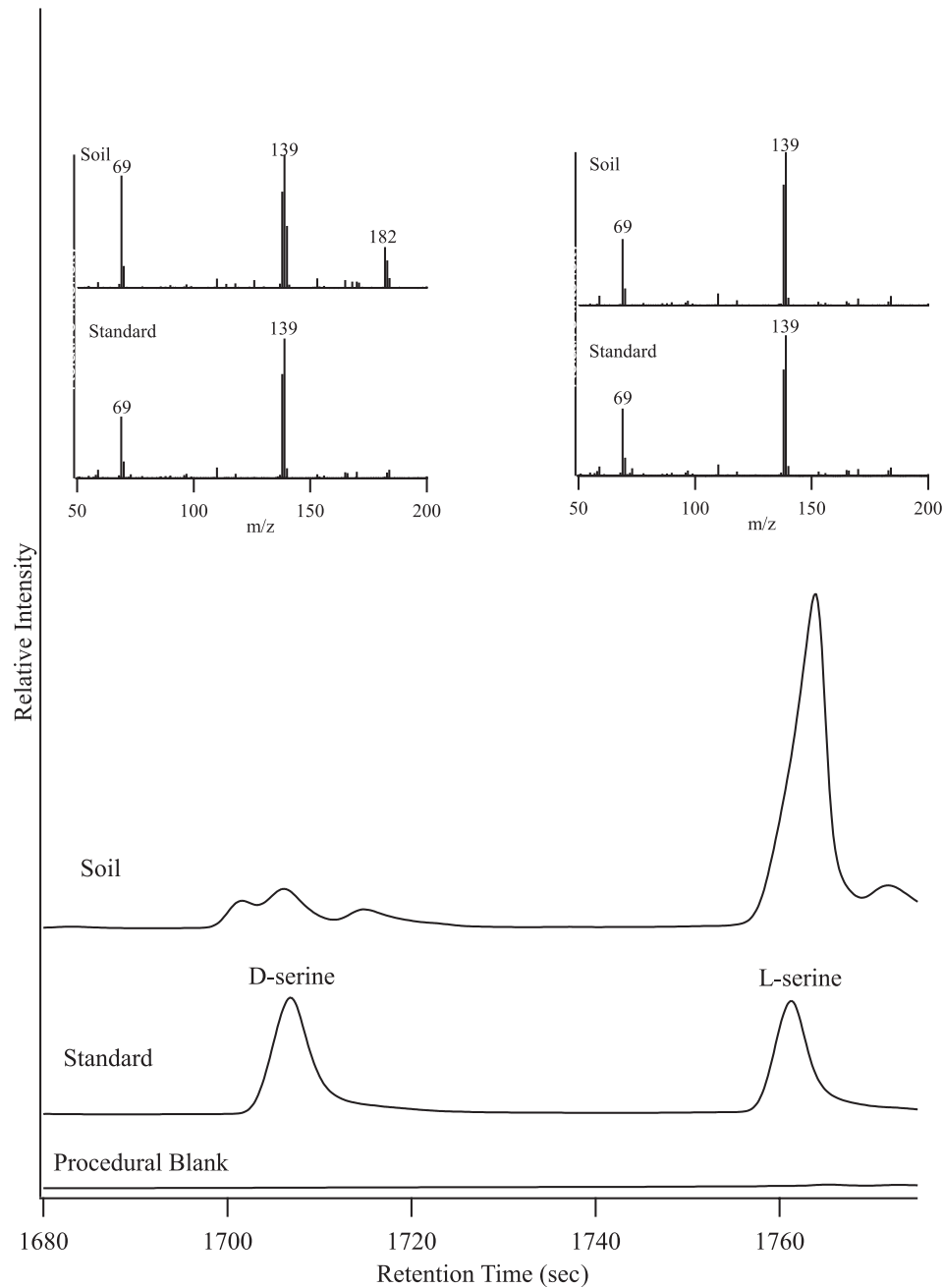
Fig. 2. Gas chromatography separation and mass spectrometry analysis of D- and L-serine in the TFAA/IPA-derivatized hydrolyzed extract of the Sutter's Mill soil, the procedural blank, and a standard. The bottom trace show the m/z 44 ($^{12}CO_2$) peak produced and measured from GC-IRMS for the peaks assigned to D- and L-serine. The upper inset traces show the simultaneously collected mass spectral fragmentation pattern for these peaks in the soil and standard. The D-serine mass spectrum clearly reveals the presence of a coeluting compound with mass fragment 182, preventing isotopic analysis.

3 nmol for δD measurements, and approximately 6 nmol for $δ^{15}N$. In the case of SM2, approximately 0.5 g (of 4.0 g in total recovered) would need to be extracted to get 1 nmol of glycine, the most abundant amino acid in SM2. Fortunately, there are other indicators that can help address the indigenous nature of amino acids extracted from the SM meteorites.

The chiral distribution of amino acids commonly found in biology can also help us assess whether these compounds are indigenous to the meteorite or are the result of terrestrial contamination. Biology shows a strong preference for L-amino acids because D-amino acids are not used in proteins. In contrast, abiotic amino acid–forming reactions produce roughly equal

Table 2. Free-to-total ratios of potentially extraterrestrial amino acids.

Amino acid	SM2 (%)	SM12 (%)	SM51 (%)	Murchison (%)	Soil (%)
Gly	42	1	29	44	18
β-Ala	41	6	61	39	20
γ-ABA	50	11	95	26	34

amounts of D- and L-amino acids. As a result, the D/L ratio of proteinogenic amino acids extracted from meteorites provides a qualitative indication of the extent of terrestrial contamination that a meteorite has experienced; values of approximately 1 indicate an essentially uncontaminated sample and, in the absence of compelling evidence to the contrary, values less than 1 suggest increasing contamination. In the case of the Sutter's Mill meteorites analyzed here, the D/L ratios for Asp, Glu, Ser, Thr, Ala, and Val are all generally very low, ranging from 0.02 to 0.54, compared to 0.44–0.87 for these same amino acids in the Murchison meteorite (Table 3). For both SM12 and SM51, the D/L ratios are virtually indistinguishable from the corresponding amino acids in the recovery site soil. We note that these two meteorite stones were recovered a week and 10 days postfall, respectively, after a period of heavy rains (Jenniskens et al. 2012). The D/L ratios for SM2, which was found in a parking lot 2 days after the fall, prior to the rain, and collected with aluminum foil to minimize contamination, are higher, particularly for Asp and Ala, suggesting that this stone experienced less contamination than did SM12 and SM51. Taken together, the amino acid data suggest that the rain played a role in the increased levels of terrestrial contamination observed in SM12 and SM51. This hypothesis is further supported by the increase in total amino acids among the three meteorites that is positively correlated with the amount of time they spent on the ground prior to recovery. The elevated D/L ratios for some proteinogenic amino acids in SM2 above the levels of the soil suggest that at least some fraction of these compounds could be indigenous to the meteorite. We should point out that there are cases where proteinogenic amino acids with L-excesses in meteorites have been classified as indigenous: we recently reported an indigenous L-excess of 45–59% for aspartic acid in the Tagish Lake meteorite based on indistinguishable δ^{13}C isotopic values for D- and L-aspartic acid that were unambiguously extraterrestrial (Glavin et al. 2012); and Pizzarello and coworkers concluded that L-isoleucine excesses were indigenous in a suite of 8 CR chondrites based on experimental and theoretical considerations (Elsila et al. 2012b; Pizzarello and Monroe 2012; Pizzarello et al. 2012). In the absence of compelling

evidence (e.g., compound-specific isotopic data) in support of an extraterrestrial origin for the proteinogenic amino acids in the Sutter's Mill meteorites, however, the most straightforward interpretation of the D/L ratios is that the proteinogenic amino acids are the result of terrestrial contamination. Unfortunately, as discussed above, confirmation of the indigenous nature of these compounds through compound-specific isotope ratio measurements would require sample masses not currently available for these types of analysis.

Another useful indicator that a meteorite contains indigenous amino acids is the presence of compounds that are not commonly found in the terrestrial biosphere, as many of these compounds can be observed even in the presence of terrestrial contamination. For example, comparing the C4 and C5 traces for the Murchison meteorite and the soil sample in Fig. 1 reveals a number of peaks corresponding to amino acids known to be extraterrestrial in origin in the Murchison sample that are not present in the soil. Thus, many indigenous compounds, if present, could still be identified in a contaminated sample despite the overprint of terrestrial amino acids. Trace levels of β-aminoisobutyric acid (DL-β-AIB; 0.02–0.04 nmol g^{-1}) were identified above background in all three acid-hydrolyzed hot water extracts of Sutter's Mill (Table 1), while β-AIB was not found in the terrestrial soil sample above 0.01 nmol g^{-1}. As β-AIB is rare on Earth, it is possible that this nonprotein amino acid is indigenous to the meteorite. The SM meteorites also contain trace amounts of several other nonproteinogenic amino acids that are less commonly found in nature, including α- and β-amino-n-butyric acid (α-, and β-ABA), α-aminoisobutyric acid (α-AIB), and ε-amino-n-caproic acid (ε-ACA). However, these compounds were also detected in the soil. Although the soil sample is not directly relevant to SM2 and SM12, which were collected a few km from SM 51, the presence of these amino acids in the soil from the SM51 collection site suggests that they may be present near the recovery sites of SM2 and SM12 as well. Because they are present in higher abundances in the soil than in SM51, it is more likely that these compounds were transferred from the soil to the meteorites than from the meteorites to the soil. In addition to α-AIB, the soil sample also contained isovaline (Iva). These two compounds are not found in translated proteins in biology, but do appear frequently in fungal peptide antibiotics (Brückner et al. 2009; Elsila et al. 2011). A fungal peptide origin for these compounds in the soil is consistent with significantly higher abundances in the bound form, as well as the D-excesses, as most fungal peptides contain either D-Iva exclusively or a mix of D- and L-Iva (Elsila et al. [2011] and references therein).

Table 3. D/L ratios for proteinogenic amino acids in meteorite samples in this study and in the Murchison meteorite.

Amino acid	SM2	SM12	SM51	Soil	Murchison USNM 5453
D/L aspartic acid	0.44 ± 0.09	0.26 ± 0.07	0.27 ± 0.04	0.24 ± 0.10	0.44 ± 0.09
D/L glutamic acid	0.26 ± 0.07	0.17 ± 0.01	0.19 ± 0.07	0.26 ± 0.07	0.76 ± 0.15
D/L serine	0.05 ± 0.01	0.02 ± 0.01	0.05 ± 0.01	0.08 ± 0.01	0.51 ± 0.15
D/L threonine	n.d.	<0.05	<0.01	<0.01	0.89 ± 0.24
D/L alanine	0.54 ± 0.47	0.16 ± 0.03	0.14 ± 0.03	0.13 ± 0.05	0.57 ± 0.20
D/L valine	<0.35	0.17 ± 0.10	0.06 ± 0.02	0.06 ± 0.01	0.87 ± 0.17

Comparing Sutter's Mill Amino Acids with Those of Other Meteorites

Perhaps the most interesting aspect of the amino acid analyses performed here is the generally low abundances of amino acids in the Sutter's Mill meteorites that are commonly found in other CM2 carbonaceous meteorites. SM2, the least contaminated of the SM meteorites analyzed here, contains <10 nmol g^{-1} of total amino acids. In comparison, in the CM2 meteorites Murchison and Murray over 80 amino acids have been identified with total amino acid abundances ranging from 15 to 60 ppm (150–600 nmol g^{-1} assuming an average amino acid molecular weight of 100 g mol^{-1}; Pizzarello et al. 2006; Glavin et al. 2010b), many of which are not found or are extremely rare on Earth. Similarly, Antarctic CM2s such as Lewis Cliffs (LEW) 90500 and Lonewolf Nunataks (LON) 94102 contain similar amino acid distributions in abundances ranging from 90 to 160 nmol g^{-1} (Glavin et al. 2010b). In addition, two of the most abundant amino acids in many CM2 chondrites, α-AIB and Iva (Glavin et al. 2006, 2010b), are virtually absent in all of the SM meteorites analyzed here (Fig. 1; compounds 8, 12, and 13).

While the SM meteorites experienced similar degrees of aqueous alteration as other CM2 chondrites, a feature that distinguishes the SM meteorites from other CM2 chondrites is their much higher metamorphic temperatures (150–400 °C; Jenniskens et al. 2012) within the parent body compared with the temperatures experienced by other CM2 chondrites, which were typically <50 °C (Zolensky et al. 1993; Krot et al. 2006). Most amino acids have solid-phase thermal decomposition temperatures ranging from approximately 200 to 600 °C (Rodante 1992), and a significant fraction (>50%) of the amino acids in the Murchison meteorite was destroyed when heated to temperatures above 200 °C in a laboratory experiment (Glavin and Bada 2001). We have previously observed that parent body composition and alteration conditions can have large effects on both the abundances and structural distributions of amino acids in meteorites. Nevertheless, meteorites that experienced primarily aqueous alteration (CI, CM, CR, and CH chondrites spanning types 1–3) and those that experienced primarily thermal metamorphism (CV, CO, ordinary chondrites, and ureilites) have all been shown previously to contain indigenous amino acids (Ehrenfreund et al. 2001; Martins et al. 2007; Pizzarello et al. 2008; Glavin et al. 2010a, 2010b; Burton et al. 2011, 2012a, 2013). Although it is difficult to estimate the fraction of amino acids in the SM meteorites that is indigenous, even if we ignore the potential terrestrial contamination and assume that all of the amino acid total for the least contaminated sample, SM2 (approximately 8 nmol g^{-1}), is indigenous, these levels are comparable to those observed in CV and CO chondrites and fragments of Almahata Sitta (Burton et al. 2011, 2012a), and an order of magnitude less than typically observed in a CM2 chondrite.

One explanation for the apparent lack of indigenous amino acids in the Sutter's Mill meteorites, then, is that the combination of aqueous alteration and thermal metamorphism in the parent body led to the destruction of any amino acids that may have been originally present. This hypothesis is most recently supported by the observation of the rapid decomposition of n-alkyl-α-amino acids through the loss of CO_2 and NH_3 by decarboxylation and deamination when heated to temperatures above 150 °C in the presence of water and minerals (McCollom 2013). While further work is needed, there could be significant implications for the survival of prebiotically relevant compounds in a variety of hydrothermal environments both in parent bodies and on Earth. These implications include perhaps a further limitation of the hospitality of thermally altered environments than has been previously discussed (e.g., Miller and Lazcano 1995).

Isotopic Analyses of Pyrolysis Products from Bulk Samples

We used EA-IRMS to measure the bulk $\delta^{13}C$ and $\delta^{15}N$ isotopic ratios of the terrestrial soil for comparison with our previous EA-IRMS analyses (Jenniskens et al. 2012) of the three SM samples. The

Table 4. Stable isotope values measured for bulk SM samples and recovery site soil as well as values for individual amino acids extracted from the soil.

Sample	Abundance C (wt%)	$\delta^{13}C$ (‰ VPDB)	Abundance N	$\delta^{15}N$ (‰ AIR)
Bulk SM2 meteorite[a]	1.32 ± 0.03	-13 ± 1	397 ± 7 ppm	$+16.7 \pm 0.3$
Bulk SM12 meteorite[a]	1.56 ± 0.01	$+2 \pm 3$	404 ± 29 ppm	-0.2 ± 0.6
Bulk SM51 meteorite[a]	1.62 ± 0.04	-2.8 ± 0.9	405 ± 8 ppm	$+6.2 \pm 0.4$
Bulk soil	6 ± 1	-21 ± 3	$0.4 \pm 0.1\%$	$+6 \pm 1$
Soil amino acids				
D-Ala		-24 ± 2		$+6 \pm 5$
L-Ala		-20 ± 2		$+7 \pm 4$
L-Ser		-8 ± 9		-3 ± 4
L-Val		-6 ± 1		$+1 \pm 5$
L-Asp		-21 ± 1		$+7 \pm 4$
L-Glu		-17 ± 4		$+12 \pm 2$
Gly		-15 ± 4		-5 ± 3
β-Ala		-27 ± 3		-12 ± 9
γ-ABA		-31 ± 3		[b]

[a]Values from Jenniskens et al. (2012).
[b]Not measurable due to low abundance.

bulk isotopic compositions of the three SM samples varied widely (Table 4). These variations may reflect differing levels of terrestrial contamination caused by length of exposure and differences in recovery sites. The $\delta^{13}C$ values for all three meteorite samples were measurably higher than those for the soil, implying the presence of indigenous C of extraterrestrial origin, although it may be mixed with terrestrial sources of C. Conversely, the $\delta^{15}N$ values for SM51 are indistinguishable within error from the values for the soil collected from the SM51 site, suggesting that either the predominant component of the indigenous N in the meteorite coincidentally has the same isotopic composition as that of the soil, or, more likely, that terrestrial N from soil contamination has overprinted any indigenous N signal. While other nitrogenous compounds may be important, this conclusion is in agreement with our finding that SM51 contains a significant amount of N-bearing amino acids probably of terrestrial origin as the measured value of +6‰ is also well within the range of $\delta^{15}N$ values we measured for individual amino acids in the soil (discussed in more detail below); the measured $\delta^{15}N$ value of -0.2‰ for SM12 suggests a similar interpretation. On the other hand, the $\delta^{15}N$ value of $+16.7$‰ for SM2 implies that there could be an indigenous N-bearing component, although amino acids of extraterrestrial origin are typically enriched in $\delta^{15}N$ to values of $+50$‰ or greater (Elsila et al. [2012a] and references therein).

Isotopic Analyses of Amino Acids in Terrestrial Soil

Compound-specific stable isotope ratios have proven invaluable in distinguishing amino acids of extraterrestrial origin from terrestrial amino acids. This is particularly true of amino acids in aqueously altered types 2–3 CM and CR chondrites, which show significant enrichment of the heavier isotopes ^{15}N, ^{13}C, and D (Engel et al. 1990; Engel and Macko 1997; Pizzarello et al. 2004, 2008; Pizzarello and Huang 2005; Martins et al. 2007; Pizzarello and Holmes 2009; Elsila et al. 2012a). Interpretation of these measurements from extraterrestrial samples requires comparisons with similar measurements of amino acids from known terrestrial sources. Most published terrestrial stable isotope data were acquired to address metabolic questions and have thus focused on stable carbon isotope ratios ($\delta^{13}C$) for L-proteinogenic amino acids (e.g., Scott et al. 2006). Terrestrial values for $\delta^{13}C$ for many D-amino acids and nonproteinogenic amino acids such as β-ALA and γ-ABA, as well as amino acid values for other isotopes including $\delta^{15}N$ are often not available in the published literature. To that end, we measured the $\delta^{13}C$ and $\delta^{15}N$ values of a suite of amino acids extracted from the terrestrial soil sample (Table 4).

It is important to note that we are analyzing an extract of a bulk sample containing a community of microorganisms both viable and dead, presumably in isotopic equilibrium with the environment, rather than analyzing individual microbial species (which may be isotopically contaminated by the method of extraction or via culture on nutrient media). Nevertheless, our $\delta^{13}C$ values for L-amino acids are in good agreement with the ranges of values obtained previously and reflect ^{13}C depletion that is a hallmark of terrestrial biology (Scott et al. 2006). For Ala, the amino acid for which we were able to measure $\delta^{13}C$ values for both

the D- and L-enantiomer, we did not observe differences between the enantiomers greater than our measurement errors. We note that β-Ala and γ-ABA were isotopically lighter than the rest of the amino acids in the soil sample, at −27 and −31‰, respectively. The presence of these two amino acids in marine sediments is commonly attributed to bacterially mediated α-decarboxylation of aspartic acid and glutamic acid, respectively (e.g., Schroeder 1975). If this was the case here, it would imply that fractionation of −6‰ to −10‰ was occurring during the decarboxylation. It appears unlikely that this is the only source of β-Ala (at least), however, because the $\delta^{15}N$ values for aspartic acid and β-Ala are different outside of measurement error. The $\delta^{15}N$ for the amino acids from the soil ranged from −12 to +12‰, well below accepted $\delta^{15}N$ values for amino acids of extraterrestrial origin (Pizzarello et al. 1994; Engel and Macko 1997; Pizzarello and Holmes 2009; Elsila et al. 2012a). As with the $\delta^{13}C$ measurements, the $\delta^{15}N$ values for D- and L-Ala were essentially the same, well within the measurement errors. While these measurements are by no means comprehensive, they provide previously unavailable reference values for $\delta^{15}N$ ratios in a suite of proteinogenic and nonproteinogenic amino acids of terrestrial origin, and $\delta^{13}C$ ratios previously unavailable for nonproteinogenic, terrestrial amino acids.

CONCLUSION

We analyzed three individual fragments of the Sutter's Mill meteorite, one collected prior to a heavy rainfall (SM2) and two collected after (SM12 and SM51). All three samples experienced some degree of terrestrial contamination as evidenced by the presence of high amounts of L-proteinogenic amino acids relative to their D-counterparts. There are a number of factors that contribute to the extent of terrestrial contamination, including the abundance of biota at the landing site, time in the field, weather, handling procedures during collection and storage, and storage conditions. However, as the indigenous abundances of amino acids are low, the amino acid homogeneity of the parent body is unknown, and the samples were collected from different locations by different people, it is difficult to assess the absolute contributions of each factor to the SM meteorites. From a qualitative standpoint, the amino acid evidence presented here is consistent with an increase in contamination from the prerain meteorite to the postrain meteorites (SM2 versus SM12 and SM51), and an increase in amino acid contamination corresponding to handling, collection, and storage procedures (SM2 and SM12 versus SM51). It is now clear that even a freshly fallen meteorite, such as the SM

meteorites, rapidly accretes amino acid contamination after a fall, similar to what was observed previously for the Martian meteorite Nakhla (Glavin et al. 1999). Several of the factors related to organic contamination are often not within our control (meteorite fall location, time in the field, weather). Thus, to minimize organic contamination in future meteorite recovery efforts, it will be important to make efforts to minimize contamination during recovery and storage. Specific practices that have been shown to be effective are: limiting the handling, even in gloves, of the meteorite stones themselves; collecting and storing the meteorites in materials that are relatively free of organic contamination such as aluminum foil, ideally folded to keep the surface that will contact the meteorite free from contamination and sterilized by heating at 500 °C for several hours; and minimizing the exposure of the sample to moisture by storing it with a desiccant, preferably inorganic. Finally, collecting a terrestrial sample from the recovery site in the same manner as the meteorite was collected provides an appropriate reference sample that can be invaluable in providing context for future results.

None of the three meteorites contained appreciable levels of the extraterrestrial, nonproteinogenic amino acids that are commonly observed in CM2 chondrites, such as isovaline and α-aminoisobutyric acid. However, the presence of trace levels of the unusual nonprotein amino acid β-AIB and the relatively high abundances of free glycine and β-alanine found in Sutter's Mill compared with the terrestrial soil sample suggest that there could be low levels of indigenous amino acids in this meteorite. The Sutter's Mill meteorite fragments analyzed in this study are distinct from other CM2 carbonaceous chondrites in that they have experienced both aqueous alteration and thermal metamorphism, and recent research has shown that this combination of conditions in the presence of minerals leads to the rapid degradation of amino acids. This finding has implications for origins-of-life scenarios that rely on hydrothermal conditions.

from the collection site of SM51, and T. McCoy and L. Welzenbach for providing the sample of Murchison.

Editorial Handling—Dr. Scott Sandford

REFERENCES

Botta O., Martins Z., and Ehrenfreund P. 2007. Amino acids in Antarctic CM1 meteorites and their relationship to other carbonaceous chondrites. *Meteoritics & Planetary Science* 42:81–92, doi:10.1111/j.1945-5100.2007.tb00219.x.

Brückner H., Becker D., Gams W., and Degenkolb T. 2009. Aib and Iva in the biosphere: Neither rare nor necessarily extraterrestrial. *Chemistry & Biodiversity* 6:38–56, doi:10.1002/cbdv.200800331.

Burton A. S., Glavin D. P., Callahan M. P., Dworkin J. P., Jenniskens P., and Shaddad M. H. 2011. Heterogeneous distributions of amino acids provide evidence of multiple sources within the Almahata Sitta parent body, asteroid 2008 TC3. *Meteoritics & Planetary Science* 46:1703–1712, doi:10.1111/j.1945-5100.2011.01257.x.

Burton A. S., Elsila J. E., Callahan M. P., Martin M. G., Glavin D. P., Johnson N. M., and Dworkin J. P. 2012a. A propensity for n-ω-amino acids in thermally altered Antarctic meteorites. *Meteoritics & Planetary Science* 47:374–386, doi:10.1111/j.1945-5100.2012.01341.x.

Burton A. S., Stern J. C., Elsila J. E., Glavin D. P., and Dworkin J. P. 2012b. Understanding prebiotic chemistry through the analysis of extraterrestrial amino acids and nucleobases in meteorites. *Chemical Society Reviews* 41:5459–5472, doi:10.1039/c2cs35109a.

Burton A. S., Elsila J. E., Hein J. E., Glavin D. P., and Dworkin J. P. 2013. Extraterrestrial amino acids identified in metal-rich CH and CB carbonaceous chondrites from Antarctica. *Meteoritics & Planetary Science* 48:390–402, doi:10.1111/maps.12063.

Callahan M. P., Smith K. E., Cleaves H. J., 2nd, Ruzicka J., Stern J. C., Glavin D. P., House C. H., and Dworkin J. P. 2011. Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases. *Proceedings of the National Academy of Sciences of the United States of America* 108:13995–13998, doi:10.1073/pnas.1106493108.

Cooper G., Kimmich N., Belisle W., Sarinana J., Brabham K., and Garrel L. 2001. Carbonaceous meteorites as a source of sugar-related organic compounds for the early Earth. *Nature* 414:879–883. doi:10.1038/414879a.

Cronin J. R. and Moore C. B. 1971. Amino acid analyses of the Murchison, Murray, and Allende carbonaceous chondrites. *Science* 172:1327–1329, doi:10.1126/science.172.3990.1327.

Cronin J. R. and Pizzarello S. 1990. Aliphatic hydrocarbons of the Murchison meteorite. *Geochimica et Cosmochimica Acta* 54:2859–2868, doi:10.1016/0016-7037(90)90020-L.

Cronin J., Pizzarello S., Epstein S., and Krishnamurthy R. 1993. Molecular and isotopic analyses of the hydroxy acids, dicarboxylic acids, and hydroxydicarboxylic acids of the Murchison meteorite. *Geochimica et Cosmochimica Acta* 57:4745–4752, doi:10.1016/0016-7037(93)90197-5.

Ehrenfreund P., Glavin D. P., Botta O., Cooper G. and Bada J. L. 2001. Extraterrestrial amino acids in Orgueil and Ivuna: Tracing the parent body of CI type carbonaceous chondrites. *Proceedings of the National Academy of Sciences of the United States of America* 98:2138–2141, doi:10.1073/pnas.051502898.

Elsila J. E., Glavin D. P., and Dworkin J. P. 2009. Cometary glycine detected in samples returned by Stardust. *Meteoritics & Planetary Science* 44:1323–1330, doi:10.1111/j.1945-5100.2009.tb01224.x.

Elsila J. E., Callahan M. P., Glavin D. P., Dworkin J. P., and Brückner H. 2011. Distribution and stable isotopic composition of amino acids from fungal peptaibiotics: assessing the potential for meteoritic contamination. *Astrobiology* 11:123–133, doi:10.1089/ast.2010.0505.

Elsila J. E., Charnley S. B., Burton A. S., Glavin D. P., and Dworkin J. P. 2012a. Compound-specific carbon, nitrogen, and hydrogen isotopic ratios for amino acids in CM and CR chondrites and their use in evaluating potential formation pathways. *Meteoritics & Planetary Science* 47:1517–1536, doi:10.1111/j.1945-5100.2012.01415.x.

Elsila J. E., Glavin D. P., Dworkin J. P., Martins Z., and Bada J. L. 2012b. Inconclusive evidence for nonterrestrial isoleucine enantiomeric excesses in primitive meteorites. *PNAS* 109:E3288–E3288, doi:10.1073/pnas.1213261109.

Engel M. H. and Macko S. A. 1997. Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite. *Nature* 389:265–268, doi:10.1038/38460.

Engel M. H., Macko S. A., and Silfer J. A. 1990. Carbon isotope composition of individual amino acids in the Murchison meteorite. *Nature* 348:47–49, doi:10.1038/348047a0.

Glavin D. P. and Bada J. L. 2001. Survival of amino acids in micrometeorites during atmospheric entry. *Astrobiology* 1:259–269, doi:10.1089/15311070152757456.

Glavin D. P. and Dworkin J. P. 2009. Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies. *Proceedings of the National Academy of Sciences of the United States of America* 106:5487–5492, doi:10.1073/pnas.0811618106.

Glavin D. P., Bada J. L., Brinton K. L. F., and McDonald G. D. 1999. Amino acids in the Martian meteorite Nakhla. *PNAS* 96:8835–8838, doi:10.1073/pnas.96.16.8835.

Glavin D. P., Dworkin J. P., Aubrey A., et al. 2006. Amino acid analyses of Antarctic CM2 meteorites using liquid chromatography-time-of-flight-mass spectrometry. *Meteoritics & Planetary Science* 41:889–902, doi:10.1111/j.1945-5100.2006.tb00493.x.

Glavin D. P., Aubrey A. D., Callahan M. P., Dworkin J. P., Elsila J. E., Parker E. T., Bada J. L., Jenniskens P., and Shaddad M. H. 2010a. Extraterrestrial amino acids in the Almahata Sitta meteorite. *Meteoritics & Planetary Science* 45:1695–1709, doi:10.1111/j.1945-5100.2010.01094.x.

Glavin D. P., Callahan M. P., Dworkin J. P., and Elsila J. E. 2010b. The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteoritics & Planetary Science* 45:1948–1972, doi:10.1111/j.1945-5100.2010.01132.x.

Glavin D. P., Elsila J. E., Burton A. S., Callahan M. P., Dworkin J. P., Hilts R. W., and Herd C. D. K. 2012. Unusual nonterrestrial l-proteinogenic amino acid excesses in the Tagish Lake meteorite. *Meteoritics & Planetary Science* 47:1347–1364, doi:10.1111/j.1945-5100.2012.01400.x.

Herd C. D. K., Blinova A., Simkus D. N., Huang Y., Tarozo R., Alexander C. M. O.'D., Gyngard F., Nittler L. R., Cody G. D., Fogel M. L., Kebukawa Y., Kilcoyne A. L. D., Hilts R. W., Slater G. F., Glavin D. P., Dworkin J. P., Callahan M. P., Elsila J. E., De Gregorio B. T., and Stroud R. M. 2011. Origin and evolution of prebiotic organic matter as inferred from the Tagish Lake meteorite. *Science* 332:1304–1307, doi:10.1126/science.1203290.

Jenniskens P., Fries M. D., Yin Q.-Z., Zolensky M., Krot A. N., Sandford S. A., Sears D., Beauford R., Ebel D. S., Friedrich J. M., Nagashima K., Wimpenny J., Yamakawa A., Nishiizumi K., Hamajima Y., Caffee M. W., Welten K. C., Laubenstein M., Davis A. M., Simon S. B., Heck P. R., Young E. D., Kohl I. E., Thiemens M. H., Nunn M. H., Mikouchi T., Hagiya K., Ohsumi K., Cahill T. A., Lawton J. A., Barnes D., Steele A., Rochette P., Verosub K. L., Gattacceca J., Cooper G., Glavin D. P., Burton A. S., Dworkin J. P., Elsila J. E., Pizzarello S., Ogliore R., Schmitt-Kopplin P., Harir M., Hertkorn N., Verchovsky A., Grady M., Nagao K., Okazaki R., Takechi H., Hiroi T., Smith K., Silber E. A., Brown P. G., Albers J., Klotz D., Hankey M., Matson R., Fries J. A., Walker R. J., Puchtel I., Lee C.-T. A., Erdman M. E., Eppich G. R., Roeske S., Gabelica Z., Lerche M., Nuevo M., Girten B., and Worden S. P. 2012. Radar-Enabled Recovery of the Sutter's Mill meteorite, a carbonaceous chondrite regolith breccia. *Science* 338:1583–1587, doi:10.1126/science.1227163.

Jungclaus G. A., Yuen G. U., Moore C. B., and Lawless J. G. 1976. Evidence for the presence of low molecular weight alcohols and carbonyl compounds in the Murchison meteorite. *Meteoritics* 11:231–237.

Krot A. N., Hutcheon I. D., Brearley A. J., Pravdivtseva O. V., Petaev M. I., and Hohenberg C. M. 2006. Timescales and settings for alteration of chondritic meteorites. In *Meteorites and the early solar system II*, edited by Lauretta D. and McSween H. Jr. Tucson, Arizona: University of Arizona Press. pp. 525–553.

Kvenvolden K., Lawless J., Pering K., Peterson E., Flores J., Ponnamperuma C., Kaplan I. R., and Moore C. 1970. Evidence for extraterrestrial amino-acids and hydrocarbons in the Murchison meteorite. *Nature* 228:923–926, doi:10.1038/228923a0.

Martins Z., Alexander C. M. O'D., Orzechowska G. E., Fogel M. L., and Ehrenfreund P. 2007. Indigenous amino acids in primitive CR meteorites. *Meteoritics & Planetary Science* 42:2125–2136.

Martins Z., Botta O., Fogel M. L., Sephton M. A., Glavin D. P., Watson J. S., Dworkin J. P., Schwartz A. W., and Ehrenfreund P. 2008. Extraterrestrial nucleobases in the Murchison meteorite. *Earth and Planetary Science Letters* 270:130–136, doi:10.1016/j.epsl.2008.03.026.

McCollom T. M. 2013. The influence of minerals on decomposition of the n-alkyl-α-amino acid norvaline under hydrothermal conditions. *Geochimica et Cosmochimica Acta* 104:330–357, doi:10.1016/j.gca.2012.11.008.

Miller S. L. and Lazcano A. 1995. The origin of life—did it occur at high temperatures? *Journal of Molecular Evolution* 41:689–692, doi:10.1007/BF00173146.

Peltzer E. T. and Bada J. L. 1978. [alpha]-Hydroxycarboxylic acids in the Murchison meteorite. *Nature* 272:443–444, doi:10.1038/272443a0.

Pizzarello S. and Holmes W. 2009. Nitrogen-containing compounds in two CR2 meteorites: 15N composition, molecular distribution and precursor molecules. *Geochimica et Cosmochimica Acta* 73:2150–2162, doi:10.1016/j.gca.2009.01.022.

Pizzarello S. and Huang Y. 2005. The deuterium enrichment of individual amino acids in carbonaceous meteorites: A case for the presolar distribution of biomolecule precursors. *Geochimica et Cosmochimica Acta* 69:599–605, doi:10.1016/j.gca.2004.07.031.

Pizzarello S. and Monroe A. A. 2012. Reply to Elsila et al.: Large enantiomeric excesses in primitive meteorites, an analytical and computational supplement. *PNAS* 109: E3289–E3289, doi:10.1073/pnas.1213714109.

Pizzarello S., Feng X., Epstein S., and Cronin J. R. 1994. Isotopic analyses of nitrogenous compounds from the Murchison meteorite: Ammonia, amines, amino acids, and polar hydrocarbons. *Geochimica et Cosmochimica Acta* 58:5579–5587, doi:10.1016/0016-7037(94)90251-8.

Pizzarello S., Huang Y., and Fuller M. 2004. The carbon isotopic distribution of Murchison amino acids. *Geochimica et Cosmochimica Acta* 68:4963–4969, doi:16/j.gca.2004.05.024.

Pizzarello S., Cooper G., and Flynn G. 2006. The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. In *Meteorites and the early solar system II*, edited by Lauretta D., Leshin L., and McSween H. Jr. Tucson, Arizona: University of Arizona Press. pp. 625–651.

Pizzarello S., Huang Y., and Alexandre M. R. 2008. Molecular asymmetry in extraterrestrial chemistry: Insights from a pristine meteorite. *Proceedings of the National Academy of Sciences of the United States of America* 105:3700–3704, doi:10.1073/pnas.0709909105.

Pizzarello S., Wang Y., and Chaban G. M. 2010. A comparative study of the hydroxy acids from the Murchison, GRA 95229 and LAP 02342 meteorites. *Geochimica et Cosmochimica Acta* 74:6206–6217, doi:10.1016/j.gca.2010.08.013.

Pizzarello S., Schrader D. L., Monroe A. A., and Lauretta D. S. 2012. Large enantiomeric excesses in primitive meteorites and the diverse effects of water in cosmochemical evolution. *PNAS*, doi:10.1073/pnas.1204865109.

Rodante F. 1992. Thermodynamics and kinetics of decomposition processes for standard [alpha]-amino acids and some of their dipeptides in the solid state. *Thermochimica Acta* 200:47–61, doi:10.1016/0040-6031(92)85105-5.

Schroeder R. A. 1975. Absence of β-alanine and γ-aminobutyric acid in cleaned foraminiferal shells: Implications for use as a chemical criterion to indicate removal of non-indigenous amino acid contaminants. *Earth and Planetary Science Letters* 25:274–278, doi:10.1016/0012-821X(75)90241-1.

Scott J. H., O'Brien D. M., Emerson D., Sun H., McDonald G. D., Salgado A., and Fogel M. L. 2006. An examination of the carbon isotope effects associated with amino acid biosynthesis. *Astrobiology* 6:867–880, doi:10.1089/ast.2006.6.867.

Vandervelden W. and Schwartz A. 1977. Search for purines and pyrimidines in the Murchison meteorite. *Geochimica et Cosmochimica Acta* 41:961–968, doi:10.1016/0016-7037(77)90155-7.

Yuen G. U. and Kvenvolden K. A. 1973. Monocarboxylic acids in Murray and Murchison carbonaceous meteorites. *Nature* 246:301–303, doi:10.1038/246301a0.

Zolensky M., Barrett R., and Browning L. 1993. Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 57:3123–3148, doi:10.1016/0016-7037(93)90298-B.