Extraterrestrial amino acids identified in metal-rich CH and CB carbonaceous chondrites from Antarctica

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Abstract–Carbonaceous chondrites contain numerous indigenous organic compounds and could have been an important source of prebiotic compounds required for the origin of life on Earth or elsewhere. Extraterrestrial amino acids have been reported in five of the eight groups of carbonaceous chondrites and are most abundant in CI, CM, and CR chondrites but are also present in the more thermally altered CV and CO chondrites. We report the abundance, distribution, and enantiomeric and isotopic compositions of simple primary amino acids in six metal-rich CH and CB carbonaceous chondrites that have not previously been investigated for amino acids: Allan Hills (ALH) 85085 (CH3), Pecora Escarpment (PCA) 91467 (CH3), Patuxent Range (PAT) 91546 (CH3), MacAlpine Hills (MAC) 02675 (CBb), Miller Range (MIL) 05082 (CB), and Miller Range (MIL) 07411 (CB). Amino acid abundances and carbon isotopic values were obtained by using both liquid chromatography time-of-flight mass spectrometry and fluorescence, and gas chromatography isotope ratio mass spectrometry. The $\delta^{13}C/^{12}C$ ratios of multiple amino acids fall outside of the terrestrial range and support their extraterrestrial origin. Extracts of CH chondrites were found to be particularly rich in amino acids (13–16 parts per million, ppm) while CB chondrite extracts had much lower abundances (0.2–2 ppm). The amino acid distributions of the CH and CB chondrites were distinct from the distributions observed in type 2 and 3 CM and CR chondrites and contained elevated levels of β-, γ-, and δ-amino acids compared to the corresponding α-amino acids, providing evidence that multiple amino acid formation mechanisms were important in CH and CB chondrites.

INTRODUCTION

Carbonaceous chondrites are primitive stony meteorites that contain many indigenous organic molecules including some relevant to biochemistry, such as sugar acids, carboxylic acids, aldehydes, ketones, nucleobases, and amino acids (Kvenvolden et al. 1970; Yuen and Kvenvolden 1973; Jungclaus et al. 1976; Cooper et al. 2001; Callahan et al. 2011). Consequently, it has been proposed that these meteorites could have been a significant source of molecules necessary for the origin of life on Earth (Dodd 1981; Chyba and Sagan 1992). Our knowledge of the organic contents of

meteorites has been largely based on studies of the CM2 chondrite Murchison because it contains a diverse inventory of organic molecules and a large amount (approximately 100 kg) was recovered. The Murchison meteorite has often been considered the prototypical carbonaceous meteorite (Pizzarello and Shock 2010), with its amino acid distributions used as a benchmark for evaluating the relevance of amino acid-forming reactions in the lab (e.g., Hayatsu et al. 1971; Wolman et al. 1972).

The high prevalence of α-amino acid isomers in Murchison has now been observed in many CM2, CR2, and CR3 chondrites (Cronin and Pizzarello 1983;

Glavin et al. 2006, 2010b; Pizzarello et al. 2006; Martins et al. 2007; Pizzarello and Holmes 2009). Based on the predominance of α-amino isomers in these meteorites as well as in residues formed from spark discharge experiments, it has been generally accepted that extraterrestrial amino acid formation was dominated by the Strecker-cyanohydrin pathway (Miller 1953; Peltzer et al. 1984). The CI chondrites have been perceived as outliers in terms of amino acid composition because they contain the three-carbon amino acid β-alanine in higher abundance than both α-alanine and glycine (Ehrenfreund et al. 2001; Glavin et al. 2010b). This was interpreted as evidence for the existence of chemically distinct parent bodies for CI and CM carbonaceous chondrites; based on the relatively simple amino acid compositions of Orgueil and Ivuna, it was even suggested that the CI chondrite parent body may have been an extinct comet (Ehrenfreund et al. 2001), a hypothesis supported by analysis of its atmospheric trajectory and calculated orbit (Gounelle et al. 2006).

Advances in analytical methodology and instrumentation have recently enabled the detection of trace amounts of primarily straight-chain, amine-terminal amino acids (*n*-ω-amino acids) in thermally altered meteorites such as CV and CO chondrites and ureilites (Burton et al. 2012a). Like Orgueil, but in contrast with the CM2, CR2, and CR3 chondrites, these meteorites do not contain predominantly α-amino acids, suggesting that mechanisms besides the Strecker-cyanohydrin pathway must have been dominant. Because these meteorites experienced thermal metamorphism but minimal aqueous alteration, their amino acids may have formed from high temperature Fischer-Tropsch type reactions (Lancet and Anders 1970; Glavin et al. 2010a; Burton et al. 2011, 2012a; Pizzarello 2012). Analyses of meteorites from the various carbonaceous chondrite groups spanning alteration types 1–3 have revealed interesting trends that suggest that parent body composition and alteration history have a profound impact on the abundances and structural and isotopic distributions of meteoritic amino acids, and that the amino acid distribution observed in Orgueil may not be so rare (Glavin et al. 2010b; Elsila et al. 2012). The discoveries of amino acids in CV and CO chondrites, in addition to an H5 chondrite from the Alamahata Sitta fall and several ureilites (Burton et al. 2011) suggest that amino acids are far more widespread across carbon-containing meteorites than previously assumed.

The present work focuses on amino acid analyses of metal-rich CH and CB chondrites, which to our knowledge have never been analyzed for amino acids. CH and CB chondrites have been grouped into the CR clan based on several similar chemical and mineralogical properties (Weisberg et al. 2006). Specifically, they are all metal rich, though to varying degrees (CR chondrites are approximately 5 vol% metal; CH chondrites are approximately 20 vol% metal, and CB chondrites are 60–80 vol% metal) and all three groups contain heavily hydrated matrix material (Greshake et al. 2002). The CB chondrites are divided into subgroups CBa and CBb, differentiated by chondrule size and metal abundance, with CBbs having smaller chondrules and higher metal contents. We measured the abundance, distribution, and enantiomeric composition (when possible) of the simple two- to five-carbon amino acids in hot water extracts of three Antarctic CH chondrites and three Antarctic CB chondrites by ultrahigh performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS). In addition, the carbon isotope ratios of several amino acids were determined in two of the CH chondrites and one of the CB chondrites by gas chromatography with mass spectrometry and combustion isotope ratio mass spectrometry (GC-MS/IRMS), confirming their extraterrestrial origin.

MATERIALS AND METHODS

Chemicals and Reagents

To remove organic residue, sample-handling tools, porcelains, 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 pyrolyzed in air at 500 °C for 18–24 h. Porcelain mortar and pestles (CoorsTek) were bead-blasted, rinsed with water, and pyrolyzed. Most of the chemicals used 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 decahydrate (Sigma Ultra 99.5–100% purity) that was pyrolyzed in air at 500 °C for 3 h to remove any organic contaminants prior to dissolution in water. All other solutions were prepared as described by Glavin et al. (2006).

Antarctic Meteorites and Controls

Meteorite samples were provided by the meteorite curator at the NASA Johnson Space Center. For this

Table 1. Summary of the meteorites and control samples analyzed in this study.

Sample name	Classification	Mass extracted (mg)
ALH 85085	CH3	120.5
PCA 91467	CH3	477.1
PAT 91546	CH3	340.2
MAC 02675	CBb	528.4
MIL 05082	CB	325.5
MIL 07411[a]	CB	631.1
Pestle[a]	Control	74.7
Serpentine	Control	478.1

[a]Pestle fractured during powdering of MIL 07411; some fragments remained in the meteorite sample.

study, we analyzed three CH chondrites: Allan Hills (ALH) 85085 (Parent/Specific: 0/36), Pecora Escarpment (PCA) 91467 (12/34), and Patuxent Range (PAT) 91546 (0/30), and three CB chondrites: MacAlpine Hills (MAC) 02675 (0/18), Miller Range (MIL) 05082 (0/16), and MIL 07411 (0/5) (may be paired with MIL 05082). Specific details for each sample are given in Table 1. Samples 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. The CB chondrites were much more difficult to crush and homogenize than the CH chondrites, presumably due to their higher metal contents. During the powdering of MIL 07411, the porcelain pestle fractured, introducing some porcelain fragments to the sample. As many of the fragments as possible were removed from the MIL 07411 sample and analyzed in parallel with the meteorite samples, along with procedural blanks and a serpentine control sample that had been heated in air at 500 °C for 3 h prior to extraction. The largest uncrushed pieces of metal were also removed.

Extraction Procedures and Analytical Techniques

The powdered meteorite samples and controls were flame sealed in 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 under ambient pressure for 5 min (Labconco Centrivap) to separate solid particulate from water supernatant. Half of the water extract was dried under vacuum and subjected to acid hydrolysis under 6 M HCl vapor at 150 °C for 3 h to liberate amino acids in bound or precursor forms. The remaining unhydrolyzed water extract (containing free amino acids only) and the HCl-hydrolyzed extract (containing free and bound amino acids) were dried separately under vacuum (Labconco Centrivap) and re-dissolved in 1 mL of water. Both HCl-hydrolyzed and unhydrolyzed extracts were desalted by cation exchange chromatography using pre-packed columns from BioRad (AG-50W X8 resin, 100–200 mesh), and their NH_4OH 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 in order to estimate the desalting and derivatization recovery of amino acids in each sample used to correct for the reported amino acid abundances (see Tables 3 and 4).

OPA/NAC amino acid derivatives were analyzed by LC-FD/ToF-MS using a Waters ACQUITY ultraperformance LC 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 tuned either for general separation (Glavin et al. 2010b) or focusing on the C5 amino acids (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.

Amino Acid Carbon Isotopic Measurements by GC-MS/IRMS

Of the six carbonaceous meteorites studied, three contained sufficiently abundant amino acids to enable determination of their $\delta^{13}C/^{12}C$ ratios. For two of the three CH chondrites, PAT 91546 and PCA 91467, we measured the $\delta^{13}C$ values of amino acids in both the HCl-hydrolyzed and unhydrolyzed samples, while $\delta^{13}C$ values could only be determined from the hydrolyzed fraction of one CB chondrite, MIL 05082. Roughly 10% of each meteorite extract was used for LC-FD/ToF-MS analysis and the remaining 90% was used for GC-MS/IRMS. The extracts were 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,
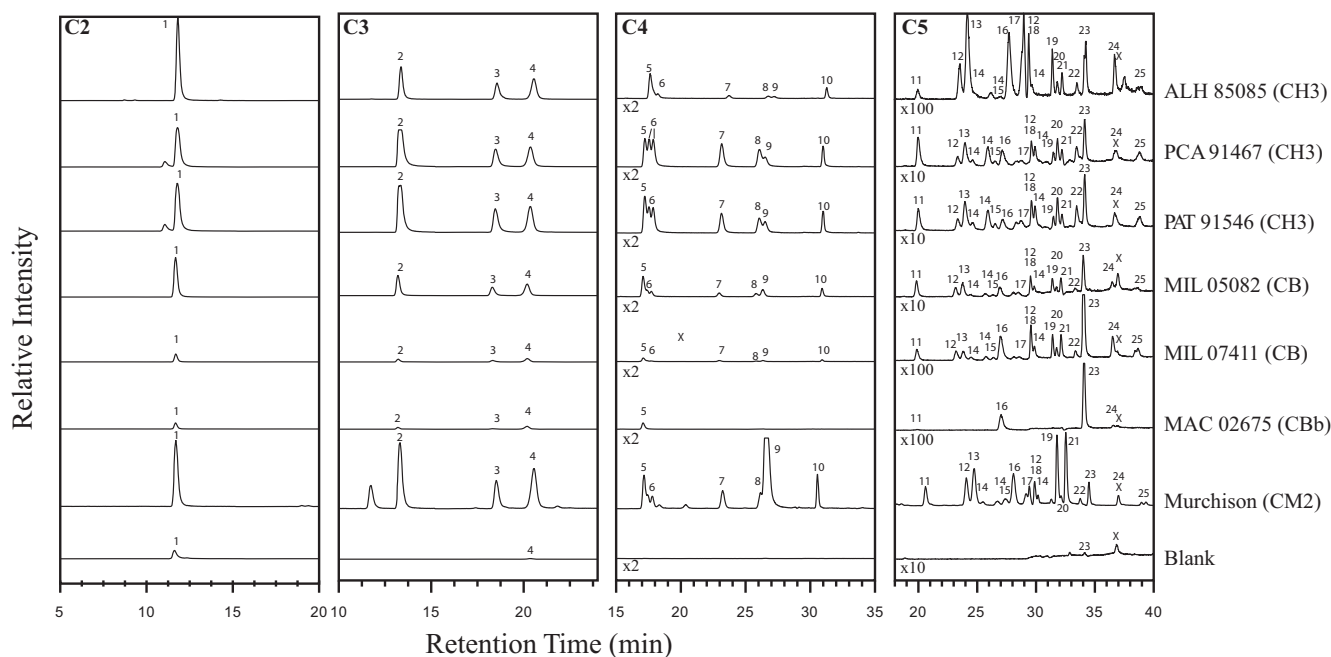
Fig. 1. Representative liquid chromatography-mass spectrometry chromatograms for the acid-hydrolyzed meteorite samples analyzed in this study. Chromatograms shown are for the C2, C3, C4, and C5-carbon primary, aliphatic, acyclic amino acids (derivatized positive ionization mass-to-charge ratios of 337.0859, 351.1015, 365.1171, and 379.1328, respectively). The masses plotted represent a 0.07 Da window (the peak width at half maximum) centered around the corresponding theoretical monoisotopic masses of the mono-protonated positive ions of C2 to C5 OPA/NAC amino acid derivatives and are all set to the same scale; in the C4 and C5 traces, peaks have been amplified by the factors given below each trace. Chromatograms of Murchison, an aqueously altered CM2 carbonaceous chondrite, have been included for comparison. Peak numbers correspond to amino acid assignments in Table 2; the "X" denotes a non-fluorescent contaminant with a mass similar to the C5 aliphatic amino acids. Similar chromatograms were obtained for the nonhydrolyzed fractions. The chromatographic conditions were as follows: column temperature, 30 °C; flow rate, 150 μL min^{-1}; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (0), 35 (55), 45 (100). To improve separation of the five-carbon amino acids, a different gradient was used: solvent A (50 mm ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (15), 25 (20), 25.1 (35), 44.5 (40), 45 (100).

which provides compound-specific structural and stable isotopic information from a single sample injection. GC-MS/IRMS analysis begins 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 amino acids are oxidized to carbon dioxide. The CO_2 is passed into a Thermo MAT 253 isotope ratio mass spectrometer (IRMS) for stable isotopic measurement.

Stock solutions of the amino acids of interest were combined to make a standard mixture that was carried through the same derivatization process and analyzed daily on the GC-MS/IRMS. A stock solution of L-alanine with a known $\delta^{13}C$ value (−23.33%, IsoAnalytical) was also derivatized and analyzed daily as a working standard. The individual, underivatized stock solutions or solid pure standards were also analyzed on a Costech ECS 4010 combustion elemental analyzer (EA) connected to the MAT 253 IRMS; this was necessary to correct for the carbon added by TFAA/IPA during derivatization

The retention times and mass spectra for amino acid peaks in the meteorite samples were carefully compared with those of the standard amino acid mix. Six pulses of CO_2 ($\delta^{13}C$ = −24.23% VPDB) that had been precalibrated against commercial reference gases (Oztech Corporation) were injected into the IRMS for computation of the $\delta^{13}C$ values of the eluting compounds. Analysis of the MAT 253 data was performed with Thermo Isodat 2.5 software. The final $\delta^{13}C$ values of the amino acids in the samples and their precision were calculated as described elsewhere (Elsila et al. 2009). Isotopic values are generally reported only
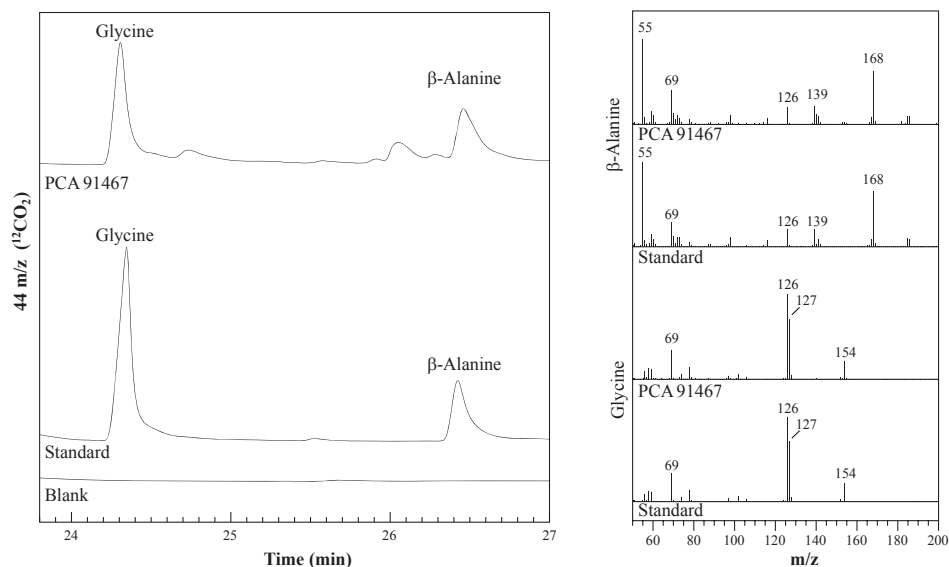
Fig. 2. Gas chromatography separation and mass spectrometry analysis of glycine and β-alanine of the TFAA/ IPA-derivatized unhydrolyzed extract of the PCA 91467 (CH3) meteorite and the procedural blank, and a standard. The traces on the left show the m/z 44 ($^{12}CO_2$) peak produced and measured from GC-IRMS for the peaks assigned to glycine and β-alanine. The traces on the right show the simultaneously collected mass spectral fragmentation pattern for these peaks in the meteorite and standard. GC separation used a 5 m base-deactivated fused silica guard column (Restek) coupled with four 25 m Chirasil L-Val columns (Restek) and the following temperature program: initial oven temperature 50 °C, ramped at 10 °C min^{-1} to 85 °C, ramped at 2 °C min^{-1} to 120 °C, ramped at 4 °C min^{-1} to 200 °C, and held for 10 min. Peaks were identified by comparison of retention time and mass spectral fragmentation with the amino acid standard run on the same day.

for those peaks in which no coelutions were detected, as indicated by the absence of additional mass fragments in the sample compared to the standard (see Fig. 2). In rare cases, isotopic values were calculated for amino acids with co-eluting compounds, but this is noted in Table 5.

RESULTS AND DISCUSSION

Amino Acid Analyses

Representative LC-ToF-MS chromatograms of the hydrolyzed meteorite extracts are shown in Fig. 1. We determined the abundances of all of the simple two- to five-carbon aliphatic, acyclic, primary, mono-amino, mono-carboxylic amino acids in the samples detected above blank levels, as well as several additional proteinogenic amino acids and the six-carbon amino acid ε-amino-n-caproic acid (Table 2 contains a list of compounds searched for in this study and their abbreviations). These values are given in Tables 3 and 4 for the CH and CB chondrites, respectively. Due to a lack of standards and insufficient chromatographic resolution, we were unable to identify several additional six-carbon amino acids detected in the CH chondrites as well as many six-, seven-, and eight-carbon amino acids present in the CB chondrite MIL 05082. The three CH3

chondrites had total amino acid abundances on the order of 13–16 ppm, with 36–60% of the amino acid totals present as free (found in the unhydrolyzed fraction; Table 3), similar to ratios observed for CM and CR chondrites (Glavin et al. [2010b] and references therein). Despite their mineralogical similarities to CR chondrites, the CH3 chondrites contain five-fold lower amino acid totals than the CR3 chondrite Queen Alexandra Range (QUE) 99177 and 10- to 20-fold lower abundances than the CR2 chondrites Elephant Moraine (EET) 92042 and Graves Nunataks (GRA) 95229 (Martins et al. 2007; Glavin et al. 2010b). Instead, the CH3 amino acid totals are more similar to the amino acid abundances observed in CM2 chondrites such as Murchison, Lewis Cliff (LEW) 90500, and Lonewolf Nunataks (LON) 94102 (Glavin et al. 2010b).

The CB chondrites were much less abundant in amino acids, with levels ranging from 0.2 to 2 ppm (Table 4), similar to the low amino acid abundances previously reported for aqueously altered type 1 CR, CM, and CI carbonaceous chondrites (0.6–7 ppm; Glavin et al. 2010b). A smaller fraction of the amino acids in the CB chondrites were found in the free form (approximately 10–30%) than were observed in the CH chondrites and previously in CM and CR chondrites. Intriguingly, the two CB chondrites that are proposed to be paired, MIL 05082 and MIL 07411, showed

Table 2. List of compounds measured in this study, their abbreviations, and peak numbering in the chromatograms in Fig. 1.

Peak number	Amino acid (abbreviation)
Not shown	D-aspartic acid (D-asp)
Not shown	L-aspartic acid (L-asp)
Not shown	L-glutamic acid (L-glu)
Not shown	D-glutamic acid (D-glu)
Not shown	D-serine (D-ser)
Not shown	L-serine (L-ser)
1	glycine (gly)
2	β-alanine (β-ala)
3	D-alanine (D-ala)
4	L-alanine (L-ala)
5	γ-amino-*n*-butyric acid (γ-aba)
6	D, L-β-aminoisobutyric acid (β-aib)
7	D-β-amino-*n*-butyric acid (D-β-aba)
8	L-β-amino-*n*-butyric acid (L-β-aba)
9	α-aminoisobutyric acid (α-aib)
10	D,L-α-amino-*n*-butyric acid (α-aba)
Not shown	ε-amino-*n*-caproic acid (ε-aca)
11	3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa)
12	D,L-4-aminopentanoic acid (D,L-4-apa)
13	D,L-4-amino-3-methylbutanoic acid (D,L-4-a-3-mba)
14	D,L- and *allo*-3-amino-2-methylbutanoic acid (D,L-3-a-2-mba)
15	D,L-3-amino-2-ethylpropanoic acid (D,L-3-a-2-epa)
16	5-aminopentanoic acid (5-apa)
17	4-amino-2-methylbutanoic acid (4-a-2-mba)
18	3-amino-3-methylbutanoic acid (3-a-3-mba)
19	D-isovaline (D-iva)
20	D-3-aminopentanoic acid (D-3-apa)
21	L-isovaline (L-iva)
22	L-3-aminopentanoic acid (L-3-apa)
23	L-valine (L-val)
24	D-valine (D-val)
25	D,L-norvaline (D,L-norval)

similar amino acid distributions but the total abundances of the two differ by approximately 10-fold. This discrepancy in absolute amino acid abundances may be explained by differences in sample composition, as both meteorites contained mm-scale metal grains that could not be homogenized. Analyses of the mineralogy and petrography of these meteorites are needed to better understand the observed differences in amino acid abundances.

To assess the degree of terrestrial amino acid contamination of the meteorites studied, we determined the D/L enantiomeric ratios of several chiral amino acids (Table 5). Terrestrial biological contamination is often detected by a relative increase in the abundance of the

L-isomer over the D-isomer for common proteinogenic amino acids, although some exceptions have recently been noted (e.g., Glavin et al. 2012). Several of these ratios are appreciably less than one, particularly for serine and valine, suggesting that terrestrial L-amino acid contamination of these meteorites occurred. It is worth noting, however, that these two amino acids represent only a small fraction of the total amino acids observed in the meteorites. Furthermore, amino acids rare or absent in the terrestrial biosphere (such as D,L-β-aba, α-aib, D,L-β-aib, and most of the five-carbon amino acids) are present in all of the meteorites except the CBb chondrite MAC 02675. Previous analyses of an approximately 10 kg sample of Antarctic blue ice from the Northern Graves ice field investigated the possibility of environmental contamination on Antarctic meteorites (Burton et al. 2012a). Although none of the meteorites analyzed in this study were recovered from that site, the observation that no nonproteinogenic amino acids were observed above the 0.01 part-per-trillion level in the ice, suggests, but does not completely rule out, that these compounds are unlikely to have come from the ice. We do not observe a relationship between the weathering grade of the meteorite samples and the levels of terrestrial contamination as determined by the D/L ratios of individual amino acids (Table 5); however, any such relationship may be overwhelmed by the necessarily differential effects of low levels of contamination on meteorites with less abundant amino acids compared with more amino acid-rich meteorites.

We were able to unambiguously establish an extraterrestrial origin for multiple amino acids including gly, L-ala, and β-ala in three of the meteorites (CH3 PCA 91467, CH3 PAT 91546, and CB MIL 05082) based on their specific $\delta^{13}C$ values that fall well outside the terrestrial range. The $\delta^{13}C$ values are shown in Table 6, along with values for the same amino acids in previously analyzed CM2, CR2, and CR3 chondrites for comparison. The values for gly, β-ala, and ala in the hydrolyzed and unhydrolyzed extracts from the CH3 chondrites range from +5% to +56%, comparable to those measured from other meteoritic samples and are well outside the known terrestrial range for amino acids in microorganisms (Scott et al. 2006). Although the $\delta^{13}C$ values for gly and L-ala are lower in the CB chondrite MIL 05082 than in the CH chondrites, they are still outside the terrestrial range, indicating an extraterrestrial origin. The values may be reduced by the presence of terrestrial contamination (although in the case of ala this seems unlikely as it is racemic within measurement error), or by different parent body conditions during synthesis. The measured $\delta^{13}C$ ratios for β-ala and γ-aba in the CB chondrite MIL 05082 are similar to those measured for the same compounds in

Table 3. Summary of the average blank-corrected amino acid concentrations in the unhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot water extracts of CH carbonaceous chondrites.[a] Full names of the amino acids are given in Table 2.

Amino acid	ALH 85085 (CH3)		PCA 91467 (CH3)		PAT 91546 (CH3)	
	Free	Total	Free	Total	Free	Total
D-asp	89 ± 11	99 ± 10	25 ± 12	120 ± 21	32 ± 9	158 ± 34
L-asp	90 ± 5	273 ± 40	32 ± 13	210 ± 36	37 ± 11	247 ± 51
L-glu	87 ± 19	1042 ± 91	28 ± 9	408 ± 52	39 ± 25	466 ± 52
D-glu	85 ± 15	1034 ± 97	19 ± 10	373 ± 64	25 ± 18	501 ± 55
D-ser	20 ± 1	13 ± 1	41 ± 6	45 ± 3	37 ± 5	80 ± 13
L-ser	33 ± 2	279 ± 31	145 ± 17	104 ± 14	75 ± 7	159 ± 39
gly	4991 ± 1538	4531 ± 429	1565 ± 254	4609 ± 718	2461 ± 381	5747 ± 838
β-ALA	749 ± 191	1093 ± 67	1116 ± 49	3818 ± 342	2362 ± 265	4218 ± 290
γ-ABA	615 ± 247	1996 ± 407	179 ± 16	542 ± 57	285 ± 29	809 ± 72
D,L-β-AIB[b]	102 ± 48	137 ± 28	130 ± 25	467 ± 58	283 ± 49	464 ± 81
D-ala	891 ± 243	830 ± 48	327 ± 38	238 ± 30	350 ± 32	378 ± 74
L-ala	745 ± 209	935 ± 49	355 ± 41	219 ± 34	350 ± 39	333 ± 70
D-β-ABA	139 ± 59	113 ± 10	184 ± 35	340 ± 68	451 ± 68	376 ± 42
L-β-ABA	144 ± 61	115 ± 10	192 ± 27	377 ± 66	488 ± 68	416 ± 45
α-AIB	96 ± 42	58 ± 4	95 ± 20	139 ± 20	163 ± 30	195 ± 26
DL-α-ABA[c]	566 ± 252	470 ± 32	158 ± 24	297 ± 59	260 ± 38	375 ± 52
ε-ACA	725 ± 321	3879 ± 203	2093 ± 135	2446 ± 896	1022 ± 53	5702 ± 2478
3-a-2,2-dmpa	16 ± 10	38 ± 4	21 ± 4	64 ± 6	34 ± 5	85 ± 6
D-4-apa	20 ± 12	160 ± 7	6 ± 1	41 ± 4	16 ± 3	33 ± 2
DL-4-a-3mba	115 ± 68	1,036 ± 101	40 ± 4	261 ± 30	84 ± 6	222 ± 14
DL-3-a-2-mba[b]	23 ± 13	59 ± 10	18 ± 4	61 ± 9	42 ± 6	46 ± 3
DL-3a-2-epa[c]	154 ± 83	40 ± 2	27 ± 1	93 ± 4	57 ± 3	72 ± 6
5-apa	78 ± 48	553 ± 45	24 ± 3	85 ± 9	31 ± 3	124 ± 21
DL-4-a-2mba	111 ± 70	616 ± 114	3 ± 1	25 ± 1	27 ± 4	19 ± 7
L-4-apa	22 ± 15	85 ± 6	8 ± 2	40 ± 5	17 ± 4	30 ± 2
D-iva	19 ± 6	35 ± 7	6 ± 1	40 ± 6	13 ± 1	48 ± 9
D-3-apa	26 ± 17	36 ± 3	20 ± 2	51 ± 4	51 ± 2	48 ± 5
L-iva	30 ± 13	53 ± 2	10 ± 3	52 ± 5	20 ± 1	53 ± 11
L-3-apa	14 ± 9	37 ± 1	14 ± 2	57 ± 7	42 ± 5	44 ± 4
L-val	23 ± 14	334 ± 48	23 ± 2	120 ± 49	37 ± 2	91 ± 7
D-val	54 ± 36	144 ± 7	16 ± 4	39 ± 7	28 ± 4	31 ± 6
D,L-norval[c]	10 ± 6	75 ± 15	6 ± 1	24 ± 3	12 ± 2	21 ± 1
C5 total	715 ± 147	3300 ± 168	252 ± 10	1127 ± 61	511 ± 15	1027 ± 43
Total[d]	10156 ± 1625	16319 ± 640	4845 ± 274	13434 ± 817	8209 ± 484	15948 ± 910
% free	62%		36%		51%	

[a]Values are reported in parts-per-billion (ppb) based on the bulk sample mass. Meteorite extracts were analyzed by OPA/NAC derivatization (15 min) and LC-FD∕ToF-MS detection. Monoisotopic chromatograms and fluorescence chromatograms were used for quantification of ToF-MS data and final peak integrations were background-corrected using a procedural blank. Peak areas in the sample chromatograms were compared with pure amino acid standards that were analyzed on the same day. Final values were normalized using desalting and derivatization recoveries based on the D,L-norleucine internal standard (recoveries were typically 70–80% for the meteorite extracts). Uncertainties (δ_x) were calculated from the standard error based on the number of separate measurements (n), $\delta_x = \sigma_x (n-1)^{-1/2}$. For all UV fluorescence data, coeluting peaks and ∕ or compounds with interfering peaks were not included in the average. Upper limits are presented for amino acids that were not present at levels above the procedural blank background levels.
[b]Enantiomers could be separated, but not identified, due to a lack of optically pure standards.
[c]Enantiomers could not be separated under the chromatographic conditions.
[d]The amino acid totals include all compounds in this table except ε-aca.

the CR3 chondrite QUE 99177, which was determined to be nearly free of amino acid contamination (Glavin et al. 2010b). These low values for β-ala and γ-aba in these two meteorites may instead be indicative of common formation conditions for the amino acids or their precursors. We note that although these values

technically lie in the terrestrial range for amino acids (0 to −60%), this range corresponds to proteinogenic, α-amino acids. To our knowledge, there have been no reports of stable isotopic ratios of non-α-amino acids such as β-ala and γ-aba from terrestrial sources. In the CH chondrites, the $\delta^{13}C$ ratios for D-ala were also in

Table 4. Summary of the average blank-corrected amino acid concentrations in the unhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot water extracts of CB carbonaceous chondrites and related samples.[a]

Amino acid	Porcelain		MAC 02675 (CBb)		MIL 05082 (CB)		MIL 07411 (CB)	
	Free	Total	Free	Total	Free	Total	Free	Total
D-asp	0.4 ± 0.3	1.0 ± 0.7	0.1 ± 0.1	3 ± 0.1	12 ± 7	40 ± 6	3.1 ± 1.5	6.4 ± 0.5
L-asp	21 ± 7	2.6 ± 2.0	<0.1	14 ± 5	33 ± 18	47 ± 3	2.8 ± 1.4	10 ± 1
L-glu	<0.1 ±	14 ± 9	<0.1	41 ± 2	10 ± 2	59 ± 5	1.6 ± 1.1	23 ± 2
D-glu	<0.1 ±	5.7 ± 3.3	0.2 ± 0.1	10 ± 1	2.9 ± 0.4	42 ± 4	2.3 ± 1.0	14 ± 1
D-ser	1.5 ± 1	1.0 ± 0.8	2.0 ± 0.2	3.8 ± 0.9	6.9 ± 0.9	10 ± 1	0.9 ± 0.5	0.9 ± 0.2
L-ser	25 ± 12	11 ± 7	1.5 ± 1.8	24 ± 8	42 ± 23	23 ± 9	1.7 ± 1.2	9.0 ± 1.5
gly	19 ± 8	6.8 ± 3.4	4.9 ± 4.9	39 ± 6	222 ± 57	900 ± 96	24 ± 11	55 ± 5
β-ALA	1.4 ± 0.8	1.9 ± 1.3	5.5 ± 1.4	25 ± 1	97 ± 4	267 ± 32	13 ± 2	28 ± 1
γ-ABA	2.6 ± 1.0	1.4 ± 1.0	6.4 ± 2.2	72 ± 6	31 ± 4	177 ± 13	5.9 ± 2.2	29 ± 3
D,L-β-AIB[b]	<0.1	<0.1	<0.1	<0.1	8.9 ± 0.8	21 ± 9	1.0 ± 0.1	15 ± 1
D-ala	0.2 ± 0.1	<0.1	0.1 ± 0.1	2.7 ± 1.2	42 ± 2	147 ± 11	5.7 ± 1.6	15 ± 1
L-ala	4.1 ± 2.7	<0.1	0.7 ± 0.7	11 ± 3	40 ± 2	125 ± 16	4.6 ± 2.3	<22 ±
D-β-ABA	0.4 ± 0.2	0.4 ± 0.3	<0.1	<0.1	14 ± 1	32 ± 5	3.2 ± 0.5	7.5 ± 3.2
L-β-ABA	<0.1	0.2 ± 0.2	<0.1	<0.1	13 ± 1	30 ± 4	1.5 ± 0.2	3.7 ± 2.1
α-AIB	1.6 ± 0.9	<0.1	0.2 ± 0.1	<0.1	23 ± 3	57 ± 8	2.7 ± 0.7	6 ± 1
DL-α-ABA[c]	0.1 ± 0.1	0.4 ± 0.3	<0.1	<0.1	20 ± 4	69 ± 6	4.6 ± 1.3	13 ± 1
ε-ACA	<0.1	63 ± 43	180 ± 23	532 ± 86	350 ± 38	2,811 ± 915	21 ± 2.7	249 ± 22
3-a-2,2-dmpa	<0.1	<0.1	<0.1	<0.1	7.6 ± 1.0	22 ± 1	0.4 ± 0.2	1.4 ± 0.2
D-4-apa	<0.1	<0.1	<0.1	<0.1	4.8 ± 2.4	16 ± 2	0.1 ± 0.1	1.4 ± 0.2
DL-4-a-3mba	<0.1	<0.1	<0.1	<0.1	8.4 ± 0.9	63 ± 7	0.3 ± 0.2	3.6 ± 0.6
DL-3-a-2-mba[b]	<0.1	<0.1	<0.1	<0.1	3.9 ± 0.5	11 ± 1	0.4 ± 0.3	1.6 ± 0.3
DL-3a-2-epa[c]	<0.1	<0.1	<0.1	<0.1	5.0 ± 1.8	16 ± 3	0.5 ± 0.3	2.5 ± 0.8
5-apa	<0.1	0.3 ± 0.2	3.9 ± 1.2	5.2 ± 1.2	4.1 ± 1.0	30 ± 5	0.6 ± 0.4	6.4 ± 0.7
DL-4-a-2mba	<0.1	<0.1	<0.1	<0.1	2.3 ± 1.0	18 ± 3	0.1 ± 0.1	1.0 ± 0.2
L-4-apa	<0.1	<0.1	<0.1	<0.1	2.3 ± 0.4	14 ± 1	0.2 ± 0.1	2.1 ± 0.1
D-iva	<0.1	<0.1	<0.1	<0.1	5.3 ± 0.9	17 ± 1	0.6 ± 0.2	2.1 ± 0.2
D-3-apa	<0.1	<0.1	<0.1	<0.1	1.9 ± 0.7	5 ± 1	0.4 ± 0.3	0.8 ± 0.2
L-iva	<0.1	<0.1	<0.1	<0.1	7.3 ± 0.9	20 ± 1	1.0 ± 0.3	3.0 ± 0.3
L-3-apa	<0.1	<0.1	<0.1	<0.1	1.9 ± 0.2	5 ± 1	0.2 ± 0.1	0.6 ± 0.2
L-val	1.5 ± 1.5	4.5 ± 0.2	1.9 ± 0.6	9.0 ± 1.3	8.0 ± 3.9	23 ± 2	1.3 ± 0.6	7.2 ± 0.5
D-val	<0.1	<1.2	<0.1	0.5 ± 0.1	2.3 ± 0.8	12 ± 1	1.5 ± 0.6	2.9 ± 0.2
D,L-norval[c]	<0.1	<0.1	<0.1	<0.1	1.4 ± 0.1	4 ± 1	0.3 ± 0.2	0.9 ± 0.2
C5 total	1.5 ± 1.5	6.0 ± 0.3	5.8 ± 1.4	15 ± 2	66 ± 6	276 ± 10	±	37 ± 2
Total[d]	82 ± 15	52 ± 13	27 ± 6	260 ± 13	683 ± 62	2,323 ± 106	86 ± 12	268 ± 7
%free	100%		10%		29%		31%	

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

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

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

[d]The amino acid totals include all compounds in this table except ε-aca.

the extraterrestrial range but were lower than the corresponding values for L-ala; the presence of additional fragments in the GC-MS spectra of the D-ala peaks from extracts of these meteorites indicates there is an unidentified amino acid co-eluting with these compounds.

Thus, based on the presence of many terrestrially rare amino acids including α-aib, β-aba, and β-aib, nearly racemic D/L ratios for β-aba, and the extraterrestrial isotope ratios of other amino acids, we conclude that a large majority of the amino acids in PCA 91467, PAT 91546, and MIL 05082 are

Table 5. Meteorite weathering grade and D/L ratios of chiral amino acids in the acid-hydrolyzed meteorite extracts.

Name	ALH 85085	PCA 91467	PAT 91546	MAC 02675	MIL 05082	MIL 07411
Classification	CH3	CH3	CH3	CBb	CB	CB
Weathering grade[a]	A/B	B/C	B/C	B	B	B/C
asp	0.36 ± 0.05	0.57 ± 0.14	0.64 ± 0.19	0.21 ± 0.08	0.85 ± 0.14	0.60 ± 0.08
glu	1.0 ± 0.13	0.91 ± 0.20	1.1 ± 0.17	0.24 ± 0.03	0.71 ± 0.09	0.61 ± 0.14
ser	0.05 ± 0.01	0.43 ± 0.06	0.50 ± 0.15	0.16 ± 0.06	0.43 ± 0.18	0.11 ± 0.03
ala	0.89 ± 0.07	1.1 ± 0.22	1.1 ± 0.33	0.25 ± 0.13	1.2 ± 0.17	>0.68
val	0.43 ± 0.07	0.33 ± 0.14	0.34 ± 0.14	<0.05	0.52 ± 0.06	0.40 ± 0.09

[a]The weathering grades range from A to C and are defined as A: Minor rustiness; rust haloes on metal particles and rust stains along fractures are minor; B: Moderate rustiness; large rust haloes occur on metal particles and rust stains on internal fractures are extensive; and C: Severe rustiness; metal particles have been mostly stained by rust throughout.

Table 6. Summary and comparison of $\delta^{13}C$ values (‰) of amino acids in carbonaceous chondrites.

Amino acid	PAT 91546 CH3 (this study)		PCA 91467 CH3 (this study)		MIL 05082 CB (this study)	Murchison CM2 (Elsila et al. 2012)	GRA 95229 CR2 (Elsila et al. 2012)	QUE 99177 (CR3) (Elsila et al. 2012)
Processing	Free	Total	Free	Total	Total	Total	Total	Total
Gly	46 ± 7	39 ± 4	56 ± 6	47 ± 3	11 ± 3	13 ± 3	35 ± 9	42 ± 12
β-ala	5 ± 3[a]	15 ± 2	19 ± 4	14 ± 3	−6 ± 3	21 ± 3	8 ± 20	−1 ± 6
D-ala	21 ± 1[b]	22 ± 1[b]	22 ± 5[b]	24 ± 4[b]	nd[c]	38 ± 10	40 ± 3	38 ± 10
L-ala	35 ± 3	31 ± 3	35 ± 4	29 ± 5	10 ± 3	40 ± 9	38 ± 2	39 ± 4
D-β-aib	nd	nd	nd	10 ± 5	nd	nd	nd	nd
L-β-aib	nd	nd	nd	8 ± 3	nd	nd	nd	nd
γ-aba	nd	nd	nd	nd	−22 ±8	17 ± 10	10 ± 14	−10 ± 4

[a]β-ala in this sample co-eluted with L-β-aba.
[b]Sarcosine (N-methylglycine) and D,L-N-methylalanine were found to co-elute with D-ala in these samples.
[c]Not determined.

extraterrestrial in origin. In addition, it appears reasonable to conclude that many of the amino acids in the CB chondrite MIL 07411 are also extraterrestrial because the distributions of amino acids in MIL 05082 and MIL 07411 are very similar. It is curious that in the CBb chondrite MAC 02675, the most abundant amino acids are straight-chain, amine-terminal amino acids (n-ω-amino acids; gly, β-ala, γ-aba, and 5-apa), a distribution similar to what has been observed previously in thermally altered meteorites (Burton et al. 2012a). However, because MAC 02675 has only trace levels of proteinogenic amino acids with low D/L ratios, it is difficult to ascertain whether any of its proteinogenic amino acids are indigenous since the abundances were too low to make carbon isotope measurements.

Differences in Relative Amino Acid Isomer Abundances Among Carbonaceous Chondrites

A striking feature of the amino acid contents of the CH chondrites and CB chondrites is high abundances of β-amino acids relative to their α-amino acid counterparts, particularly in the four-carbon (C4) amino acids (Fig. 3). These distributions more closely resemble those of meteorites such as GRO 95577 (CR1) and the type 2 ungrouped Bells meteorite (Monroe and Pizzarello 2011) than type 2 CR or CM chondrites, such as Murchison, that contain primarily α-aib. The CH and CB chondrites also have elevated abundances of γ-aba relative to α-amino isomers; in the case of the CBb chondrite, MAC 02675, γ-aba was the only C4 amino acid detected above 0.1 ppb. Comparing the five-carbon (C5) amino acid distributions of CI, CM, and CR chondrites revealed that the more aqueously altered meteorites (CI1, CM1, and CR1) tended to have more γ- and δ-amino acid isomers while the less altered chondrites (CM2, CR2, and CR3) predominantly contained α-amino acid isomers (Glavin et al. 2010b). The CH and CB chondrites analyzed here do not closely resemble either group, but rather have roughly equal distributions of each of the four possible isomer groups (Fig. 4).

The observed widespread prevalence of non-α-amino acid isomers in a variety of meteorites exposes a limitation in our understanding of meteoritic amino
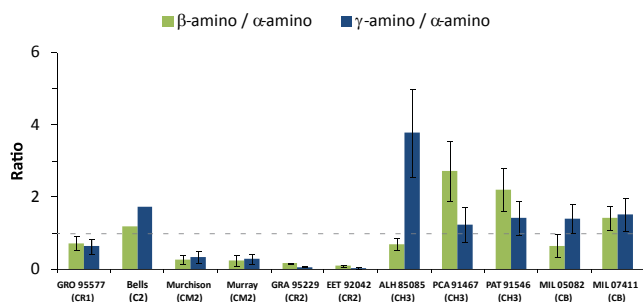
Fig. 3. Isomeric ratios of the four-carbon aliphatic, acyclic, primary mono-amino, mono carboxylic acids in carbonaceous chondrites. The β-amino/α-amino ratio was calculated from the abundances of β-aba, β-aib, α-aba, and α-aib; the γ-amino/α-amino ratio was obtained from the abundances of γ-aba, α-aba, and α-aib. Amino acid data for the following meteorites were obtained from the literature: GRO 95577 and EET 92042 (Glavin et al. 2010b); Bells (Monroe and Pizzarello 2011); Murchison and Murray (Ehrenfreund et al. 2001); GRA 95229 (Martins et al. 2007; Pizzarello and Holmes 2009). Error bars were generated from the errors reported for each meteorite, except Bells for which no errors were reported (Monroe and Pizzarello 2011). The dashed line indicates a ratio of 1.

acid chemistry. The Strecker-cyanohydrin pathway (Miller 1953; Peltzer et al. 1984) is generally accepted as the likely synthetic route to meteoritic amino acids; we note that reductive amination pathways have also been proposed for the prebiotic formation of α-amino acids from α-keto acids (Huber and Wächtershäuser 2003), although it is unclear how well these reactions translate to meteoritic conditions. The formation of β-amino acids is also plausibly explained by the Michael addition reaction under aqueous conditions within the meteorite parent body. On the other hand, the formation pathways for γ- and δ-amino acids are less clearly understood (Burton et al. 2012b). The presence of γ- and δ-lactams, cyclized forms of γ- and δ-amino acids, was previously reported for the Murchison meteorite (Cooper and Cronin 1995). The source of the lactams, however, remains unclear. The higher relative abundances of γ- and δ-amino acids observed in several aqueously altered meteorite types (Fig. 3) and in thermally altered meteorites (Glavin et al. 2010a; Burton et al. 2011, 2012a) reinforces the need for additional work to understand relevant pathways for
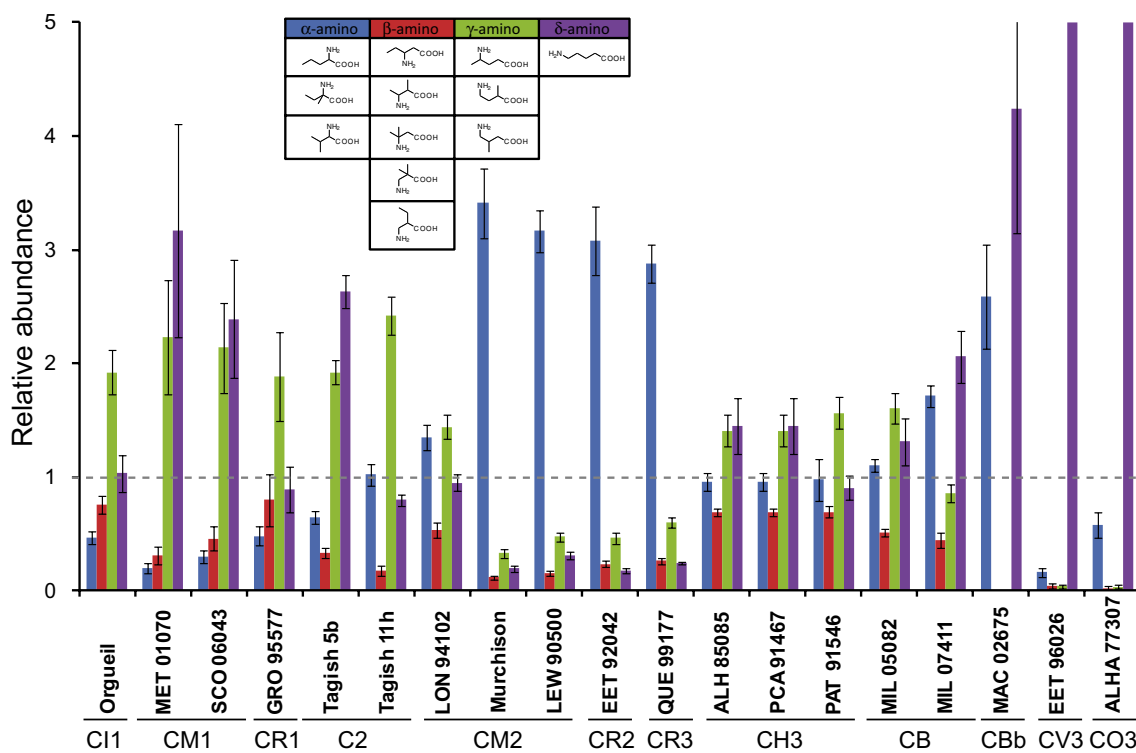

Fig. 4. A comparison of the relative molar abundances of the C5 amino acids in CI, CM, CR, CH, CB, CV, CO, and ungrouped carbonaceous chondrites as a function of amine position (α-, β-, γ-, and δ-) normalized to the total number of possible structural isomers. The dashed line corresponds to the expected relative abundance if the amino acids were formed by a completely non-selective synthetic process. The relative abundance data for the following meteorites were taken from the literature: MET 01070, SCO 06043, and GRO 95577 (Glavin et al. 2010b); Orgueil, LON 94102, Murchison (USNM 6650), LEW 90500, EET 92042, and QUE 99177 (Glavin and Dworkin 2009); Tagish Lake (Herd et al. 2011; Glavin et al. 2012); EET 96026 and ALHA 77307 (Burton et al. 2012a). In most cases there is structural similarity in C5 amino acid relative abundances within a single meteorite group; however, between meteorite groups a great deal of variability is observed.

these amino acid isomers. Irradiation of assorted aqueous solutions containing amines and carboxylic acids in the presence of CO_2 or ammonia, respectively, was shown to produce a spectrum of amino acid isomers (Getoff and Schenck 1967, 1968), and these types of reactions may satisfactorily explain the diversity of amino acid isomers observed in CI, CH, and CB chondrites; that they could be driven by γ-rays from ^{60}Co, a daughter isotope produced during the decay of ^{60}Fe to ^{60}Ni, suggests that they may be relevant to meteoritic amino acid synthesis during aqueous alteration. These experiments warrant revisiting under conditions explicitly relevant to meteorite parent bodies to assess their validity.

Enantiomeric Excesses of Isovaline in CH and CB Chondrites

Lastly, we observed L-enantiomeric excesses for the nonproteinogenic amino acid isovaline (L-ee) in all three of the CH chondrites and two of the three CB chondrites that we analyzed ranging from 5 to approximately 20% (Table 7); the third CB, MAC 02675, did not contain isovaline above 0.1 ppb. L-isovaline has now been observed in enantiomeric excess in five carbonaceous chondrite groups: CH and CB (this study), CI and CM (Cronin and Pizzarello 1997; Glavin and Dworkin 2009), and CR chondrites (Glavin et al. 2010b) as well as the ungrouped C2 carbonaceous chondrite Tagish Lake (Glavin et al. 2012). We previously reported a correlation between the degree of aqueous alteration in a given meteorite and its L-isovaline ee (Glavin and Dworkin 2009; Glavin et al. 2010b). It is difficult to assess how well the CB and CH chondrites fit this trend despite the nominal designation of type 3 for the CH chondrites because both CB and CH chondrites are composed of a heterogeneous mix of heavily hydrated and anhydrous materials (Greshake et al. 2002). However, we have previously observed that the β-ala/α-aib ratio (Glavin and Dworkin 2009) and β-ala/gly (Herd et al. 2011) empirically appears to correlate with the aqueous alteration with higher ratios found in more altered material. While there is currently no rationale for the relationship, when comparing the CB and CH chondrites studied here, we observe a similar correlation with higher L-isovaline excesses in samples with higher β-ala/gly ratios within the same meteorite group. The overall abundances of the isovaline in the CH and CB chondrites appear to more closely resemble type 1 chondrites than type 3, as do the observed isovaline enantiomeric excesses in MIL 05082, MIL 07411, and PCA 91467. In any case, the presence of slight to significant L-ee of isovaline appears to be

Table 7. L-isovaline enantiomeric excesses in carbonaceous chondrites.

Sample	Classification	Isovaline (% ee)
ALH 85085	CH3	20.5 ± 7.1[a]
Orgueil	CI1	15.2 ± 4.0[b]
SCO 06043	CM1	16.5 ± 7.5[c]
GRO 95577	CR1	11.0 ± 7.2[c]
Murchison	CM2	17.2–18.5[c]
Murchison	CM2	8.4[d]
Murchison	CM2	0–15.2[e]
MIL 07411	CB	14 ± 4[a]
PCA 91467	CH3	13 ± 3[a]
MIL 05082	CB	9.7 ± 3.0[a]
Murray	CM2	6.0[f]
PAT 91546	CH3	5 ± 2[a]
LEW 90500	CM2	3.3 ± 1.8[b]
QUE 99177	CR3	0.3 ± 2.1[b]
Tagish Lake 5b	C2	7.0+/−1.9[g,h]

[a]This study; [b]Glavin and Dworkin (2009); [c]Glavin et al. (2010b); [d]Cronin and Pizzarello (1997); [e]Pizzarello et al (2003); [f]Pizzarello and Cronin (2000); [g]Herd et al. (2011); [h]Glavin et al. (2012).

common in aqueously altered meteorites, even across a wide range of mineralogical compositions and degrees of aqueous alteration. Intriguingly, *in every case where a meteoritic enantiomeric excess of isovaline has been measured, it is in favor of the L-enantiomer*. That the L-enantiomer, the same chirality used in the proteins of all forms of life on Earth, is the favored isomer in so many different meteorites suggests that life on Earth, and perhaps elsewhere in the solar system, was biased from the very beginning.

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