

Amino acid analyses of R and CK chondrites

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Abstract—Exogenous delivery of amino acids and other organic molecules to planetary surfaces may have played an important role in the origins of life on Earth and other solar system bodies. Previous studies have revealed the presence of indigenous amino acids in a wide range of carbon-rich meteorites, with the abundances and structural distributions differing significantly depending on parent body mineralogy and alteration conditions. Here we report on the amino acid abundances of seven type 3–6 CK chondrites and two Rumuruti (R) chondrites. Amino acid measurements were made on hot water extracts from these meteorites by ultrahigh-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry. Of the nine meteorites analyzed, four were depleted in amino acids, and one had experienced significant amino acid contamination by terrestrial biology. The remaining four, comprised of two R and two CK chondrites, contained low levels of amino acids that were predominantly the straight chain, amino-terminal (*n*- ω -amino) acids β -alanine, and γ -amino-*n*-butyric acid. This amino acid distribution is similar to what we reported previously for thermally altered ureilites and CV and CO chondrites, and these *n*- ω -amino acids appear to be indigenous to the meteorites and not the result of terrestrial contamination. The amino acids may have been formed by Fischer–Tropsch-type reactions, although this hypothesis needs further testing.

INTRODUCTION

Amino acids are the monomers of proteins; they are ubiquitous in life and likely trace to the earliest ancestral biochemistry. Indigenous amino acids have been found in many classes of meteorites, suggesting they were delivered to the prebiotic Earth by meteorites as well. Our knowledge of meteoritic amino acids, and indeed, prebiotic chemistry in general, has been greatly informed by analyses of type 2 CM chondrites, notably Murchison and Murray (Degens and Bajor 1962; Kvenvolden et al. 1970; Cronin and Moore 1971; Cronin and Chang 1993). A combination of advances in analytical technology and a steady

supply of relatively uncontaminated meteorites recovered as falls and Antarctic finds have led to several important discoveries in the last three decades. These include the detection of amino acids in meteorites with varied mineralogies and petrographies, including extensive aqueous alteration and thermal metamorphism (Ehrenfreund et al. 2001; Glavin et al. 2006, 2010a, 2010b; Botta et al. 2007; Martins et al. 2007; Pizzarello and Holmes 2009; Burton et al. 2011, 2012a, 2012b, 2013; Callahan et al. 2013). In addition, chiral excesses of multiple amino acids of extraterrestrial origin have been observed in some carbonaceous meteorites, suggesting that the origins of homochirality, a hallmark of life on Earth, may have

originated prior to the origins of life (Cronin and Pizzarello 1997; Engel and Macko 1997; Pizzarello and Cronin 2000; Glavin and Dworkin 2009; Elsilá et al. 2012b; Glavin et al. 2012; Pizzarello and Monroe 2012; Pizzarello et al. 2012; Burton et al. 2013).

Of the meteorites that have been analyzed for amino acids, these compounds are found to be most abundant in carbonaceous chondrites. To date, seven of the eight distinct groups of carbonaceous chondrites have been reasonably well studied, with multiple meteorites from each group having been analyzed for amino acids. CK chondrites are the exception, with only one published analysis of a single CK meteorite in the literature (Botta et al. 2008). Trace levels (<20 ppb each) of glycine, β -alanine, and γ -amino-*n*-butyric acid were reported in the CK5 chondrite La Paz Icefield (LAP) 03874 (Botta et al. 2008). Analyses of Antarctic ice samples collected from beneath the meteorite revealed amino acid levels that were much lower and in very different distributions than was observed in the meteorite, indicating that the amino acids detected in this meteorite were likely indigenous. The amino acid distributions observed in this meteorite resemble what we have observed for other thermally metamorphosed meteorites including CV and CO chondrites, ureilites, and the Martian shergottite Roberts Massif (RBT) 04262 (Burton et al. 2012a; Callahan et al. 2013). This observation coupled with the assertion that CV and CK chondrites may have come from a common parent body (Greenwood et al. 2010; Wasson et al. 2013) led us to revisit amino acid analyses of CK chondrites. The CK chondrites, like the oxidized CV chondrite subgroups (oxA and oxB), were highly oxidized on their parent body during hydrothermal alteration and exhibit the whole range of metamorphic petrologic types from 3 to 6 (Greenwood et al. 2010). We also analyzed two R chondrites, another group of highly oxidized meteorites that also have experienced a range of thermal metamorphism (Rubin and Kallemeyn 1994; Kallemeyn et al. 1996; Bischoff 2000; Bischoff et al. 2011). Here we report the amino acid contents of seven CK chondrites spanning alteration types 3–6: CK3 Northwest Africa (NWA) 5956, CK4 Larkman Nunatak (LAR) 04318, CK4 Allan Hills (ALH) 85002, CK4/5 Pecora Escarpment (PCA) 82500, CK5 Elephant Moraine (EET) 92002, CK6 Lewis Cliff (LEW) 87009, and CK6 LAR 06872; and two R chondrites: R3 La Paz Icefield (LAP) 03834 and R4 LAP 031135, by ultrahigh-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (UPLC-FD/ToF-MS).

Table 1. Summary of samples analyzed in this study.

Sample name	Classification	Parent, split	Mass extracted (mg)
NWA 5956	CK3	N/A	268
LAR 04318	CK4	23, 0	427
ALH 85002	CK4	88, 75	426
PCA 82500	CK4/5	43, 19	456
EET 92002	CK5	46, 21	420
LEW 87009	CK6	51, 38	466
LAR 06872	CK6	13, 0	465
LAP 03834	R3	13, 0	316
LAP 031135	R4	4	38
Serpentine	Control	N/A	474

MATERIALS AND METHODS

Chemicals and Reagents

Sample-handling tools, ceramics, and glassware were all rinsed with Millipore Integral 10 UV (18.2 M Ω cm, <3 parts-per-billion [ppb] total organic carbon) ultrapure water, hereafter referred to as water, wrapped in aluminum foil, and heated in air at 500 °C for 18–24 h to clean them of organic residue. Most of the chemicals used were purchased from Fischer Scientific, Sigma-Aldrich, or Acros Organics. Details on the sources of specific five-carbon (C₅) amino acids used as standards are available in 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 heated in air at 500 °C for 3 h prior to dissolution in water. All other solutions were prepared as described by Glavin et al. (2006).

Meteorite Samples and Controls

Antarctic meteorite samples were allocated by the Meteorite Working Group and provided by NASA Johnson Space Center. NWA 5956, found in Northwest Africa, was purchased from a private seller. Additional information about specific samples is given in Table 1. Samples were crushed into a powder using a clean mortar and pestle in a Class 100 Labconco laminar flow hood under HEPA-filtered positive pressure. Crushed serpentine that had been heated at 500 °C in air for 3 h and procedural reagent blanks were processed in parallel to the meteorite samples as controls.

Extraction Procedures and Analytical Techniques

The meteorite samples and controls described above were sealed in glass ampoules with 1 mL water and placed in an oven set at 100 °C for 24 h. After extraction, the tubes were cooled and centrifuged for 5 min. (Labconco Centrивap) to separate solid particulate from water supernatant. Half of the water extract was dried under vacuum and subjected to acid hydrolysis under 6 M HCl vapor at 150 °C for 3 h to liberate amino acids in bound or precursor forms. The remaining water extract (unhydrolyzed extract) and the acid-hydrolyzed extract, containing free and free + bound amino acids, respectively, were dried under vacuum (Labconco Centrивap) and redissolved in 1 mL of water. Both hydrolyzed and nonhydrolyzed water extracts were desalted by cation exchange chromatography using prepacked columns (AG 50W-X8 resin, 100–200 mesh, hydrogen form, BioRad), and the NH₄OH eluates derivatized with *o*-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC) fluorescent derivatization as previously described (Glavin et al. 2006).

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

RESULTS AND DISCUSSION

Amino Acid Analyses and Terrestrial Contamination

We endeavored to quantitate a broad suite of amino acids in the CK and R chondrites analyzed

here, including the proteinogenic amino acids aspartic acid, glutamic acid, glycine, alanine, serine, threonine, and valine, as well as many other two- to five-carbon aliphatic, monoamino, monocarboxylic acid amino acids, and the six-carbon amino acid ϵ -amino-*n*-caproic acid (Tables 2–4). Other primary amines and amino acids, had they been present, would also have been detected and characterized. Representative LC–MS chromatograms are given in Fig. 1. Most of the meteorites were highly depleted in amino acids, with five of the eight samples containing fewer than 200 ppb of total amino acids (Tables 2–4). Amino acids were most abundant in NWA 5956, PCA 82500, and LEW 87009, ranging from 400 to 3000 ppb, similar to levels observed previously in Antarctic CO and CV chondrites (Burton et al. 2012a). To assess the degree of biological contamination these samples experienced, we considered the total and relative abundances of the D- and L-enantiomers of several chiral amino acids found in proteins including aspartic acid, glutamic acid, serine, alanine, and valine. Were these amino acids to be extraterrestrial in origin, we would expect them to be racemic (L ≈ D). All of the proteinogenic amino acid D/L ratios we measured were significantly less than one and many were lower than 0.4 (Table 5); in the absence of compelling evidence to the contrary, such as extraterrestrial values for stable isotopic ratios of the individual amino acid enantiomers (e.g., Glavin et al. 2012), we assume that these proteinogenic amino acids are the result of terrestrial contamination, potentially originating from one or more of the following sources: transit through the atmosphere; the impact and residence environment; handling for collection, curation, and allocation; and laboratory processing. However, several of the meteorites also contain nonproteinogenic amino acids that do appear to be of extraterrestrial origins. More detailed discussions of the amino acid contents of individual meteorites are given in the following sections.

Many of the Antarctic meteorites contain elevated levels of ϵ -amino-*n*-caproic acid (ϵ -aca). This compound is likely to be a contaminant, as Antarctic meteorites collected prior to 2007 were stored in bags made of Nylon-6, the monomer of which is ϵ -aca (since 2007, it has become standard practice to collect meteorites in Teflon bags [Harvey et al. 2014]). In most of the meteorites we analyzed, more than 90% of the ϵ -aca is present in a bound form (either as part of the Nylon-6 polymer or as the activated monomer ϵ -aminocaprolactam), and ϵ -aca derived from the Nylon sample collection bags is found overwhelmingly in the bound form (Glavin et al. 2006), suggesting the bags are the likely source for

Table 2. Summary of the average blank-corrected amino acid concentrations (ppb) in the unhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot water extracts of CK3-4 carbonaceous chondrites.^a

Amino acid	NWA 5956 (CK3)		LAR 04318 (CK4)		ALH 85002 (CK4)	
	Free	Total	Free	Total	Free	Total
D-asp	15 ± 6	60 ± 34	0.1 ± 0.1	<1	0.1 ± 0.1	<1
L-asp	151 ± 84	166 ± 5	1.2 ± 0.3	<5	12 ± 1	<3
L-glu	26 ± 13	486 ± 202	1.9 ± 0.9	<3	35 ± 2	<2
D-glu	4.2 ± 0.8	115 ± 27	5.7 ± 0.4	<1	6.9 ± 0.7	<1
D-ser	68 ± 23	100 ± 28	0.3 ± 0.1	<1	0.2 ± 0.1	<1
L-ser	263 ± 81	270 ± 57	1.2 ± 0.1	<19	33 ± 1	<13
gly	207 ± 61	623 ± 193	5.3 ± 0.8	19 ± 2	9.8 ± 0.4	13 ± 1
β-ala	248 ± 99	734 ± 259	13 ± 1	18 ± 2	0.3 ± 0.1	6.3 ± 0.8
γ-aba	8.4 ± 3.1	56 ± 12	6.1 ± 0.3	12 ± 1	0.9 ± 0.1	17 ± 2
D,L-β-aib ^b	0.9 ± 0.2	7.0 ± 1.0	<0.1	<0.1	<0.1	<0.1
D-ala	61 ± 26	143 ± 49	0.2 ± 0.2	<2	0.1 ± 0.1	<1
L-ala	166 ± 66	212 ± 64	1.0 ± 0.8	<10	47 ± 0.2	<6
D-β-ABA	0.7 ± 0.1	3.4 ± 0.4	0.1 ± 0.1	<0.2	0.1 ± 0.1	<0.1
L-β-ABA	0.7 ± 0.2	1.6 ± 0.5	<0.1	<0.2	0.1 ± 0.1	<0.1
α-AIB	2.8 ± 1.6	22 ± 6	0.4 ± 0.1	<0.8	<0.1	<0.7
D,L-α-ABA ^b	0.4 ± 0.3	4.1 ± 0.5	<0.1	<0.1	<0.1	<0.1
ε-aca	4.0 ± 1.0	41 ± 10	1.9 ± 0.2	15 ± 1	10 ± 1	358 ± 3
3-a-2,2-dmpa	<0.1	5.1 ± 0.6	<0.1	<0.1	<0.1	<0.1
D,L-4-apa ^c	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-4-a-3-mba	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-3-a-2-mba ^c	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3-a-3-mba ^d	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-3-a-2-epa ^b	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-apa	0.1 ± 0.1	2.6 ± 0.5	0.1 ± 0.1	0.3 ± 0.3	0.1 ± 0.1	1.2 ± 0.4
D,L-4-a-2mba	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D-iva	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-3-apa ^c	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
L-iva (2-a-2mba)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
L-val (2-a-3-mba)	24 ± 1	57 ± 10	<0.1	<5	22 ± 11	<3
D-val (2-a-3-mba)	<0.1	2.2 ± 0.8	<0.1	<0.1	<0.1	<0.1
D,L-norval (2-apa)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total ^e	1247 ± 181	3068 ± 397	36 ± 2	94 ± 3	168 ± 11	68 ± 3
% free	41%		38.3%		100%	

^aAll values are reported in ppb on a bulk sample basis. Extracts 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-ToF-MS data, the monoisotopic masses of each protonated OPA/NAC amino acid derivative ($M+H^+$) was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The uncertainties (δx) are based on the standard deviation of the average value of at least three separate measurements (n) with a standard error, $\delta x = \sigma x \cdot (n - 1)^{-1/2}$.

^bEnantiomers could not be separated under the chromatographic conditions.

^cEnantiomers were separated but could not be identified due to a lack of optically pure standards.

^d3-amino-3-methylbutanoic acid co-elutes with one of the enantiomers of D,L-4-aminopentanoic acid; therefore, upper limits for 3-amino-3-methylbutanoic acid were estimated by taking the difference in peak areas of the two D,L-4-aminopentanoic acid enantiomers.

^eTotal (free + bound) amino acid abundances are the sum of all amino acids included in the table except ε-aca.

most, if not all, of this amino acid. In the two most metamorphosed samples analyzed here (petrologic type 6), LEW 87009 and LAR 06872, however, closer to 50% of the ε-aca is present in its free form, making it possible that some of the ε-aca in these samples was indigenous as less than 0.06% of total ε-aca in hot water extracts of Nylon-6 bag material was in the free form (Glavin et al. 2006).

Evidence for Extraterrestrial Amino Acids in LAP 03834 (R3), LAP 031135 (R4), PCA 82500 (CK4/5), and LEW 87009 (CK6)

Discounting ε-aca for the reasons discussed above, the most abundant amino acids in these four meteorites are the straight chain, amine-terminal amino acids (n -ω-amino acids) glycine, β-ala, and γ-aba, in order of

Table 3. Summary of the average blank-corrected amino acid concentrations (ppb) in the unhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot water extracts of CK4-6 carbonaceous chondrites.^a

Amino acid	PCA 82500 (CK4/5)		EET 92002 (CK5)		LEW 87009 (CK6)		LAR 06872 (CK6)	
	Free	Total	Free	Total	Free	Total	Free	Total
D-asp	<0.1	2.2 ± 1.5	0.4 ± 0.1	0.5 ± 0.2	0.8 ± 0.1	1.1 ± 0.2	0.4 ± 0.1	0.5 ± 0.1
L-asp	0.2 ± 0.1	10 ± 6	0.4 ± 0.2	2.2 ± 0.3	0.6 ± 0.1	2.0 ± 0.1	0.1 ± 0.1	1.7 ± 0.2
L-glu	1.0 ± 0.1	18 ± 4	0.2 ± 0.1	8.1 ± 0.1	0.3 ± 0.1	6.9 ± 0.2	0.1 ± 0.1	1.7 ± 0.2
D-glu	1.7 ± 0.2	5 ± 2	0.1 ± 0.1	1.7 ± 0.5	0.4 ± 0.2	2.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1
D-ser	0.1 ± 0.1	0.4 ± 0.1	<0.1	<0.1	<0.1	0.1 ± 0.1	<0.1	0.1 ± 0.1
L-ser	1.8 ± 0.2	25 ± 2	0.7 ± 0.3	3.0 ± 0.3	<0.1	2.4 ± 0.8	0.9 ± 0.8	7.8 ± 0.9
gly	16 ± 1	59 ± 9	6.1 ± 1.5	21 ± 1	3.8 ± 1.2	45 ± 6	3.0 ± 1.8	14 ± 1
β-ala	36 ± 2	162 ± 20	11 ± 2	19 ± 2	16 ± 2	101 ± 13	7.7 ± 1.0	12 ± 1
γ-aba	42 ± 3	113 ± 18	2.7 ± 0.2	7.1 ± 0.7	37 ± 1	453 ± 137	2.5 ± 0.1	11 ± 1
D,L-β-aib ^b	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D-ala	0.1 ± 0.1	2.6 ± 1.0	0.1 ± 0.1	0.9 ± 0.1	<0.1	0.5 ± 0.4	<0.1	0.2 ± 0.1
L-ala	0.8 ± 0.7	11 ± 4	1.0 ± 0.2	3.2 ± 0.6	<0.1	0.7 ± 0.6	<0.1	3.1 ± 0.1
D-β-ABA	<0.1	<0.1	<0.1	0.1 ± 0.1	<0.1	0.1 ± 0.1	<0.1	<0.1
L-β-ABA	<0.1	<0.1	<0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	<0.1	<0.1
α-AIB	<0.1	<1	0.4 ± 0.1	0.2 ± 0.1	0.5 ± 0.1	<0.1	0.3 ± 0.2	<0.1
D,L-α-ABA ^b	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
ε-aca	52 ± 1	459 ± 19	1.1 ± 0.2	14 ± 4	434 ± 54	870 ± 144	53 ± 12	127 ± 33
3-a-2,2-dmpa	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-4-apa ^c	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-4-a-3mba	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-3-a-2-mba ^c	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3-a-3-mba ^d	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-3-a-2-epa ^b	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-apa	0.7 ± 0.5	3.0 ± 1.3	0.2 ± 0.1	0.1 ± 0.1	5.3 ± 0.2	20 ± 1	0.2 ± 0.1	0.3 ± 0.1
D,L-4-a-2mba	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D-iva	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-3-apa	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
L-iva (2-a-2mba)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
L-val (2-a-3-mba)	12 ± 10	<8	0.3 ± 0.3	2.7 ± 0.5	1.3 ± 0.2	1 ± 0.3	0.1 ± 0.1	2.3 ± 0.4
D-val (2-a-3-mba)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D,L-norval (2-apa)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total ^e	112 ± 13	419 ± 28	24 ± 2	70 ± 2	66 ± 2	635 ± 138	15 ± 2	55 ± 2
%free	26.7%		34.3%		10.4%		27.2%	

^aAll values are reported in ppb on a bulk sample basis. Extracts 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-ToF-MS data, the monoisotopic masses of each protonated OPA/NAC amino acid derivative ($M + H^+$) was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The uncertainties (δx) are based on the standard deviation of the average value of at least three separate measurements (n) with a standard error, $\delta x = \sigma x \cdot (n - 1)^{-1/2}$.

^bEnantiomers could not be separated under the chromatographic conditions.

^cEnantiomers were separated but could not be identified due to a lack of optically pure standards.

^d3-amino-3-methylbutanoic acid co-elutes with one of the enantiomers of D,L-4-aminopentanoic acid; therefore, upper limits for 3-amino-3-methylbutanoic acid were estimated by taking the difference in peak areas of the two D,L-4-aminopentanoic acid enantiomers.

^eTotal (free + bound) amino acid abundances are the sum of all amino acids included in the table except ε-aca.

increasing abundance (Figs. 2 and 3). This matches previous observations of elevated levels of n - ω -amino acids relative to glycine in thermally metamorphosed CO and CV chondrites, shergottites, and ureilites (Burton et al. 2012a; Chan et al. 2012; Callahan et al. 2013). The finding that these amino acids are far more abundant than chiral proteinogenic amino acids in the meteorites suggests that they are not the result of

biological contamination. In addition, we note that only trace amounts of β-ala and γ-aba (0.2 and <0.1 parts-per-trillion [ppt]) were detected in a sample of Antarctic ice from the La Paz Icefield and neither was detected above 0.01 ppt in ice from the Northern Graves Nunataks region, nor was δ-ava; in both ice samples, L-amino acids such as L-serine, L-aspartic acid, and L-alanine were more abundant than β-ala and γ-aba

Table 4. Summary of the average blank-corrected amino acid concentrations (ppb) in the unhydrolyzed (free) and 6 M HCl acid-hydrolyzed (total), hot water extracts of R3-4 chondrites.^a

Amino acid	LAP 03834 (R3)		LAP 031135 (R4)	
	Free	Total	Free	Total
D-asp	<0.1	<1	<0.1	<0.1
L-asp	0.3 ± 0.1	<5	<0.1	<0.1
L-glu	0.4 ± 0.2	<4	<0.1	<0.1
D-glu	0.3 ± 0.1	<1	<0.1	<0.1
D-ser	0.4 ± 0.1	<1	<0.1	<0.1
L-ser	1.3 ± 0.3	<20	<0.1	<0.1
Gly	4.8 ± 2.4	21 ± 3	<0.1	<0.1
β-ala	4.1 ± 0.5	37 ± 5	6.1 ± 0.5	39 ± 2
γ-aba	5.5 ± 0.3	74 ± 6	31 ± 3	94 ± 1
D,L-β-aib ^b	<0.1	<0.1	<0.1	<0.1
D-ala	0.1 ± 0.1	<2	<0.1	<0.1
L-ala	0.6 ± 0.4	<9	<0.1	<0.1
D-β-ABA	<0.1	<0.2	<0.1	<0.1
L-β-ABA	<0.1	<0.1	<0.1	<0.1
α-AIB	0.1 ± 0.1	<1	<0.1	<0.1
D,L-α-ABA ^b	<0.1	<0.1	<0.1	<0.1
ε-aca	9.3 ± 0.1	508 ± 9	665 ± 82	2030 ± 940
3-a-2,2-dmpa	<0.1	<0.1	<0.1	<0.1
D,L-4-apa ^c	<0.1	<0.1	<0.1	<0.1
D,L-4-a-3mba	<0.1	<0.1	<0.1	<0.1
D,L-3-a-2-mba ^c	<0.1	<0.1	<0.1	<0.1
3-a-3-mba ^d	<0.1	<0.1	<0.1	<0.1
D,L-3-a-2-epa ^b	<0.1	<0.1	<0.1	<0.1
5-apa	0.2 ± 0.1	1.1 ± 0.5	<0.1	<0.1
D,L-4-a-2mba	<0.1	<0.1	<0.1	<0.1
D-iva	<0.1	<0.1	<0.1	<0.1
D,L-3-apa	<0.1	<0.1	<0.1	<0.1
L-iva (2-a-2mba)	<0.1	<0.1	<0.1	<0.1
L-val (2-a-3-mba)	0.6 ± 0.3	<5	<0.1	<0.1
D-val (2-a-3-mba)	<0.1	<0.1	<0.1	<0.1
D,L-norval (2-apa)	<0.1	<0.1	<0.1	<0.1
Total ^e	19 ± 3	180 ± 9	37 ± 4	133 ± 3
% free	10.5%		27.8%	

^aAll values are reported in ppb on a bulk sample basis. Extracts 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-ToF-MS data, the monoisotopic masses of each protonated OPA/NAC amino acid derivative ($M + H^+$) was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The uncertainties (δx) are based on the standard deviation of the average value of at least three separate measurements (n) with a standard error, $\delta x = \sigma x \cdot (n - 1)^{-1/2}$.

^bEnantiomers could not be separated under the chromatographic conditions.

^cEnantiomers were separated but could not be identified due to a lack of optically pure standards.

^d3-amino-3-methylbutanoic acid co-elutes with one of the enantiomers of D,L-4-aminopentanoic acid; therefore, upper limits for 3-amino-3-methylbutanoic acid were estimated by taking the difference in peak areas of the two D,L-4-aminopentanoic acid enantiomers.

^eTotal (free + bound) amino acid abundances are the sum of all amino acids included in the table except ε-aca.

(Glavin et al. 2006; Burton et al. 2012a). Consequently, the most plausible explanation for the *n*-ω-amino acids β-ala, γ-aba, and δ-ava in these meteorites is that these nonprotein amino acids are extraterrestrial in origin. The D/L ratios of the trace chiral proteinogenic amino acids in these meteorites are relatively low (Table 5), however, suggesting these amino acids are derived from biological contamination of the meteorites after fall. It is unclear how

much of the glycine in these meteorites is extraterrestrial, as it is both the most common biological amino acid and found only in low abundance in other thermally metamorphosed meteorites (Burton et al. 2012a). Nevertheless, it appears that these CK and R chondrites do contain some indigenous nonprotein amino acids.

In principle, stable isotope measurements could be used to confirm an extraterrestrial origin for the amino

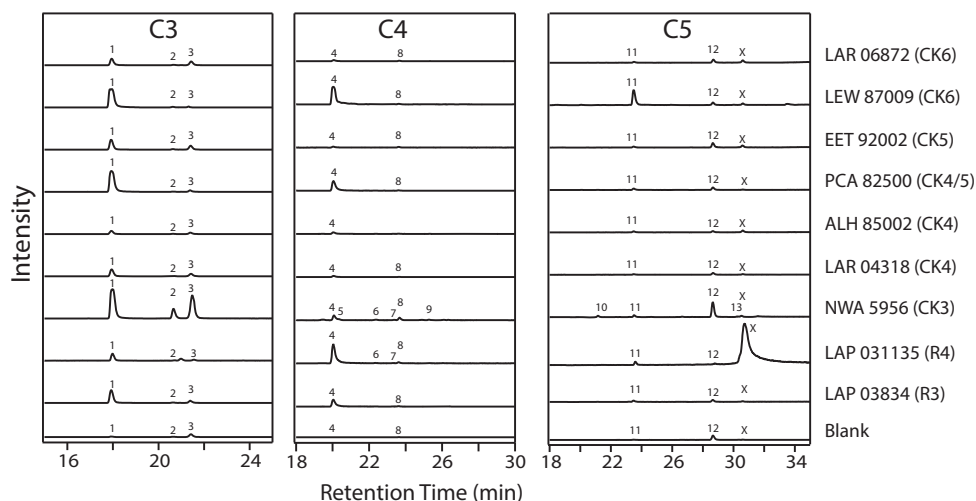


Fig. 1. Representative liquid chromatography–mass spectrometry chromatograms for the acid-hydrolyzed meteorite samples analyzed in this study. Chromatograms shown are for the C3, C4, and C5-carbon primary, aliphatic, acyclic amino acids (derivatized positive ionization mass-to-charge ratios of 351.1015, 365.1171, and 379.1328, respectively). The masses plotted represent a ~ 0.07 Da window (the peak width at half maximum) centered on the corresponding theoretical monoisotopic masses of the mono-protonated positive ions of C3 to C5 OPANAC amino acid derivatives. The C3 and C4 traces are all set to the same scale, while the C5 traces are multiplied by 2. Similar chromatograms were obtained for the nonhydrolyzed fractions. Peak assignments are (1) β -alanine; (2) D-alanine; (3) L-alanine; (4) γ -amino-*n*-butyric acid; (5) D,L- β -aminoisobutyric acid; (6) D- β -amino-*n*-butyric acid; (7) L- β -amino-*n*-butyric acid; (8) α -aminoisobutyric acid; (9) D,L- α -amino-*n*-butyric acid; (10) 3-amino-2,2-dimethylpropanoic acid; (11) δ -amino-*n*-valeric acid; (12) L-valine; (13) D-valine; (X) denotes a nonfluorescent molecule of similar mass to the derivatized amino acids.

Table 5. Summary of D/L-amino acid ratios for the meteorites analyzed in this study.^{a,b}

Amino acid	NWA 5956	LAR 04318	ALH 85002	PCA 82500	EET 92002	LEW 87009	LAR 06872	LAP 03834
Aspartic acid	0.36 ± 0.21	~ 0.2	~ 0.33	0.22 ± 0.2	0.23 ± 0.10	0.55 ± 0.10	0.29 ± 0.07	~ 0.2
Glutamic acid	0.24 ± 0.11	~ 0.3	~ 0.5	0.28 ± 0.13	0.21 ± 0.07	0.30 ± 0.02	0.12 ± 0.06	~ 0.3
Serine	0.37 ± 0.13	~ 0.05	~ 0.08	<0.02	<0.03	0.04 ± 0.04	0.01 ± 0.01	~ 0.05
Alanine	0.67 ± 0.27	~ 0.2	~ 0.2	0.24 ± 0.10	0.28 ± 0.04	0.71 ± 0.83	0.06 ± 0.03	~ 0.2
Valine	0.04 ± 0.02	~ 0.02	~ 0.03	~ 0.01	0.04 ± 0.01	0.10 ± 0.03	0.04 ± 0.01	~ 0.2

^aD/L ratios are approximate where only upper limits were determined for amino acid abundances.

^bValues are not included for LAP 031135 as the listed amino acids were below detection limits.

acids, as amino acids found in CI, CR, CM, CH, and CB chondrites tend to be enriched in heavier isotopes including ^{13}C (Ehrenfreund et al. 2001; Martins et al. 2007; Elsila et al. 2012a; Burton et al. 2013). However, the *n*- ω -amino acids β -ala and γ -aba that are predominant in the CK and R chondrites have $\delta^{13}\text{C}$ ratios that fall below zero in ureilites, shergottites, and CV chondrites, and even in some CM, CR, and CB chondrites with α -amino acids that are significantly enriched in ^{13}C (Burton et al. 2012a, 2013; Elsila et al. 2012a; Callahan et al. 2013). Although only limited $\delta^{13}\text{C}$ data are available for β -ala and γ -aba from terrestrial sources (Burton et al. 2014a), the data that are known indicate that these measurements are not useful for distinguishing between terrestrial and extraterrestrial sources for β -ala and γ -aba in many

meteorites. Other stable isotopes such as δD and $\delta^{15}\text{N}$ may be more useful for differentiating between terrestrial and extraterrestrial origins. Unfortunately, the amounts of sample required for stable isotope measurements are significant (~ 1 nmol for $\delta^{13}\text{C}$, ~ 3 nmol for δD , and ~ 6 nmol for $\sim \delta^{15}\text{N}$). Thus, even for LEW 87009, the meteorite with the highest abundances of β -ala and γ -aba of the four discussed in this section, insufficient material remains from our originally allocated sample to perform even $\delta^{13}\text{C}$ measurements after taking into account desalting recoveries and replicate analyses already performed. Because $\delta^{13}\text{C}$ data alone would likely not be sufficient to determine an extraterrestrial origin, all three stable isotopes would need to be analyzed for LEW 87009. For γ -aba, the most abundant plausibly indigenous

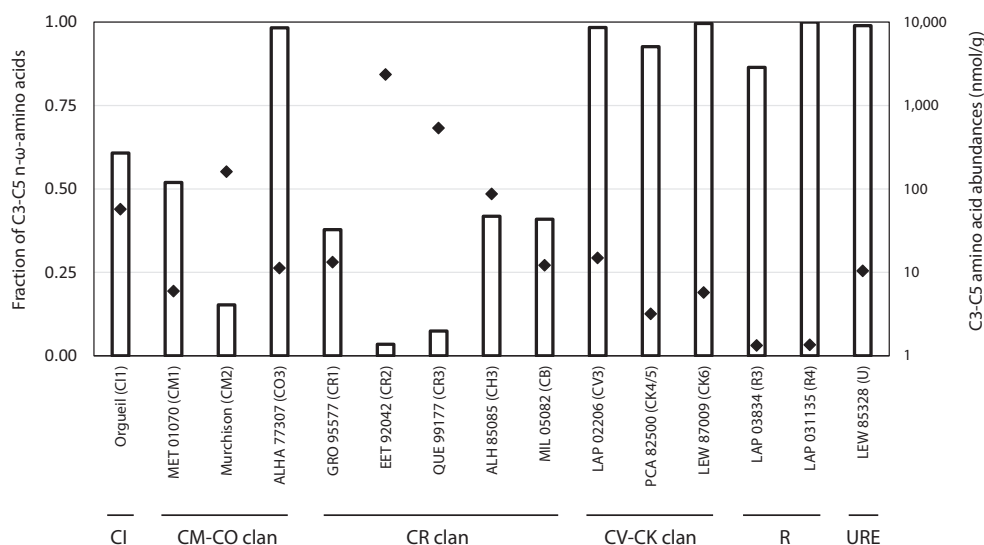


Fig. 2. A comparison of structural distributions and abundances of C3–C5 amino acids in a wide range of amino acid-containing meteorites. The primary axis shows the fraction of C3–C5 amino acids that are *n*- ω -isomers among the eight carbonaceous chondrites groups, R chondrites, and ureilites. Meteorites are ordered according to the classification system in Weisberg et al. (2006). Data are from this study, Burton et al. (2012a), and Glavin et al. (2010b). The secondary axis shows the total abundances of C3–C5 amino acids in these meteorites (black diamonds, nmol g⁻¹). The proportion of amino acids present as *n*- ω -amino acids in the R and CK chondrites analyzed here are very similar to the amino acid distributions of CO and CV chondrites and ureilites measured previously, and differ appreciably from aqueously altered CI, CM, and CR chondrites.

amino acid in LEW 87009, this would require more than 3 g of meteorite (~ 4.5 nmol g⁻¹ abundance, assuming 70% extraction and workup recovery), or more than 9% of the remaining sample mass of 35.2 g. At present, use of such a large sample relative to the mass available is difficult to justify.

The Amino Acid-Depleted Meteorites: LAR 04318 (CK4), ALH 85002(CK4), EET 92002 (CK5), and LAR 06872 (CK6)

These four meteorites contained very low amino acid abundances (<100 ppb total). The extent of biological contamination appears to be relatively low, as most of the amino acids were measured at abundances lower than 10 ppb (Tables 2 and 3). Nevertheless, the low D/L ratios of chiral proteinogenic amino acids support a terrestrial origin for the proteinogenic amino acids in these meteorites. In contrast with LAP 03834 (R3), LAP 031135 (R4), PCA 82500 (CK4/5), and LEW 87009 (CK6), these meteorites contain only low levels of β -ala, γ -aba, and δ -ava, and these compounds are all less abundant than glycine. Of the four depleted meteorites, ALH 85002 best fits the general trend of γ -aba > β -ala > δ -ava. However, we note that the amino acid abundances in ALH 85002 decreased after hydrolysis (Table 2, free versus total), rather than the typical two-fold or greater increase normally observed for meteoritic amino acids. One possible cause for the

observed decrease in amino acid abundance after acid hydrolysis could be carryover of mineral grains or metal ions into the acid hydrolysis step. It has been previously shown that significant amino acid destruction can occur when meteorite grains are directly exposed to 6 M HCl (Glavin et al. 1999). Based on the current data, there is not sufficient evidence to conclude that any of the amino acids in LAR 04318, ALH 85002, EET 92002, and LAR 06872 are extraterrestrial.

NWA 5956 (CK3)

The meteorite recovered from Northwest Africa, NWA 5956, has relatively high abundances of proteinogenic amino acids with low D/L ratios (Tables 2 and 5). As a result, in the absence of stable isotopic measurements indicating an extraterrestrial origin, we assume that these chiral proteinogenic amino acids likely came from contamination by terrestrial biology (Glavin et al. 2012). After replicate measurements, the remaining sample was not sufficient to permit compound-specific isotopic measurements (discussed above). The bulk of this meteorite is privately held, making it difficult to acquire additional material to perform these measurements. We did observe several amino acids that are less common in biology, including α -aib, 3-a-2,2-dmpa, β -ala, γ -aba, and δ -ava. Although α -aib is commonly found as an extraterrestrial amino acid in aqueously altered meteorites (Kvenvolden et al. 1971), it is also found in fungal

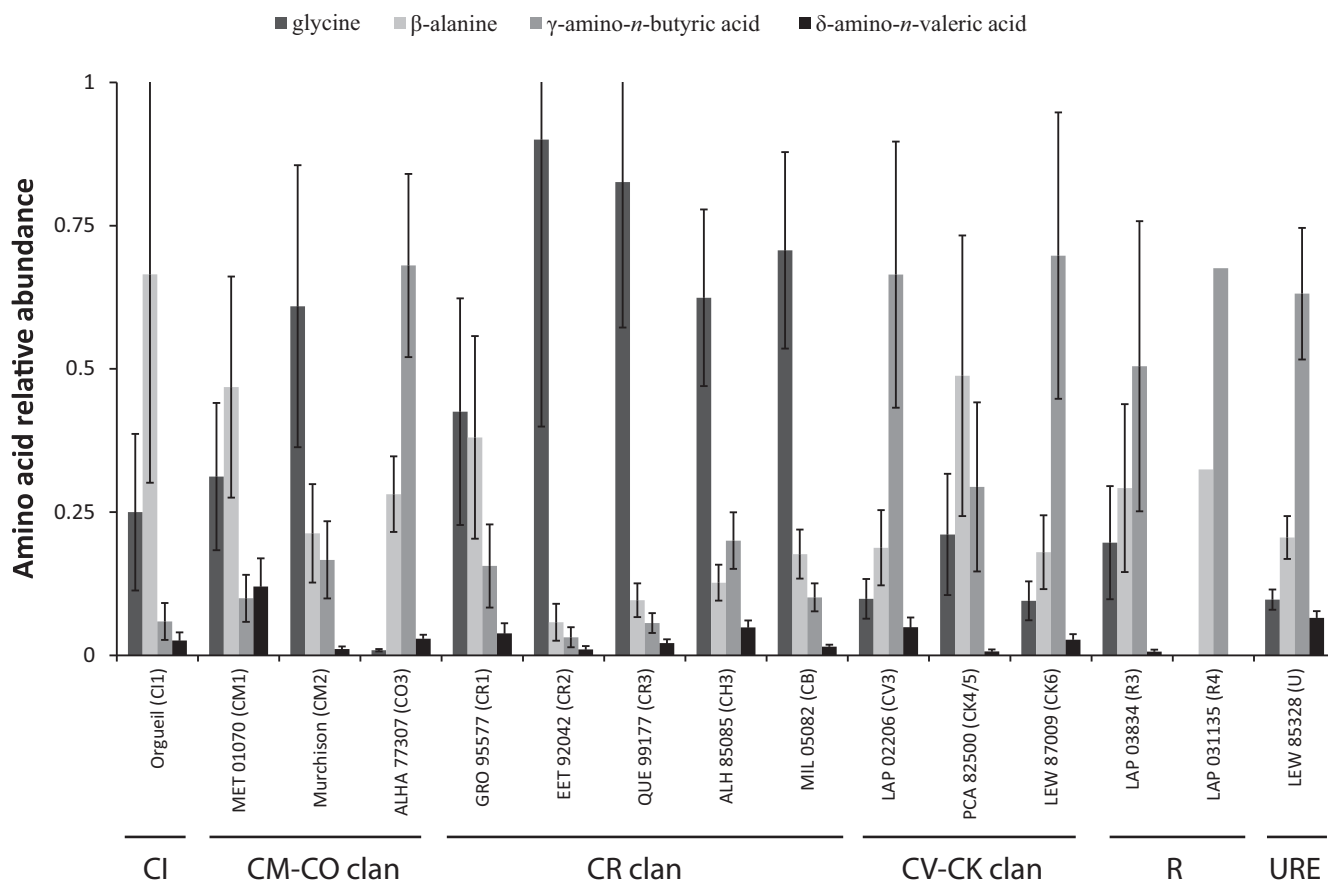


Fig. 3. A comparison of the relative abundances of glycine, β -alanine, γ -amino-*n*-butyric acid, and δ -amino-*n*-valeric acid in a range of meteorites. Bars represent the mole fraction of each amino acid relative to all four amino acids. Aqueously altered meteorites (CI, CM, and CR) tend to predominantly contain glycine and β -alanine, while the thermally altered meteorites (CO, CV, CK, R, and URE) tend to predominantly contain γ -amino-*n*-butyric acid. Meteorites are ordered according to the classification system in Weisberg et al. (2006). Data are from this study, Burton et al. (2013, 2012a, 2013), and Glavin et al. (2010b); error bars were obtained from the standard error propagation from the abundance data in the various sources.

peptides (Brückner et al. 2009; Elsila et al. 2011), and thus could have been introduced along with the chiral proteinogenic amino acid contaminants prior to recovery or during subsequent handling. The observation that 3-*a*-2,2-dmpa was not detected in any of the other meteorites analyzed here makes its presence puzzling; however, the lack of magnetite in NWA 5956 (Martin et al. 2013), which is typically abundant in CK chondrites (e.g., Greenwood et al. 2010), suggests that it may have been misclassified and is not a CK chondrite. The nearly equal molar abundances of glycine and β -ala in NWA 5956 is similar to what was seen in the other thermally altered meteorites; however, γ -aba is always present in even greater abundance in ureilites and CV and CO chondrites, whereas NWA 5956 contains relatively little γ -aba. Thus, while it is plausible that at least some of the β -ala in NWA 5956 is indigenous, determining the fraction of the measured total that is extraterrestrial in origin is

impossible for this sample with the current set of data. Therefore, it remains unclear whether any of the amino acids in NWA 5956 were synthesized extraterrestrially.

The substantial increase in contamination levels between non-Antarctic and Antarctic meteorite finds in the meteorites analyzed here reinforces the importance of Antarctic meteorites in the search for biologically relevant organic molecules of extraterrestrial origin such as amino acids. In fact, despite in some cases spending hundreds of thousands of years on the Earth and experiencing significant terrestrial weathering (e.g., Nishiizumi et al. 1989; Huber et al. 2006; Wasson et al. 2013), many of the Antarctic meteorites show little or no evidence of biological amino acid contamination. Unfortunately, there are no recognized CK chondrites of petrologic type 3 in any of the Antarctic meteorite collections, so performing amino acid analyses on a relatively uncontaminated CK3 sample may not be possible currently.

Amino Acid Formation Pathways in Thermally Metamorphosed Meteorites

The *n*- ω -amino acids we observed in LAP 03834, LAP 031135, PCA 82500, and LEW 87009 appear to be indigenous to the meteorites, and the predominance of these amino acid isomers matches what has been observed previously in thermally metamorphosed CV and CO chondrites, ureilites, and the Martian shergottite RBT 04262 (Burton et al. 2012a; Callahan et al. 2013). The amino acid-containing R and CK chondrites analyzed here are of types 3, 4/5, and 6, corresponding to peak metamorphic temperatures in the range of 300–600 °C or warmer. These temperatures are roughly in line with the range of temperatures experienced by CO3 and CV3 chondrites of 250–600 °C (Busemann et al. 2007). It has been shown that CK and R chondrites experienced aqueous alteration as well (Noguchi 1993; Rubin 1993; Righter and Neff 2007; McCanta et al. 2008; Greenwood et al. 2010; Davidson et al. 2014). However, we note that the amino acid abundances in the R and CK chondrites are lower than observed for CV and CO chondrites and ureilites; furthermore, several of the CK chondrites only had trace levels of amino acids. Compared to CV and CO chondrites and ureilites, the CK and R chondrites show increased oxidation as reflected by their high abundance of oxidized phases such as magnetite and Fe-rich silicates, and general paucity of reduced phases like metal. Perhaps the increased oxidation is unfavorable to amino acid formation and/or survival. In addition, measurements of the bulk carbon content in Rumuruti (R3-6), the only R chondrite fall, yield between 420 and 740 ppm (Schulze et al. 1994), much lower than the CV (5600 ppm) or CO (4500 ppm) chondrites (Wasson and Kallemeyn 1988). Whether this low carbon content is a pre-accretionary feature or the result of parent body processing, it is plausible that it is related to the low abundance of amino acids in the R chondrites. Furthermore, we have also observed that aqueously altered CM and CI-like chondrites that have experienced parent body heating above ~200 °C also are depleted in amino acids (Jenniskens et al. 2012; Burton et al. 2014a, 2014b).

We also observe that, of the *n*- ω -amino acids, γ -aba is almost always predominant in the thermally altered meteorites, whereas in aqueously altered meteorites, the most abundant *n*- ω -amino acids are glycine and β -ala (Fig. 3). The driving force for the shift in predominant amino acid from two- to three-carbon amino acids in aqueously altered meteorites to the four-carbon amino acid γ -aba in thermally altered meteorites could be related to thermal stability, as previous studies have shown that amino acid stability increases as the amino

group is moved farther away from the carboxylic acid group. More specifically, Li and Brill (2003) showed that α - and β -aminobutyric acids have much higher decarboxylation rates than γ -aba in aqueous solution at elevated temperatures. Thus, one possibility is that the elevated relative abundances of γ -aba are not due to its preferential synthesis but rather that glycine and β -ala are more rapidly destroyed.

We previously hypothesized that the amino acids observed in thermally altered ureilites, and CV and CO chondrites were likely formed by Fischer–Tropsch-type (FTT) reactions (e.g., Burton et al. 2012a, 2012b); the similar amino acid distributions observed for the R and CK chondrites suggest they had similar formation mechanisms as the amino acids in ureilites, and CV and CO chondrites. Since then, Pizzarello (2012) demonstrated the catalytic potential of meteorite powder of the Murchison CM2 chondrite for amino acid synthesis, although the observed amino acid distributions differed from what we find in thermally altered meteorites. There are several possible explanations for the differences in amino acid distributions (1) the amino acids in the thermally altered meteorites were not formed by FTT chemistry; (2) differences in meteorite mineralogy and parent body conditions could have a significant effect on the final product distribution; and (3) differences in analytical methodology including the resolving power and sensitivity of the analytical methods, and identities of the products searched for, affected the relative abundances reported in the meteoritic amino acid analyses and the laboratory FTT studies. Differentiating between these possibilities will require revisiting laboratory FTT studies, an undertaking with considerable merit but beyond the scope of the present work.

CONCLUSION

We report here on the presence of plausibly indigenous amino acids in several CK and R chondrites. The predominance of the *n*- ω -amino acids β -ala, γ -aba, and δ -ava was consistent with the distributions observed in ureilites and CO and CV chondrites, although the amino acid abundances were lower than previously observed in other carbonaceous chondrites and ureilites. This discovery expands the range of meteorite types and parent body environments compatible with amino acid synthesis and preservation. Furthermore, the observation that several of the CK and R chondrites were devoid of or contained only trace levels of amino acids is evidence that the composition and/or parent body processing of these meteorites does not enhance amino acid synthesis or survival. Further study of these

meteorites should provide additional constraints on the formation and preservation of compounds relevant to biology in our early solar system and beyond.

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