

Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies

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The distribution and enantiomeric composition of the 5-carbon (C₅) amino acids found in CI-, CM-, and CR-type carbonaceous meteorites were investigated by using liquid chromatography fluorescence detection/TOF-MS coupled with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine derivatization. A large L-enantiomeric excess (ee) of the α -methyl amino acid isovaline was found in the CM meteorite Murchison ($L_{ee} = 18.5 \pm 2.6\%$) and the CI meteorite Orgueil ($L_{ee} = 15.2 \pm 4.0\%$). The measured value for Murchison is the largest enantiomeric excess in any meteorite reported to date, and the Orgueil measurement of an isovaline excess has not been reported previously for this or any CI meteorite. The L-isovaline enrichments in these two carbonaceous meteorites cannot be the result of interference from other C₅ amino acid isomers present in the samples, analytical biases, or terrestrial amino acid contamination. We observed no L-isovaline enrichment for the most primitive unaltered Antarctic CR meteorites EET 92042 and QUE 99177. These results are inconsistent with UV circularly polarized light as the primary mechanism for L-isovaline enrichment and indicate that amplification of a small initial isovaline asymmetry in Murchison and Orgueil occurred during an extended aqueous alteration phase on the meteorite parent bodies. The large asymmetry in isovaline and other α -dialkyl amino acids found in altered CI and CM meteorites suggests that amino acids delivered by asteroids, comets, and their fragments would have biased the Earth's prebiotic organic inventory with left-handed molecules before the origin of life.

enantiomeric excess | homochirality | origin of life | carbonaceous chondrite

Meteorites provide a record of the chemical processes that occurred in the early solar system before life began on the Earth. In particular, the carbonaceous chondrites are carbon-rich meteorites with up to 2 wt % organic carbon (1). The delivery of organic compounds by carbonaceous chondrites to the early Earth could have been an important source of the Earth's prebiotic organic inventory (2). The amino acid composition of carbonaceous meteorites has been characterized extensively because these prebiotic molecules are the monomers of proteins and enzymes in all life on Earth. Over 80 different amino acids have been identified in the CM meteorites Murchison and Murray, and they comprise a mixture of 2- to 8-carbon cyclic and acyclic monoamino alkanolic and alkanedioic acids of nearly complete structural diversity, many of which are completely nonexistent in the terrestrial biosphere (1, 3–5). In addition, many amino acids are structurally chiral. With a few very rare exceptions, only left-handed amino acids (L) are found in biology, whereas all known abiotic syntheses of amino acids result in equal mixtures of left- and right-handed (L \approx D) amino acids. The origin of "homochirality" has been investigated for well over a century since Louis Pasteur discovered chirality, and it continues to be a topic of great importance in the origin of life field. There appear to be no biochemical reasons why left-handed amino acids should be favored over right-handed amino acids in enzymes (6), and therefore some have argued that the selection of left-handed amino acid homochirality by life on Earth was a random process (7).

The finding of slight to significant enantiomeric excess (ee) for several indigenous amino acids in the Murchison and Murray

CM2-type meteorites could point toward a possible prebiotic contribution to the origin of biological homochirality by the delivery of extraterrestrial organic material from asteroids and comets to the early Earth. These analyses showed enantiomeric excesses of the left-handed form (L_{ee}) ranging from 0% to 15.2% for isovaline and enantiomeric enrichments for several other α -methyl amino acids, including α -methylnorleucine, α -methylvaline, α -methylnorvaline, α -methylisoleucine, and 2-amino-2,3-dimethylpentanoic acid (8–11). Pizzarello et al. (11) also found a possible correlation between the magnitude of the L-isovaline excesses observed in individual fragments of the Murchison meteorite and the relative abundance of hydrous silicate minerals, hinting that aqueous alteration may have played a role in amino acid asymmetry in this meteorite. These α -methyl amino acids are nonbiological, and unlike the α -hydrogen amino acids used in biochemistry, they are not prone to geologically rapid racemization under aqueous or radiogenic conditions (12). Therefore, the initial enantiomeric ratios of these α -methyl amino acids are much more likely to have been preserved since the time of their formation.

The enantiomeric measurements of α -methyl amino acids in Murchison and Murray reported by Pizzarello and co-workers were made by using a gas chromatography/mass spectrometry (GCMS) technique, and great care was taken to rule out all potential sources of error. Nevertheless, to date these results have not been independently confirmed by using a different analytical technique. Moreover, very few meteorites have been investigated for isovaline asymmetry. To further constrain enantiomeric excesses in CM carbonaceous meteorites and to investigate the possibility that aqueous alteration on the parent body may have contributed to amplification of amino acid asymmetry, we reinvestigated the Murchison meteorite by using the very sensitive and selective liquid chromatography fluorescence detection (LC-FD)/TOF-MS technique that we optimized for the separation and enantiomeric determination of the 5-carbon (C₅) amino alkanolic acids, including isovaline. We also report here the results of analyses of C₅ amino acids in the aqueous altered CI1 meteorite Orgueil, the less altered Antarctic CM2 meteorite Lewis Cliffs (LEW) 90500, ungrouped C2 meteorite Lonewolf Nunataks (LON) 94102, and the most pristine Antarctic CR2 meteorites Elephant Moraine (EET) 92042 and Queen Alexandra Range (QUE) 99177.

Results and Discussion

Amino Acid Analyses. Examination of the exact mass chromatogram of the acid-hydrolyzed, hot-water extracts of the carbonaceous meteorites by LC-FD/TOF-MS shows the C₅ α -, β -, γ , and δ -amino alkanolic acid isomers that eluted in the 20- to 45-min region [Fig. 1 and supporting information (SI) Fig. S1]. All identified peaks were confirmed by comparison with standards, fluorescence, and

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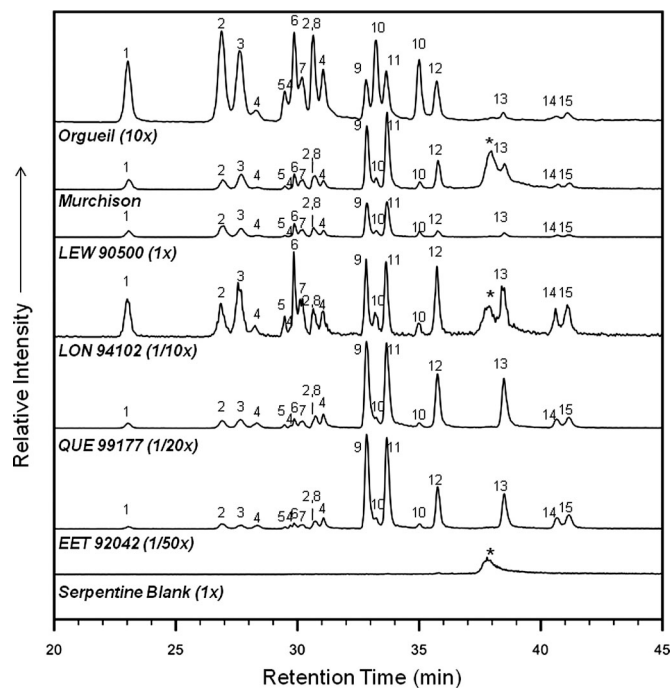


Fig. 1. The 20- to 45-min region of the LC-FD/TOF-MS single-ion chromatograms ($m/z = 379.13 \pm 0.015$) in positive electrospray ionization mode. OPA/NAC derivatization (15 min) of amino acids in the 6 M HCl-hydrolyzed, hot-water extracts from the CI carbonaceous chondrite Orgueil, the CM chondrites Murchison, LEW 90500, and LON 94102, the CR chondrites QUE 99177 and EET 92042, and the serpentine blank are shown. Peak heights were normalized to the total meteorite mass on column and scaled as indicated in parentheses. Separation was achieved using a Waters BEH C18 column (2.1×50 mm, $1.7\text{-}\mu\text{m}$ bead) followed by a second Waters BEH phenyl column (2.1×150 mm, $1.7\text{-}\mu\text{m}$ bead). The conditions for amino acid separations for the mobile phase at 30.0°C were as follows: flow rate, $150\ \mu\text{L}/\text{min}$; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (15), 25 (20), 25.06 (35), 44.5 (40), 45 (100). The peaks were identified by comparison of the retention time and exact molecular mass to those in the C_5 amino acid standard run on the same day. Peak identifications: 1, 3-amino-2,2-dimethylpropanoic acid; 2, DL-4-aminopentanoic acid; 3, DL-4-amino-3-methylbutanoic acid; 4, DL-3-amino-2-methylbutanoic acid; 5, DL-3-amino-2-ethylpropanoic acid; 6, 5-aminopentanoic acid; 7, DL-4-amino-2-methylbutanoic acid; 8, 3-amino-3-methylbutanoic acid; 9, D-2-amino-2-methylbutanoic acid (D-isovaline); 10, DL-3-aminopentanoic acid; 11, L-2-amino-2-methylbutanoic acid (L-isovaline); 12, L-2-amino-3-methylbutanoic acid (L-valine); 13, D-2-amino-3-methylbutanoic acid (D-valine); 14, D-2-aminopentanoic acid (D-norvaline); 15, L-2-aminopentanoic acid (L-norvaline). Asterisks indicate a nonfluorescent artifact.

mass. Although complete resolution of all 23 amino acid isomers and enantiomers was not achieved under the chromatographic conditions used, we were able to obtain baseline separation of the D- and L-isovaline enantiomers (Fig. 1, peaks 9 and 11) from all other possible C_5 amino acids, which was the primary goal of this study. The total concentration of the C_5 amino acids in Murchison was 3,100 parts per billion (ppb), composed predominately of DL-isovaline ($\approx 2,400$ ppb) (Table S1). The high relative abundance of the α -amino isomer isovaline in Murchison is consistent with previous work on this meteorite (3, 13). In a previous study by Cronin et al. (14), only approximate upper limits for the β -, γ -, and δ -isomers of the C_5 amino alkanic acids were reported (Table S1), because contributions from other coeluting amino acids in the Murchison extract by GCMS could not be ruled out. However, in this study we were able to completely eliminate interference from all other amino acids by using LC-FD/TOF-MS by plotting only the full width at half maximum centered at the exact mass ($m/z = 379.13 \pm 0.02$) corresponding to the *o*-phthaldialdehyde/*N*-acetyl-

L-cysteine (OPA/NAC) derivatives of the C_5 amino acids of interest (Fig. 1).

The amino acid concentrations of the β -, γ -, and δ -isomers in Murchison ranged from <14 to 103 ppb and are consistent with the upper limits (<120 or <590 ppb) previously reported for Murchison (14). A similar distribution and total abundance of C_5 amino acids were found in the Antarctic CM2 meteorite LEW 90500 (1,800 ppb) and the C2 meteorite LON 94102 (5,900 ppb); however, for LON 94102, the relative abundance of the α -isomers ($\alpha/\text{total } \text{C}_5 \approx 0.1$) was much lower than those in the other two CM2 meteorites ($\alpha/\text{total } \text{C}_5 \approx 0.8$). Like Murchison and LEW 90500, LON 94102 is a carbonaceous chondrite of petrologic type 2 containing fine-grained matrix and hydrated minerals (15); however, LON 94102 has not yet been classified into any specific group. The C_5 amino acid data suggest that the parent body of LON 94102 was chemically distinct from the parent body of the two CM2 meteorites analyzed in this study. We detected only one nonfluorescent peak in the LC-FD/TOF-MS $379.13\ m/z$ trace of the serpentine blank that had a different retention time from those of all other C_5 amino acids (denoted by an asterisk in Fig. 1), which means that no C_5 amino acid contamination occurred during the processing procedure. However, the low abundance of C_5 amino acids in the serpentine blank does not rule out the possibility of amino acid contamination of the meteorites during collection, storage, or handling of the samples.

The detection of all C_5 amino acids in the CI1 meteorite Orgueil, including isovaline, which had a total concentration of 85 ± 5 ppb, was unexpected. In a previous amino acid analysis of Orgueil, the two most abundant amino acids detected by standard HPLC with UV fluorescence detection were glycine (2,052 ppb) and β -alanine (707 ppb); isovaline was not detected above UV fluorescence background levels (<200 ppb) when this technique was used (16). Glycine and β -alanine in Orgueil could have formed from HCN polymerization and Michael addition during an aqueous alteration phase (17) on a parent body that was rich in water ice, ammonia, HCN, and cyanoacetylene, possibly an extinct comet (16). All of these volatiles have been detected in the comae of comets Hyakutake and Hale-Bopp (18). In contrast to Orgueil, the complex distribution of amino acids and high abundances of α -aminoisobutyric acid (AIB) and isovaline found in Murchison are believed to have been the result of the Strecker-cyanohydrin synthesis on an asteroid parent body rich in aldehydes and ketones, HCN, water, and ammonia (19), because it is difficult to form these α -amino acids by any other pathway. The possibility that the Strecker-cyanohydrin synthesis could represent a pathway of formation for α -amino acids in carbonaceous meteorites is further supported by the detection of hydroxy- and imino acids in Murchison (19, 20), compounds that are also predicted to be present by the Strecker mechanism. The amino acid isovaline, detected in Orgueil, has not previously been identified in a CI chondrite. This result is significant because it suggests that the Strecker mechanism may not have been completely inactive on the CI meteorite parent body as previously thought (16). The distinct C_5 amino acid distribution (low relative abundance of the α -amino isomers and enhanced abundances of the β - and γ -amino isomers) in Orgueil compared to that of Murchison provides additional support that the CI and CM parent bodies were chemically distinct.

The CR chondrites are believed to contain the most primitive organic material of any carbonaceous chondrite group (21, 22), and it has recently been discovered that two Antarctic CR2 meteorites, EET 92042 and Graves Nunataks (GRA) 95229, have the highest total amino acid concentrations (180,000 and 249,000 ppb, respectively) in any meteorite reported to date, with isovaline concentrations ranging from 23,000 to 29,000 ppb (23). However, the more altered CR1 meteorite Grosvenor Mountains (GRO) 95577 had a much lower total amino acid abundance of ≈ 900 ppb (23), suggesting that some of the amino acids or their precursors were destroyed or leached from this meteorite during aqueous alteration.

chiral β - and γ -amino isomers because these amino acid enantiomers were not separated or optically pure standards were not available for their identification. We observed very low D/L ratios for isovaline in Murchison (0.69 ± 0.04) and Orgueil (0.73 ± 0.07), which correspond to L-isovaline excesses of $18.5 \pm 2.4\%$ for Murchison and $15.2 \pm 4.0\%$ for Orgueil (Table 1). The Murchison value measured in this study exceeds the highest value of 15.2% previously measured for Murchison (11). The L-isovaline excess measured in Orgueil has not previously been reported in this or any CI meteorite and is similar to the Murchison value within error. Because isovaline is highly resistant to racemization (12), the measured D/L ratios should not have increased since the time of formation. Some radioracemization ($\approx 5\%$) of isovaline could have occurred based on the expected ionizing radiation dose from radioactive decay inside the Murchison and Orgueil meteorite parent bodies (24). However, radioracemization would only act to decrease the isovaline excesses observed in these meteorites; therefore, the values measured in this study should be considered lower limits for the initial L-isovaline excess.

Another possibility is enhancement of the L-isovaline excess in meteorites by terrestrial L-amino acid contamination after their fall; however, isovaline is a nonprotein amino acid that is extremely rare on the Earth, is found predominately in its D configuration in fungal peptides (25) and was not identified above the 10 ppb detection limit in a soil sample collected from the Murchison meteorite fall site (26). Furthermore, carbon isotopic measurements of D- and L-isovaline in Murchison did not display any significant difference in their $^{12}\text{C}/^{13}\text{C}$ ratios, which would have been detected if significant terrestrial contamination of one of the enantiomers had occurred (11). We were unable to make carbon isotope measurements of isovaline in Orgueil given the extremely low concentrations (≈ 85 ppb) and limited meteorite sample available for analysis. The finding of large L-isovaline excesses in Murchison and Orgueil suggests that enantiomeric enrichment occurs after the formation of this amino acid in the meteorite parent body because the most plausible ketone precursor for the synthesis of isovaline (2-butanone) is achiral, and laboratory abiotic simulations of the Strecker–cyanohydrin synthesis produce racemic mixtures of α -amino and α -dialkyl amino acids (27, 28). The formation of isovaline by the Strecker synthesis in Murchison is supported further by the detection of the α -hydroxy acid (α -hydroxy- α -methyl butyric acid) predicted to form by the Strecker mechanism from the same chemical precursors as isovaline (29). The enantiomeric ratio of α -hydroxy- α -methyl butyric acid is currently unknown, and it cannot be detected by the OPA/NAC derivatization technique used in this study.

With the exception of Orgueil and LON 94102, the D/L ratio of the protein amino acid valine in the other meteorites was nearly racemic (Table 1 and Table S1), indicating that very little terrestrial L-amino acid contamination occurred in these samples. Assuming that the extraterrestrial D/L valine ratios in Orgueil and LON 94102 were racemic, as found for the other meteorites, the currently measured D/L values of 0.39 ± 0.10 for Orgueil and 0.74 ± 0.05 for LON 94102 suggest that some terrestrial L-valine amino acid contamination of these meteorites occurred after their fall to Earth. The Orgueil meteorite fell in France in 1864, and its varying levels of contamination are well known. In contrast to valine, the non-protein amino acids isovaline and norvaline are much less abundant in the terrestrial biosphere and are therefore unlikely amino acid contaminants. We found that, for all of the carbonaceous meteorites analyzed, the D/L ratio of norvaline was racemic (≈ 1.0) within experimental error (Table 1 and Table S1), providing additional evidence that this nonprotein amino acid is extraterrestrial in origin. Because of the lack of pure standards, the individual D- and L-enantiomers of 3-apa were not identified. However, the meteoritic 3-apa appears to be as racemic as the commercial DL standard. We cannot rule out the possibility that these chiral C_5 amino acids had L-enantiomeric excesses at the time of formation. However,

these C_5 amino acids are not resistant to racemization; therefore, any initial enantiomeric excess could have been rapidly eliminated during periods of aqueous alteration on the meteorite parent body.

The measured D/L ratios for isovaline in the CR meteorites QUE 99177 and EET 92042 were racemic within measurement uncertainty, $\text{D/L} = 0.99 \pm 0.04$ and 1.02 ± 0.08 , respectively (Table S1). Although D/L isovaline ratios for these two CR meteorites have not previously been reported, amino acid enantiomeric measurements for another Antarctic CR meteorite, GRA 95229, using GCMS also showed low L-isovaline excesses of $\approx 3\%$ (22). In the same meteorite, Pizzarello et al. (22) found that the C_6 amino acid diastereomers L-isoleucine and D-alloisoleucine had enantiomeric enrichments of $\approx 12\text{--}14\%$, which was similar to the chiral distribution of these amino acids found in the more altered meteorite Murchison. If one invokes the Strecker–cyanohydrin synthesis, then the asymmetries in isoleucine and alloisoleucine in GRA 95229 and Murchison possibly were derived from asymmetry in their C_5 aldehyde precursor (22); however, isovaline would not likely have obtained its asymmetry by the same mechanism because 2-butanone is achiral. These observations suggest that the chemical processes and environments that led to the asymmetry in isovaline in Murchison were different from those for the aldehyde precursors that led to the asymmetry in isoleucine and alloisoleucine. The large L-isovaline excesses in Murchison and Orgueil and apparent lack of L-isovaline excesses in pristine CR2 meteorites indicate that aqueous alteration was an important process for isovaline enantioenrichment on the CM2 and CI1 parent bodies.

Amplification of Amino Acid Asymmetry During Aqueous Alteration.

On the basis of mineralogical and chemical evidence, in situ aqueous alteration was an important process on the CM meteorite parent body, with liquid water timescale estimates ranging from 10^2 to 10^4 years (30, 31). Aqueous alteration of the CM meteorites is believed to have been the result of the melting of ice inside the asteroid by radioactive heating, largely by the short-lived radionuclides ^{26}Al and ^{60}Fe (17, 32). The CI meteorites also experienced alteration, as demonstrated by their high abundance of hydrated minerals, oxygen isotope values, and high water-to-rock ratio compared with those of other groups of carbonaceous meteorites (33, 34). Although it has been suggested that the CI meteorites could be fragments of comets or extinct cometary nuclei (35, 36), the idea that liquid water was present in the interior of comets has been controversial, with some models suggesting that it is unlikely (37). The primitive nature of the insoluble organic matter found in Antarctic CR meteorites compared with that of CI and CM meteorites (38) suggests that some CR meteorites experienced only minimal aqueous alteration and thermal metamorphism. However, we should emphasize that even meteorites within the same class show evidence for various degrees of aqueous alteration and thermal metamorphism (38).

In addition to changing the mineralogy and volatile contents, aqueous alteration can also modify the soluble organic composition. It has been observed that the relative distribution of amino acids in carbonaceous chondrites is influenced by the degree of aqueous alteration on the parent body (13). In general, the more altered meteorites have a higher relative abundance of the amino acid β -alanine, whereas meteorites experiencing a lower degree of alteration have a much higher relative abundance of AIB. The variation in $\beta\text{-Ala}/\text{AIB}$ ratios follows a consistent trend with aqueous alteration, and this pattern was observed for the meteorites analyzed in this study (Fig. 3). In fact, the least altered CM meteorite, Yamato 791198, analyzed to date (39) has the highest relative abundance of AIB (40). A similar trend was previously observed in several Antarctic CR meteorites, where the least altered CR2 meteorites EET 92042 and GRA 95229 exhibit higher relative abundances of AIB, whereas the more altered CR1 meteorite GRO 95577 has a higher relative abundance of β -alanine (23).

The D/L ratios of chiral amino acids in meteorites have not been

(150 °C for 1 week). Enantiomerically pure samples of 4-a-2-mba were also supplied by R. Duke (University of Sydney, Sydney, Australia).

Meteorite Samples and Processing Procedures. All glassware and sample handling tools used for the meteorite samples were rinsed with Millipore water, wrapped in aluminum foil, and then heated in an oven at 500 °C overnight. Several fragments of the Murchison meteorite (6.3 g obtained from the Smithsonian National Museum of Natural History, USNM 6650,2), an interior chip of the Orgueil meteorite (1.0 g from the Musée National, Paris), the Antarctic meteorites LEW 90500 (5.0 g, split 69, parent 1), LON 94102 (0.6 g, split 19, parent 7), QUE 99177 (0.5 g, split 29, parent 10), and EET 92042 (0.6 g, split 58, parent 0) provided by the Antarctic meteorite curator at the National Aeronautics and Space Administration Johnson Space Center were crushed separately into fine powders and homogenized by using a mortar and pestle in a positive pressure high-efficiency particulate air-filtered laminar flow bench. As controls, a sample of serpentine (a hydrated magnesium silicate mineral common in carbonaceous meteorites) that had been heated at 500 °C for 3 h and standard mix of C₅ amino acids were carried through the identical procedure as the meteorites.

A portion of each sample (~100–200 mg) was sealed separately in a glass ampoule with 1 mL of Millipore water and extracted at 100 °C for 24 h, and the water supernatants were subjected to a 6 M HCl acid vapor hydrolysis procedure

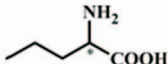
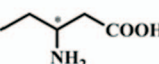
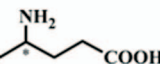
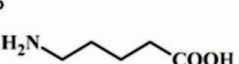
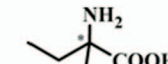
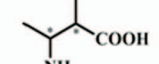
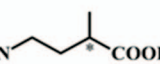
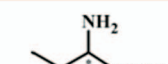
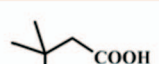
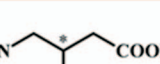

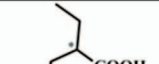
(150 °C for 3 h). The acid-hydrolyzed, hot-water extracts were desalted by using cation-exchange resin (AG50W-X8, 100–200 mesh, hydrogen form, Bio-Rad), and the amino acids were recovered by elution with 2 M NH₄OH (prepared from NH₃(g) (Air Products and Chemicals) in vacuo). The amino acids in the NH₄OH eluates were derivatized with OPA/NAC followed by positive electrospray ionization LC-FD/TOF-MS (Waters ACQUITY UltraPerformance LC and Waters LCT Premier) or LC-QQ-Q-MS (Waters Quattro micro API). The C₅ amino alkanolic acids and their enantiomeric ratios in the meteorite extracts were then quantified from the peak areas generated from the exact mass chromatogram of their OPA/NAC derivatives (379.1328 Da) from a minimum of 8 separate analyses. A more detailed description of the processing procedures, analytical technique, and quantification method is provided elsewhere (13).

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Supporting Information

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	α -amino isomer	β -amino isomer	γ -amino isomer	δ -amino isomer
<i>n</i> -	14 (D) 15 (L)  2-Aminopentanoic acid (norvaline; Nva)	10  3-Aminopentanoic acid (3-apa)	2  4-Aminopentanoic acid (4-apa)	6  5-Aminopentanoic acid (5-apa)
<i>sec</i> -	9 (D) 11 (L)  2-Amino-2-methylbutanoic acid (isovaline; Iva)	4  3-Amino-2-methylbutanoic acid (3-a-2-mba & allo-3-a-2-mba)	7  4-Amino-2-methylbutanoic acid (4-a-2-mba)	
<i>iso</i> -	13 (D) 12 (L)  2-Amino-3-methylbutanoic acid (valine; Val)	8  3-Amino-3-methylbutanoic acid (3-a-3-mba)	3  4-Amino-3-methylbutanoic acid (4-a-3-mba)	
<i>neo</i> -		1  3-Amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa)		
<i>sec</i> -		5  3-Amino-2-ethylpropanoic acid (3-a-2-epa)		

* = chiral carbon

Fig. S1. Structures, names, and abbreviations of all possible five-carbon (C_5) α -, β -, γ -, and δ -amino alkanolic acids. Chiral centers are denoted by an asterisk. These compounds represent all possible (23) C_5 acyclic primary amino acid isomers and enantiomers with the chemical formula $C_5H_{11}NO_2$. The numbers in the upper left corner correspond to liquid chromatography peaks in the order of elution as identified in Fig. 1.

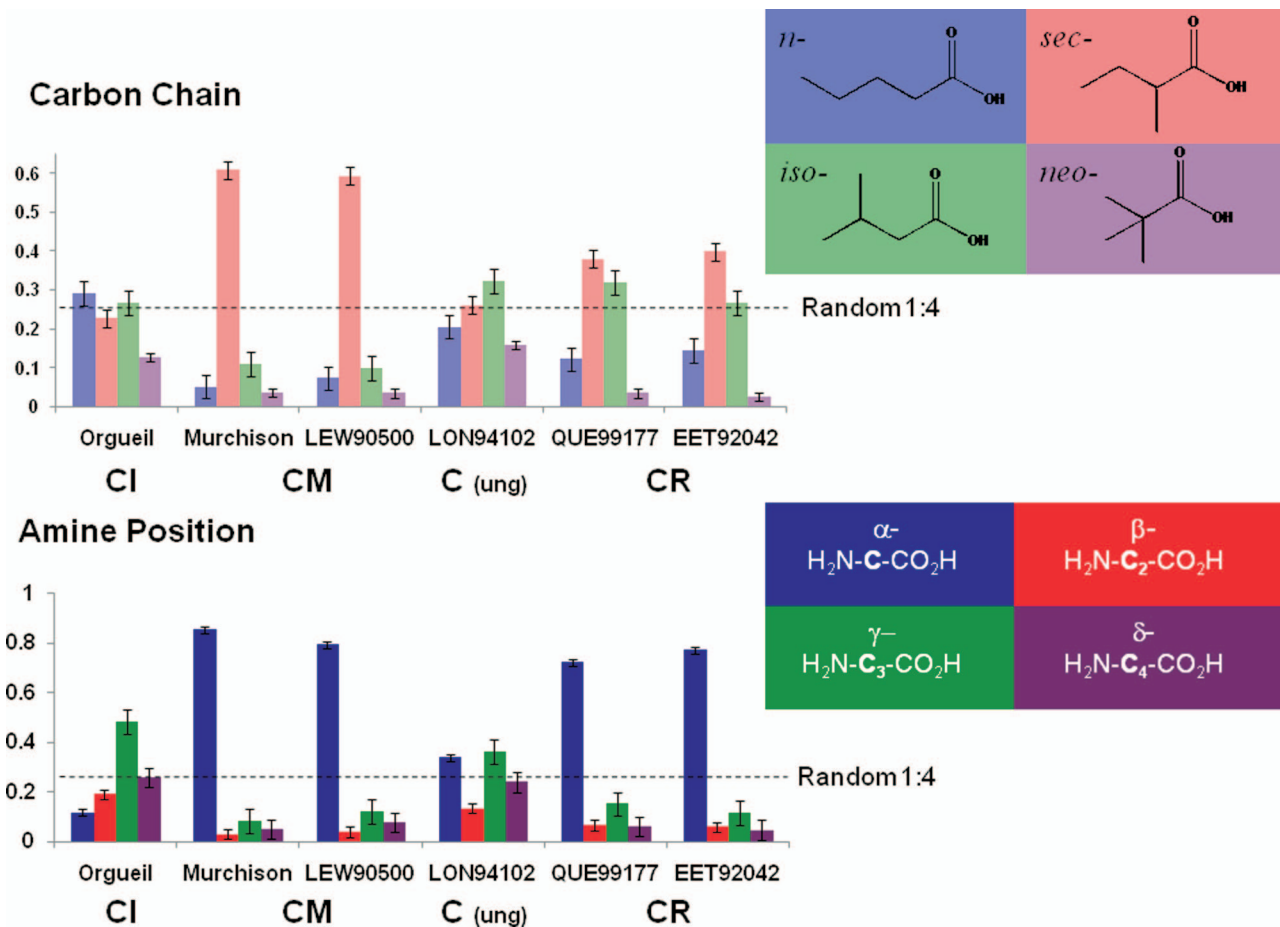


Fig. S2. The relative abundances of the five-carbon (C_5) amino acids in several carbonaceous meteorites as a function of carbon chain structure (*n*-, *sec*-, *iso*-, and *neo*-valeric acid) and amine position (α -, β -, γ -, and δ -) normalized to the total number of structures in the respective column or row in Fig. S1. It is apparent from the data that there is structural similarity in C_5 amino acid abundances within a meteorite class and between classes. For the purpose of this article these plots illustrate that it is unlikely that there were systematic errors in the detection of these amino acids. Furthermore, it is possible that this analysis method may aid in the assignment of new meteorite classes [e.g., LON 94102 (C2 ungrouped) is clearly distinct from the other CI, CM, and CR meteorites].

Table S1. Summary of the average abundances of the 5-carbon α -, β -, γ -, and δ -amino acids in the 6 M HCl acid-hydrolyzed, hot-water extracts of the carbonaceous meteorites analyzed

C ₅ amino acid detected	CI1	CM2			C2	CR2	
	Orgueil	Murchison		LEW 90500	LON 94102	QUE 99177	EET 92042
		This study	Previous work*				
α D-norvaline (D-2-apa)	13 ± 1	18 ± 2	180–470 [†]	9 ± 1	259 ± 20	960 ± 60	3,275 ± 391
L-norvaline (L-2-apa)	14 ± 1	19 ± 2		9 ± 1	263 ± 17	967 ± 68	3,231 ± 351
D-isovaline (D-2-a-2-mba)	36 ± 3	993 ± 43	2,800–6,800 [†]	652 ± 15	332 ± 19	5,534 ± 210	14,446 ± 625
L-isovaline (L-2-a-2-mba)	49 ± 2	1,444 ± 66		696 ± 20	348 ± 21	5,564 ± 92	14,164 ± 1,038
D-valine (D-2-a-3-mba)	22 ± 6	105 ± 15	320–2,800 [†]	48 ± 6	357 ± 20	3,442 ± 208	7,217 ± 427
L-valine (L-2-a-3-mba)	56 ± 2	111 ± 28		55 ± 8	480 ± 21	3,861 ± 137	7,647 ± 500
β DL-3-apa [‡]	181 ± 11	37 ± 4	≤120	36 ± 2	178 ± 9	804 ± 25	2,077 ± 177
DL- and allo-3-a-2-mba [‡]	64 ± 4	26 ± 5	≤120	24 ± 4	162 ± 7	962 ± 29	2,161 ± 102
3-a-3-mba [§]	<30	<14	≤120	<14	<150	<250	<286
3-a-2,2-dmpa	69 ± 3	36 ± 3	≤230	21 ± 1	320 ± 13	315 ± 20	539 ± 21
DL-3-a-2-epa [¶]	171 ± 14	37 ± 2	≤120	24 ± 3	534 ± 34	774 ± 59	1,393 ± 127
γ DL-4-apa [‡]	283 ± 24	84 ± 12	≤590	78 ± 9	475 ± 31	1,293 ± 90	2,968 ± 212
DL-4-a-2-mba [¶]	173 ± 11	67 ± 8	≤590	75 ± 3	733 ± 38	1,485 ± 60	2,396 ± 311
DL-4-a-3-mba [¶]	325 ± 17	103 ± 7	≤590	68 ± 2	973 ± 23	1,472 ± 87	2,137 ± 75
δ 5-apa	140 ± 19	50 ± 5	≤590	48 ± 5	480 ± 24	570 ± 17	973 ± 93
Total, ppb	1,600	3,100	3,300–10,000	1,800	5,900	28,000	65,000

All values are reported in parts per billion (ppb) on a bulk sample basis. Extracts were analyzed by o-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization (15 min) and HPLC separation with UV fluorescence and TOF-MS detection. For the liquid chromatography TOF-MS data, the monoisotopic masses ($m/z = 379.13 \pm 0.02$) of each protonated OPA/NAC amino acid derivative ($M + H^+$) were used for quantification, and final peak integrations included background level correction using a serpentine 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 DL-norleucine standard (recoveries ranged from 60% to 75% for the meteorite samples). The uncertainties (δx) are based on the standard deviation of the average value of between 8 and 23 separate measurements (n) with a standard error of $\delta x = \sigma_x(n - 1)^{-1/2}$.

*Total concentrations measured in acid-hydrolyzed, hot-water extracts of the Murchison meteorite reported in previous studies [Cronin JR, Pizzarello S (1983) Amino acids in meteorites. *Adv Space Res* 3:5–18; Glavin DP, et al. (2006) Amino acid analyses of Antarctic CM2 meteorites using liquid chromatography-time of flight-mass spectrometry. *Meteorit Planet Sci* 41:889–902; Cronin JR, Pizzarello S, Yuen GU (1985) Amino acids in the Murchison meteorite: II. Five carbon acyclic primary β -, γ -, and δ -aminoalkanoic acids. *Geochim Cosmochim Acta* 49:2259–2265].

[†]Range of D + L values reported for four separate Murchison meteorite fragments [Cronin JR, Pizzarello S (1983) Amino acids in meteorites. *Adv Space Res* 3:5–18; Glavin DP, et al. (2006) Amino acid analyses of Antarctic CM2 meteorites using liquid chromatography-time of flight-mass spectrometry. *Meteorit Planet Sci* 41:889–902].

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

[§]3-a-3-mba coelutes with one of the enantiomers of DL-4-apa; therefore, upper limits for 3-a-3-mba were estimated by taking the difference in peak areas of the two DL-4-apa enantiomers.

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