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Extraterrestrial amino acids and L-enantiomeric excesses in the CM2 carbonaceous chondrites Aguas Zarcas and Murchison

Daniel P. GLAVIN[1*], Jamie E. ELSILA[1], Hannah L. MCLAIN[1,2], José C. APONTE[1,2], Eric T. PARKER[1], Jason P. DWORKIN[1], Dolores H. HILL[3], Harold C. CONNOLLY Jr.[3,4], and Dante S. LAURETTA[3]

[1]NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA
[2]Catholic University of America, Washington, District of Columbia 20064, USA
[3]Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721, USA
[4]Rowan University, Glassboro, New Jersey 08028, USA
[*]Corresponding author: E-mail: daniel.p.glavin@nasa.gov

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Abstract–The abundances, distributions, enantiomeric ratios, and carbon isotopic compositions of amino acids in two fragments of the Aguas Zarcas CM2 type carbonaceous chondrite fall and a fragment of the CM2 Murchison meteorite were determined via liquid chromatography time-of-flight mass spectrometry and gas chromatography isotope ratio mass spectrometry. A suite of two- to six-carbon aliphatic primary amino acids was identified in the Aguas Zarcas and Murchison meteorites with abundances ranging from ~0.1 to 158 nmol/g. The high relative abundances of α-amino acids found in these meteorites are consistent with a Strecker-cyanohydrin synthesis on these meteorite parent bodies. Amino acid enantiomeric and carbon isotopic measurements in both fragments of the Aguas Zarcas meteorites indicate that both samples experienced some terrestrial protein amino acid contamination after their fall to Earth. In contrast, similar measurements of alanine in Murchison revealed that this common protein amino acid was both racemic (D ≈ L) and heavily enriched in ^{13}C, indicating no measurable terrestrial alanine contamination of this meteorite. Carbon isotope measurements of two rare non-proteinogenic amino acids in the Aguas Zarcas and Murchison meteorites, α-aminoisobutyric acid and D- and L-isovaline, also fall well outside the typical terrestrial range, confirming they are extraterrestrial in origin. The detections of non-terrestrial L-isovaline excesses of ~10–15% in both the Aguas Zarcas and Murchison meteorites, and non-terrestrial L-glutamic acid excesses in Murchison of ~16–40% are consistent with preferential enrichment of circularly polarized light generated L-amino acid excesses of conglomerate enantiopure crystals during parent body aqueous alteration and provide evidence of an early solar system formation bias toward L-amino acids prior to the origin of life.

INTRODUCTION

Meteorites provide a record of the chemical processes that occurred in the early solar system before life began on Earth. The exogenous delivery of organic compounds by carbonaceous chondrites to the early Earth and other planetary bodies could have been an important source of prebiotic compounds required for the emergence of life (Chyba and Sagan 1992). The amino acid contents of a variety of carbon-rich meteorites, in particular the CM2 type carbonaceous chondrite Murchison, have been studied extensively because these prebiotic molecules are essential components of life as the monomers of proteins and enzymes. The first amino acid measurements of the

[Correction added on 8 June 2020 after first online publication: The two amino acids listed on Table 1 in the right column on lines 1 and 4 and on page 11 were corrected to 'D,L-4-aminopentanoic acid' and '5-aminopentanoic acid'.]

Murchison meteorite shortly after its fall and recovery near Murchison, Australia, on September 28, 1969, led to the discovery of five common protein amino acids (glycine, alanine, valine, proline, and glutamic acid) and 12 non-proteinogenic amino acids in the meteorite, including α-aminoisobutyric acid (AIB) and isovaline that are both rare on Earth (Kvenvolden et al. 1970, 1971).

Most amino acids found in Murchison and other carbonaceous chondrites are structurally chiral; that is, they possess two non-superimposable mirror image structures or enantiomers (by convention and analogy with glyceraldehyde: left, L and right, D). L-amino acids overwhelmingly dominate the enantiomeric distribution in the biosphere, whereas amino acids formed by abiotic processes are racemic (equal mixtures of L- and D-enantiomers) unless a separate chiral bias is applied. Therefore, the structural ratios of these compounds can be a very useful tool to help discriminate between biotic and abiotic (extraterrestrial) origins of amino acids in meteorites. Kvenvolden and co-workers concluded that all of the amino acids in the Murchison meteorite were abiotic and extraterrestrial in origin since all of the chiral amino acids were racemic ($D \approx L$), indicating very little, if any, terrestrial L-amino acid contamination of the meteorite (Kvenvolden et al. 1970). To date, 96 different amino acids have been *named* in the Murchison meteorite including 12 of the 20 most common amino acids found in biology and hundreds more have been detected, but have yet to be explicitly identified (Glavin et al. 2018). The vast majority of amino acids identified in the Murchison meteorite are rare or absent in the terrestrial biosphere and are therefore unlikely to be contaminants (Cronin and Chang 1993).

One of the most significant discoveries in meteorites of relevance to prebiotic chemistry and our understanding of the origin of biological homochirality (i.e., why the majority of life on Earth uses L-amino acids and D-sugars and not the opposite handedness) was the finding of L-enantiomeric excesses in several amino acids in the CM2 meteorites Murchison and Murray. L-excesses ranging from ~3 to 15% have been found in the Murchison and Murray meteorites in several non-protein α-dialkyl amino acids including isovaline, α-methylnorleucine, α-methylvaline, α-methylnorvaline, and α-methylisoleucine (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000). An extraterrestrial origin for the α-dialkyl amino acid L-excesses in these meteorites is supported by the observations that (1) these non-protein amino acids are rare or non-existent in terrestrial biology (Cronin and Pizzarello 1997) and (2) the stable carbon and hydrogen isotopic measurements of the D- and L-isovaline enantiomers ($\delta^{13}C$ ~+12 to +22‰; δD ~3200‰) in Murchison and Murray (Pizzarello et al. 2003; Pizzarello and Huang 2005) are heavily enriched in ^{13}C and D compared to terrestrial sources of isovaline (Elsila et al. 2011).

These results have been difficult to explain since the abiotic formation of isovaline and other α-dialkyl amino acids (e.g., by Strecker-cyanohydrin synthesis) in the CM2 parent body should produce racemic mixtures (Wolman et al. 1972). However, subsequent enantiomeric measurements of isovaline in a wide range of meteorites from multiple carbonaceous chondrite groups (CI, CM, CR, CB, and CH) and the ungrouped C2 Tagish Lake meteorite have confirmed slight to significant L-isovaline excesses up to 20.5% with a general correlation between the extent of aqueous alteration and magnitude of the observed L-excess (Glavin and Dworkin 2009; Glavin et al. 2010, 2012; Burton et al. 2013). These findings support the hypothesis that amino acid exposure to water during hydrothermal alteration in these carbonaceous chondrite parent bodies played a role in the enantioenrichment of some L-amino acids over their D-enantiomers (Glavin and Dworkin 2009). Multiple mechanisms for amino acid symmetry breaking and amplification of enantiomeric excesses have been proposed and are discussed in detail elsewhere (Kondepudi et al. 1990; Soai et al. 1995; Blackmond 2004; Kawasaki et al. 2006; Klussmann et al. 2006; Fletcher et al. 2007; Pizzarello and Groy 2011; MacDermott 2012).

In addition to the α-dialkyl amino acids, large L-enantiomeric excesses for several α-H protein amino acids have been reported in Murchison and other carbonaceous meteorites; however, establishing a non-terrestrial origin has been much more problematic because unlike α-dialkyl amino acids, the α-H amino acids are common in terrestrial biology and their measurements are more susceptible to contamination. Engel and Nagy (1982) first reported large L-enantiomer excesses ranging from ~25 to 67% for several common α-H protein amino acids including alanine, aspartic acid, and glutamic acid within interior fragments of the Murchison meteorite and suggested that these L-excesses were unlikely to be the result of terrestrial contamination after the meteorite fell to Earth since other common protein amino acids (e.g., tyrosine, phenylalanine, lysine, histidine, arginine, etc.) were absent from the meteorite. Moreover, subsequent nitrogen isotopic measurements of D- and L-glutamic acid and D- and L-alanine detected in Murchison showed that both enantiomers for each amino acid were heavily enriched in ^{15}N relative to terrestrial amino acids and had similar $\delta^{15}N$ values ranging from +57 to +60‰, suggesting that the large L-glutamic acid and L-

alanine excesses were indigenous to the meteorite (Engel and Macko 1997, 2001). It was argued by others, however, that incomplete chromatographic resolution of alanine and glutamic acid and possible co-elution with other meteoritic amino acids could have affected both the enantiomeric ratios and stable N isotope values measured (Pizzarello and Cronin 1998). The reports of large non-terrestrial L-alanine and L-glutamic acids excesses in Murchison were surprising since the first amino acid measurements of a pristine interior fragment of the Murchison meteorite shortly after its fall to Earth found that these protein amino acids were nearly racemic (Kvenvolden et al. 1970).

Large L-aspartic acid excesses of up to ~60% were also measured in "pristine" fragments of the ungrouped C2 Tagish Lake meteorite that had been maintained at temperatures below 0 °C since the time of their collection a week after the meteorites fell on January 18, 2000, on the frozen Tagish Lake in northern British Columbia (Hildebrand et al. 2006; Glavin et al. 2012). Carbon isotope measurements of aspartic acid in Tagish Lake revealed that both D- and L-enantiomers were highly enriched in ^{13}C ($\delta^{13}C$ = +24‰ and +29‰, respectively), confirming that the large L-aspartic acid excesses in the meteorite were extraterrestrial in origin (Glavin et al. 2012). Interestingly, other proteinogenic amino acids in the Tagish Lake meteorite including glutamic acid, serine, and threonine were also present with large L-excesses of ~50–99%, whereas alanine, another common protein amino acid, was nearly racemic (Glavin et al. 2012). A strikingly similar observation was made for a pristine fragment of the Murchison meteorite from the Chicago Field Museum[1] where aspartic acid, glutamic acid, and serine were all present with large L-enantiomeric excesses up to 43%, but alanine was racemic (Friedrich et al. 2018). However, carbon isotope measurements of these protein amino acids required to firmly establish the origin of the measured L-excesses in Murchison were not made in that study (Friedrich et al. 2018).

The recent fall of the Aguas Zarcas meteorites in San Carlos county, Alajuela province, Costa Rica on April 23, 2019, and rapid recovery of hundreds of individual fragments from the strewn field totaling 27 kg in mass, of which 11 kg was recovered before it rained in the area 6 days after the fall (Meteoritical Bulletin Database 2020), provides a unique opportunity to investigate the amino acid composition of a carbonaceous chondrite fall that may not have experienced significant terrestrial weathering. Based on its mineralogy, elemental abundances, and O-isotope composition, the Aguas Zarcas meteorite has been classified as a CM2 carbonaceous chondrite and some of the recovered pre-rain fragments and those exposed to liquid water after the rain were noted to give off a "Murchison-like" odor (Meteoritical Bulletin Database 2020), an indication that the Aguas Zarcas meteorites were indeed volatile-rich, typical of other CM2 chondrites.

Here, we report on measurements of the abundance, distribution, enantiomeric ratios, and stable carbon isotopic compositions of amino acids extracted from two different pre-rain fragments of the CM2 Aguas Zarcas meteorite and a single fragment of the CM2 Murchison meteorite from the Chicago Field Museum whose amino acid carbon isotopic compositions have not previously been measured. Our report is based on measurements using a combination of ultra-high-performance liquid chromatography with UV fluorescence and quadrupole time-of-flight mass spectrometry (LC-FD/Q-ToF-MS) and gas chromatography-mass spectrometry coupled with isotope ratio mass spectrometry (GC-MS/IRMS) techniques.

MATERIALS AND METHODS

Chemicals and Reagents

All glassware, ceramics, and sample handling tools used in sample processing were rinsed with Milli-Q ultrapure water (18.2 MΩ, <3 ppb total organic carbon), wrapped in aluminum foil, and then heated in a furnace at 500 °C in air overnight. Most of the chemicals and reagents were purchased from Sigma-Aldrich. A stock amino acid solution (1×10^{-6} M) was prepared by mixing individual amino acid standards (97–99% purity) in Milli-Q ultrapure water (see Figs. 1 and 2). All chiral amino acid standards were purchased as racemic mixtures (D = L), except for D- and L-threonine (Sigma-Aldrich, >98% purity, *allo*-free) and D- and L-isovaline (Acros Organics, >99% purity) which were prepared as racemic mixtures by mixing the appropriate masses of each compound in Milli-Q ultrapure water to the standard mixture. The sources of the C_5 amino acid standards used are detailed elsewhere (Glavin and Dworkin 2009).

Acid vapor hydrolysis used 6 M double distilled HCl (ddHCl). Cation-exchange resin (AG50W-X8, 100-200 mesh, hydrogen form, BIO-RAD) was used for removal of salts and interfering ions from samples. During the desalting protocol, 1.5 M ddHCl, 2 M sodium hydroxide (NaOH), and 2 M ammonium hydroxide (NH_4OH) were used. The 2 M NaOH was produced by dissolution of 32 g of NaOH pellets (Sigma-Aldrich, anhydrous, ≥97%)

[1]The Murchison meteorite fragment analyzed in this study was stored in a parafilm-covered glass beaker that was sealed inside a desiccator containing P_4O_{10} and $CaCl_2$ for many years (exact duration unknown) before the desiccator was broken open at the University of Chicago on August 14, 2015.

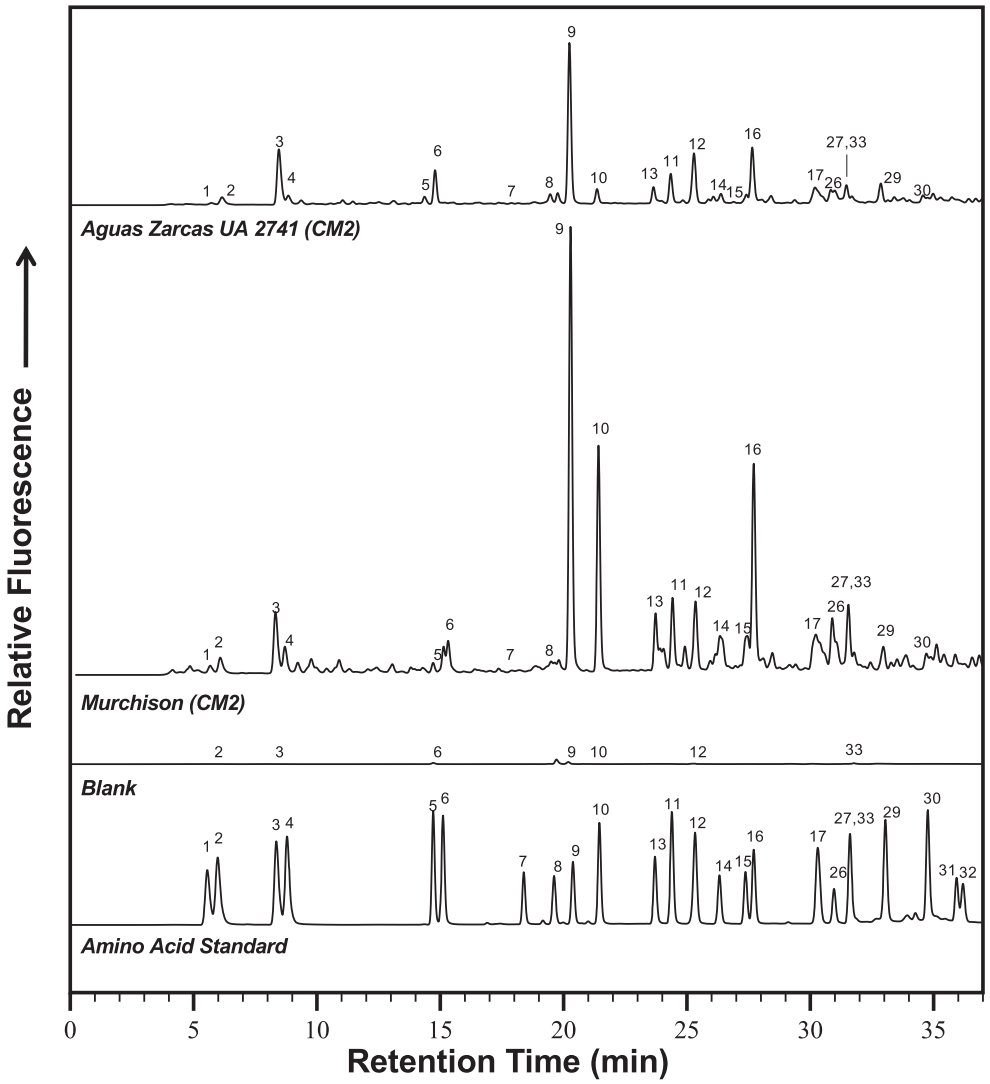

Fig. 1. The 0–37 min. region of the LC-FD chromatograms (no significant peaks were observed beyond this retention time range). *o*-phthaldialdehyde/*N*-acetyl-L-cysteine derivatization (15 min) of amino acids in the standard and of the 6 M HCl-hydrolyzed, hot-water extracts of the procedural blank and the CM2 Murchison (Chicago Field Museum, 1.0 g extract) and Aguas Zarcas (UA 2741, 0.5 g extract) meteorites are shown. Similar chromatograms were also obtained for the non-hydrolyzed extracts. Peaks were identified by comparison to the fluorescence retention time and molecular mass to those in the amino acid standard analyzed on the same day and are designated by peak number as follows: 1) D-aspartic acid; 2) L-aspartic acid; 3) L-glutamic acid; 4) D-glutamic acid; 5) D-serine; 6) L-serine; 7) D-threonine; 8) L-threonine; 9) glycine; 10) β-alanine; 11) D-alanine; 12) L-alanine; 13) γ-amino-*n*-butyric acid + D,L-β-aminoisobutyric acid; 14) D-β-amino-*n*-butyric acid; 15) L-β-amino-*n*-butyric acid; 16) α-aminoisobutyric acid; 17) D,L-α-amino-*n*-butyric acid; 26) D-isovaline; 27) D,L-3-aminopentanoic acid; 29) L-valine; 30) D-valine; 31) D-norvaline; 32) L-norvaline; and 33) ε-amino-*n*-caproic acid. The data used for this figure can be found in the supporting information.

in 400 mL Milli-Q ultrapure water and the 2 M NH_4OH was prepared from Milli-Q ultrapure water and ammonia gas (Air Products) in vacuo. Pre-column derivatization of samples prior to LC-FD/Q-ToF-MS analyses involved the use of 0.1 M sodium borate, *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC), and 0.1 M hydrazine hydrate. Sodium borate was generated by heating solid sodium borate decahydrate at 500 °C, in air, for 3 h, prior to dissolution in Milli-Q ultrapure water. The OPA/NAC derivatization reagent was prepared by firstly generating 0.1 M OPA via dissolving 0.1 g OPA in 7.5 mL methanol (Optima Grade), secondly generating 0.5 M NAC via dissolving 0.408 g NAC in 5 mL Milli-Q ultrapure water, and thirdly mixing 300 μL of 0.1 M OPA with 30 μL of 0.5 M NAC, and 670 μL of 0.1 M sodium borate. The 0.1 M

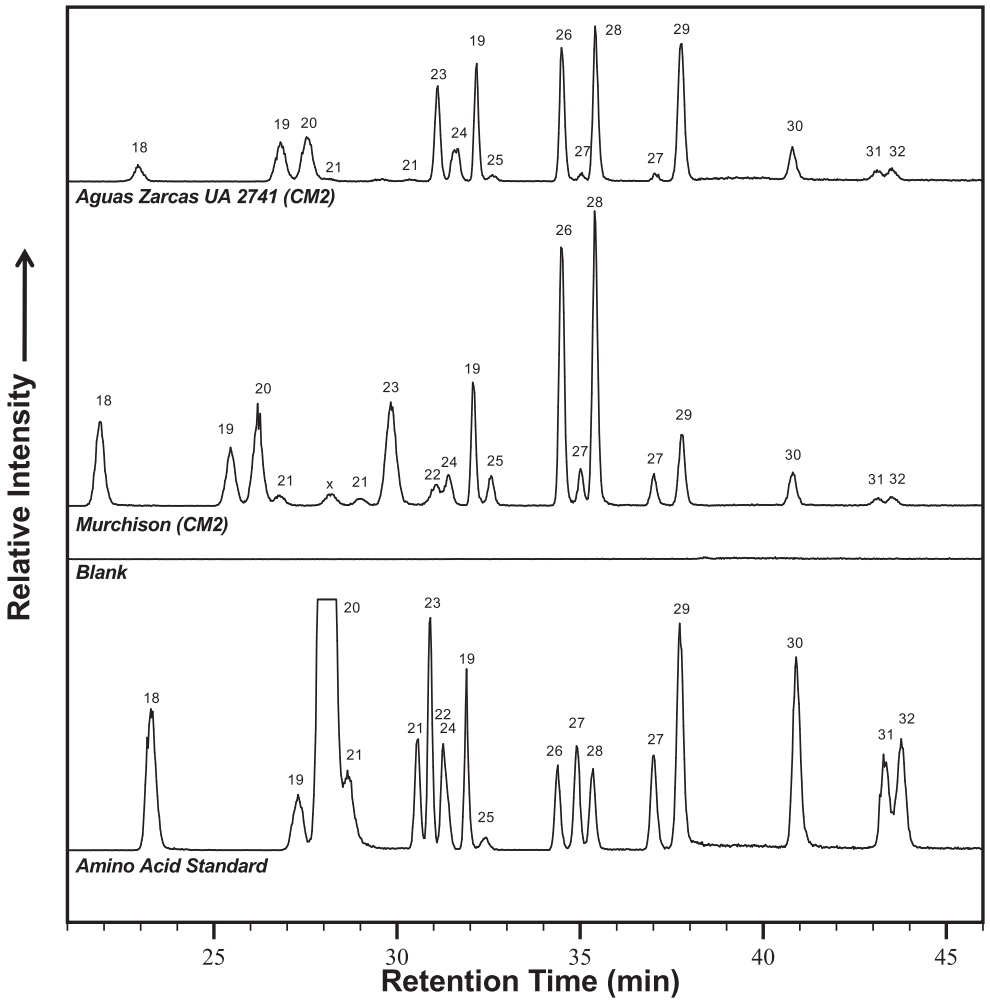

Fig. 2. The 21–46 min. region of the LC-Q-ToF-MS single ion chromatograms of the C_5 amino acids (m/z = 379.1328 ± 10 ppm). *o*-phthaldialdehyde/*N*-acetyl-L-cysteine derivatization (15 min) of amino acids in the standard and of the 6 M HCl-hydrolyzed, hot-water extracts of the procedural blank and the CM2 Murchison (Chicago Field Museum, 1.0 g extract) and Aguas Zarcas (UA 2741, 0.5 g extract) meteorites are shown. Similar LC-Q-ToF-MS single ion chromatograms were obtained for the non-hydrolyzed extracts. The peaks were identified by comparison of the retention time and exact molecular mass to those in the C_5 amino acid standard analyzed on the same day and designated by peak number as follows: 18) 3-amino-2,2-dimethylpropanoic acid; 19) D,L-4-aminopentanoic acid; 20) D,L-4-amino-3-methylbutanoic acid; 21) D,L- and *allo*-3-amino-2-methylbutanoic acid; 22) D,L-3-amino-2-ethylpropanoic acid; 23) 5-aminopentanoic acid; 24) D,L-4-amino-2-methylbutanoic acid; 25) 3-amino-3-methylbutanoic acid; 26) D-isovaline; 27) D,L-3-aminopentanoic acid; 28) L-isovaline; 29) L-valine; 30) D-valine; 31) D-norvaline; and 32) L-norvaline. The peak labeled "X" is not a C_5 primary aliphatic amino acid and could not be identified. The data used for this figure can be found in the supporting information.

hydrazine (NH_2NH_2) solution was prepared by vacuum distillation of concentrated anhydrous hydrazine (98% purity) and subsequent dilution in Milli-Q ultrapure water.

During LC-FD/Q-ToF-MS analyses, liquid chromatography was facilitated by the implementation of two solvents: solvent A (50 mM ammonium formate, 8% methanol, pH 8.0) and solvent B (Fisher Optima grade methanol). Solvent A was prepared by 2 M NH_4OH titration of a 50 mM formic acid solution to pH 8. Also, during LC-FD/Q-ToF-MS analyses, mass calibrations were performed using a 0.5 mM sodium formate solution, and real-time lock mass corrections were performed using a 200 pg/μL leucine enkephalin solution. The 0.5 mM sodium formate solution was made by first preparing a 5 mM stock sodium formate solution, and then performing a 10× dilution of this 5 mM stock sodium formate solution using 90:10 (v:v) isopropanol:water. The 5 mM stock sodium formate solution was made by mixing 1000 μL of 0.1 M sodium hydroxide with 900 μL of Milli-Q ultrapure water and 100 μL of formic acid, and diluting up to 20 mL using

a 90:10 (v:v) isopropanol:water solution. The 200 pg/μL leucine enkephalin solution was prepared by first generating a 400 ng/μL stock solution of leucine enkephalin, and then diluting the solution down to a concentration of 200 pg/μL using a 50:50 (v:v) acetonitrile:water +0.1% formic acid solution. The 400 ng/μL stock leucine enkephalin solution was prepared by dissolving 3 mg of leucine enkephalin powder in 7.5 mL of Milli-Q ultrapure water.

Meteorite Samples and Controls

Three individual pre-rain fragments of the CM2 Aguas Zarcas meteorite obtained by the University of Arizona from Mike Farmer (UA 2741, total masses = 0.11 g and 0.51 g) and Robert Ward (UA 2746, total mass = 0.53 g) that had been kept stored at the University of Arizona in sealed screw-capped glass vials in a freezer at −20 °C were warmed to room temperature and mailed to the NASA Goddard Space Flight Center (GSFC) for amino acid analyses. For this amino acid study, we also selected individual aliquots (0.08 g and 1.0 g) of a powdered 10 g chip taken from a single 47.5 g fragment of the Murchison meteorite originally from the Chicago Field Museum that had been kept stored in a 600 mL parafilm-covered glass beaker and sealed for an unknown period of time (many years) inside a glass desiccator containing both P_4O_{10} and $CaCl_2$ desiccants at the University of Chicago. On August 14, 2015, the desiccator was broken open by Dr. Robert Minard on behalf of the Clifford N. Matthews' research group and the Murchison meteorite sample wrapped in aluminum foil followed by bubble wrap, sealed in a box, and then shipped to NASA GSFC. Immediately after receipt of the Murchison sample at NASA GSFC on August 19, 2015, the meteorite was transferred to a clean aluminum foil-covered glass beaker and kept stored inside a glass desiccator at room temperature prior to its removal on July 29, 2019, for extraction and amino acid analyses in parallel with the Aguas Zarcas meteorites.

Each individual meteorite fragment was separately crushed to powder using a ceramic mortar and pestle, transferred to glass vials, and homogenized using a vortex mixer inside a positive pressure ISO 5 HEPA-filtered laminar flow hood housed in an ISO 8 white room. Tiny light green colored plant fragments were observed without magnification in the powdered Aguas Zarcas meteorite sample UA 2746, but not in UA 2741. As controls, a soil sample (Soil#2, UA 2745, total mass = 0.65 g) collected from the Aguas Zarcas meteorite strewn field by Greg Hupe and a procedural blank were prepared using the identical extraction and processing procedures as the meteorite samples. Although not analyzed as part of this study, the amino acid data from a previous LC-FD analysis of soil (Soil#1, 20–30 cm depth) collected from the Murchison meteorite fall location in Australia in 1999 by Prof. Reid R. Keays from The University of Melbourne are also discussed.

Sample Preparation

A portion of each powdered sample (mass ~0.08–1.0 g) was flame-sealed separately in a glass ampoule with 1 mL of Milli-Q ultrapure water and extracted at 100 °C for 24 h. For the extracts of the 0.08 g sample portions of Aguas Zarcas UA 2741 and the Murchison meteorite, half of the water supernatants were subjected to a 6 M HCl vapor hydrolysis procedure at 150 °C for 3 h to determine total hydrolyzable amino acid content. The HCl acid-hydrolyzed, hot water extracts were then desalted using cation-exchange chromatography. The remaining non-hydrolyzed water extracts of the meteorite samples were taken through the identical desalting procedure in parallel with the acid-hydrolyzed extracts to determine the abundances of free amino acids. For the other larger sample extractions (0.50 g Aguas Zarcas UA 2741 and 0.52 g Aguas Zarcas UA 2746 meteorites, 0.62 g Aguas Zarcas soil, and the 1.0 g Murchison meteorite), the entire hot water extract from each sample was acid-hydrolyzed under HCl vapor, desalted, and 1% of the extract analyzed by LC-FD/Q-ToF-MS to determine the total amino acid abundances and enantiomeric ratios. The remaining 99% of the acid-hydrolyzed water extracts were used to measure the stable carbon isotope values ($\delta^{13}C$) of the individual amino acids. Based on our previous analyses of amino acid standards taken through the entire extraction, acid hydrolysis, and desalting procedure, there is no evidence of significant decomposition, racemization, thermal degradation, or carbon isotopic fractionation of the amino acids (Glavin et al. 2010; Elsila et al. 2012).

LC-FD/Q-ToF-MS Analysis

Amino acid abundances, distribution, and enantiomeric ratios were analyzed by LC-FD/Q-ToF-MS. The amino acids in the NH_4OH eluates were derivatized with OPA/NAC for 15 minutes at room temperature followed by their separation and analysis using a Waters ACQUITY UPLC and Waters Xevo G2-XS Q-ToF-MS operating in positive ion mode. C_2 to C_6 amino acids were chromatographically resolved using a Waters BEH C18 column (2.1 × 50 mm, 1.7 μm bead) and a Waters BEH phenyl column (2.1 × 150 mm, 1.7-μm bead) in series. Both columns were maintained at 30.0 °C. The mobile phase conditions for amino acid

separations were as follows: flow rate, 150 μL/min; gradient, time in minutes (%B): 0 (0), 35 (55), 45 (100). C_5 amino acid isomers and enantiomers were chromatographically separated using the same chromatography conditions as for the C_2 to C_6 amino acids, but required the implementation of a different gradient. The gradient used for C_5 amino acid isomers and enantiomers was structured via time in minutes (% B): 0 (15), 25 (20), 25.06 (35), 44.5 (40), 45 (100).

During the Xevo G2-XS analysis, a dual electrospray ionization (ESI) system was used for the purpose of implementing lock mass corrections. The primary ESI source was operated using the following parameters: capillary voltage, 1.2 kV; sampling cone voltage, 40 V; cone gas (N_2) flow, 50 Lhr^{-1}, source temperature, 120 °C; desolvation gas (N_2) temperature, 500 °C; desolvation gas flow rate, 300 Lhr^{-1}. Due to the possibility that minor variations in the mass-to-charge (m/z) scale may occur during the course of executing experimental runs after instrument calibration is performed, a reference ESI source was implemented to supply an independent leucine enkephalin standard signal. The reference ESI source was operated using identical parameters to those used for the primary ESI source, except the reference ESI source used a capillary voltage of 2.8 kV and a reference cone voltage of 30 V. The ToF analyzer was operated in "Sensitivity mode," which used a reflectron to provide a full width at half maximum resolution of 22,000 based on the $[M+H]^+$ of leucine enkephalin, m/z 556.2771. The reference ESI source was operated with a scan time of 1 s at an interval of 120 s. The detector voltage was set to 3325 V. The mass range over which mass data were acquired was 50–900 m/z.

The amino acid abundances and their enantiomeric ratios in the meteorite extracts and controls were determined by comparison of the peak areas generated from the sample and control UV fluorescence chromatograms (LC-FD, λ_{ex} = 340 nm, λ_{em} = 450 nm) of their OPA/NAC derivatives to the corresponding peak areas of amino acid standards run under the same chromatographic conditions and included peak identification confirmation by accurate mass using a match tolerance of 10 ppm (Q-ToF-MS). The reported amino acid concentrations (nmol g^{-1}) in Tables 1 and 2 are the average values of between three and six separate LC-FD/Q-ToF-MS measurements.

GC-MS/IRMS Analysis

Stable carbon isotopic compositions of amino acids were analyzed by GC-MS/IRMS. For the carbon isotope measurements, amino acids in the acid-hydrolyzed water extracts were esterified with isopropanol and the isopropyl esters reacted with trifluoroacetic anhydride (TFAA). The $\delta^{13}C$ values of the TFAA-isopropyl derivatives were analyzed on a gas chromatograph coupled to both a mass spectrometer and an isotope ratio mass spectrometer (GC-MS/IRMS) instrument suite, which provides compound-specific structural and isotopic information from a single sample injection. The GC-MS/IRMS suite consists of a Thermo Trace GC whose 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 90% passes through a Thermo GC-C III interface, where eluting amino acids are oxidized to form CO_2, which is then passed into a Thermo MAT 253 isotope ratio mass spectrometer to measure the $^{13}C/^{12}C$ ratio of the amino acid derived CO_2. 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 to 85 °C, ramped at 2 °C/min to 120 °C, ramped at 4 °C/min to 200 °C, and held for 10 min. Six pulses of high-purity CO_2 gas ($\delta^{13}C$ = –27.40‰, Vienna Pee Dee Belemnite, VPDB) that had been precalibrated against two commercial reference CO_2 gases (Oztech Corporation, $\delta^{13}C$ = –3.61‰, VPDB and $\delta^{13}C$ = –40.740‰, VPDB) were injected into the IRMS for computation of the $\delta^{13}C$ values of the eluting derivatized amino acid standards and sample compounds. Analysis of the MAT 253 data was performed with Thermo Isodat 3.0 software. The reported $\delta^{13}C$ values for the individual amino acids in the Aguas Zarcas meteorites (UA 2741 and UA 2746), the Aguas Zarcas soil (UA 2745), and the Murchison meteorite extracts are the average of three separate analyses and were corrected for the carbon added during derivatization. Due to the relatively low amino acid abundances in the meteorites, there was insufficient sample available to make nitrogen and hydrogen isotope measurements of the amino acids. To do so would have required at least three times the mass of meteorite sample used for the carbon isotope measurements.

RESULTS AND DISCUSSION

Amino Acid Abundances and Relative Distributions

Typical liquid chromatography UV fluorescence and ToF-MS mass chromatograms of the 6 M HCl vapor hydrolyzed, hot-water extracts from the Aguas Zarcas meteorite UA 2741, the Murchison meteorite, and the procedural blank show several peaks corresponding to two- to six-carbon aliphatic primary amino acids (Figs. 1 and 2). Peaks in the LC-FD/Q-ToF-MS sample

Table 1. Summary of the average abundances (nmol/g) of the two- to six-carbon amino acids in the non-hydrolyzed (free) and 6 M HCl-hydrolyzed (total) water extracts of the CM2 Aguas Zarcas meteorites (UA 2741 and UA 2746), Aguas Zarcas recovery site soil (UA 2745), and the CM2 Murchison meteorite measured by LC-FD/Q-ToF-MS. Total mass extracted given under sample name.[a]

	Aguas Zarcas					Murchison			
	UA 2741		UA 2741	UA 2746	Soil#2 UA 2745	Chicago Field Museum			Soil#1[c]
	0.08 g extract		0.50 g extract	0.52 g extract	0.62 g extract	0.08 g extract		1.0 g extract	0.17 g extract
Amino acids (C_2 to C_6)	Free	Total	Total	Total	Total	Free	Total	Total	Total
D-aspartic acid	0.20 ± 0.01	2.4 ± 0.01	0.16 ± 0.06	15.1 ± 0.7	50 ± 1	0.06 ± 0.01	0.59 ± 0.02	0.95 ± 0.04	72 ± 2
L-aspartic acid	3.8 ± 0.1	10.1 ± 0.3	0.5 ± 0.2	27 ± 1	120 ± 4	0.27 ± 0.02	3.0 ± 0.1	1.7 ± 0.1	314 ± 2
D-glutamic acid	0.59 ± 0.01	2.2 ± 0.1	0.59 ± 0.01	10.3 ± 0.1	28 ± 2	0.17 ± 0.01	1.03 ± 0.03	2.7 ± 0.1	19 ± 15
L-glutamic acid	3.75 ± 0.05	19.7 ± 0.4	3.7 ± 0.1	36 ± 1	119 ± 5	0.29 ± 0.01	6.3 ± 0.1	7.6 ± 0.4	269 ± 33
D-serine	2.07 ± 0.05	3.4 ± 0.2	0.3 ± 0.2	1.9 ± 0.2	16.9 ± 0.1	0.04 ± 0.01	0.13 ± 0.03	0.4 ± 0.1	<15
L-serine	14.0 ± 0.5	18.0 ± 0.6	1.5 ± 0.9	6.6 ± 0.9	91.3 ± 0.1	0.53 ± 0.02	3.5 ± 0.1	0.6 ± 0.1	199 ± 21
D-threonine	<0.01	0.01 ± 0.01	0.2 ± 0.2	0.7 ± 0.2	4.2 ± 0.2	<0.01	0.02 ± 0.01	0.17 ± 0.01	n.d.
L-threonine	6.8 ± 0.2	14.8 ± 0.7	28 ± 1	56 ± 28	107 ± 1	0.08 ± 0.05	2.21 ± 0.05	0.32 ± 0.03	n.d.
Glycine	58 ± 4	75 ± 14	20 ± 3	158 ± 35	425 ± 10	6.7 ± 0.4	40 ± 3	32 ± 3	667 ± 35
β-alanine	1.7 ± 0.1	3.4 ± 0.2	0.9 ± 0.1	10 ± 2	26 ± 2	3.3 ± 0.1	6.0 ± 0.2	16 ± 1	8 ± 1
γ-amino-*n*-butyric acid + D,L-β-AIB[b]	1.9 ± 0.1	3.9 ± 0.3	1.4 ± 0.1	6 ± 1	25.2 ± 0.8	0.7 ± 0.1	2.4 ± 0.6	2.0 ± 0.2	4.9 ± 0.9
D-alanine	2.5 ± 0.1	3.7 ± 0.2	1.6 ± 0.1	17 ± 4	74.3 ± 0.5	0.94 ± 0.06	2.2 ± 0.1	8.3 ± 0.8	47 ± 1
L-alanine	11.7 ± 0.6	18.4 ± 0.7	3.5 ± 0.4	38 ± 6	213 ± 1	0.98 ± 0.06	3.0 ± 0.2	8.2 ± 0.7	356 ± 6
D-β-amino-*n*-butyric acid	0.21 ± 0.01	0.33 ± 0.04	0.19 ± 0.02	0.34 ± 0.03	0.48 ± 0.03	1.13 ± 0.05	1.8 ± 0.1	1.3 ± 0.2	<6
L-β-amino-*n*-butyric acid	0.18 ± 0.01	0.26 ± 0.03	0.19 ± 0.02	0.3 ± 0.2	0.6 ± 0.1	1.08 ± 0.04	1.6 ± 0.1	1.2 ± 0.2	
α-aminoisobutyric acid (α-AIB)	5.4 ± 0.9	4.6 ± 0.7	5.6 ± 0.8	5.2 ± 0.8	1.0 ± 0.6	10.8 ± 0.3	11.4 ± 0.5	10.4 ± 0.8	<0.1
D,L-α-amino-*n*-butyric acid[b]	1.8 ± 0.2	1.8 ± 0.3	1.4 ± 0.4	2.9 ± 0.4	4.0 ± 0.4	0.65 ± 0.01	2.0 ± 0.4	2.4 ± 0.3	<0.7
ε-amino-*n*-caproic acid (EACA)	4.2 ± 0.3	0.4 ± 0.5	0.7 ± 0.4	1.8 ± 0.4	1.4 ± 0.8	0.14 ± 0.03	2.2 ± 0.6	2.2 ± 0.2	n.d.
C_5 amino acids (from Table 3)	8 ± 1	40 ± 2	14 ± 3	45 ± 15	216 ± 45	11 ± 1	42 ± 3	38 ± 1	102 ± 29
Sum (nmol/g)	127 ± 7	222 ± 21	85 ± 10	438 ± 97	1523 ± 73	39 ± 2	132 ± 8	135 ± 11	2062 ± 145

n.d. = value not determined due to trace amino acid abundances and/or lack of standards.

[a]Sample extracts were analyzed by OPA/NAC derivatization (15 min.) and LC-FD/Q-ToF-MS. The reported uncertainties (δx) are based on the standard deviation of the average value of 3–6 separate measurements (n) with a standard error, $\delta x = \sigma_x \cdot (n-1)^{-1/2}$.

[b]The amino acids γ-ABA and β-AIB coelute and the D- and L-β-AIB enantiomers could not be separated under the chromatographic conditions.

[c]HPLC-UV fluorescence data from Glavin (2001).

Table 2. Summary of the average abundances (nmol/g) of five-carbon amino acids in the non-hydrolyzed (free) and 6 M HCl-hydrolyzed (total) water extracts of the CM2 Aguas Zarcas meteorites (UA 2741 and UA 2746), Aguas Zarcas landing site soil (UA 2745), and the CM2 Murchison meteorite measured by LC-FD/Q-ToF-MS. Total mass extracted given under sample name.[a]

		Aguas Zarcas					Murchison			
		UA 2741		UA 2741	UA 2746	Soil#2 UA 2745	Chicago Field Museum			Soil#1[f]
		0.08 g extract		0.50 g extract	0.52 g extract	0.62 g extract	0.08 g extract		1.0 g extract	0.17 g extract
Amino acids (C_5)		Free	Total	Total	Total	Total	Free	Total	Total	Total
α	D-norvaline (D-2-apa)	0.10 ± 0.01	0.45 ± 0.03	0.5 ± 0.2	0.15 ± 0.01	0.08 ± 0.01	<0.01	0.1 ± 0.1	0.25 ± 0.01	n.d.
	L-norvaline (L-2-apa)	0.11 ± 0.01	0.56 ± 0.01	0.5 ± 0.2	0.16 ± 0.01	0.17 ± 0.01	0.03 ± 0.02	0.05 ± 0.03	0.25 ± 0.01	n.d.
	D-isovaline (D-2-a-2-mba)	1.4 ± 0.1	4.0 ± 0.2	2.8 ± 0.2	2.9 ± 0.4	<0.1	3.5 ± 0.2	10.0 ± 0.5	9.5 ± 0.1	<0.1
	L-isovaline (L-2-a-2-mba)	2.0 ± 0.1	5.0 ± 0.2	3.5 ± 0.4	3.9 ± 0.4	<0.1	4.5 ± 0.2	11.8 ± 0.7	11.5 ± 0.1	
	D-valine (D-2-a-3-mba)	0.25 ± 0.01	0.92 ± 0.03	0.35 ± 0.03	3.6 ± 0.8	10 ± 1	0.09 ± 0.01	0.55 ± 0.02	0.62 ± 0.01	4 ± 3
	L-valine (L-2-a-3-mba)	2.5 ± 0.2	20.1 ± 0.5	1.2 ± 0.1	27 ± 11	204 ± 43	0.10 ± 0.01	2.8 ± 0.1	0.93 ± 0.04	97 ± 27
β	D,L-3-apa[b]	0.10 ± 0.01	0.27 ± 0.03	0.6 ± 0.5	0.9 ± 0.6	0.5 ± 0.4	0.53 ± 0.02	2.7 ± 0.1	2.50 ± 0.03	n.d.
	D,L- and allo-3-a-2-mba[b]	<0.01	0.04 ± 0.03	0.8 ± 0.4	1.4 ± 0.9	<0.01	0.04 ± 0.01	0.29 ± 0.04	0.3 ± 0.2	n.d.
	3-a-3-mba[c]	<0.01	1.3 ± 0.1	0.47 ± 0.06	1.0 ± 0.2	<0.01	1.2 ± 0.1	4.76 ± 0.04	5.2 ± 0.1	n.d.
	3-a-2,2-dmpa	1.17 ± 0.01	0.47 ± 0.02	0.18 ± 0.01	0.17 ± 0.01	1.0 ± 0.6	0.30 ± 0.02	1.9 ± 0.1	1.73 ± 0.01	n.d.
	D,L-3-a-2-epa[d,e]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.3	<0.3	<0.3	n.d.
γ	D,L-4-apa[b]	<0.01	2.1 ± 0.1	0.8 ± 0.2	0.7 ± 0.1	<0.01	0.30 ± 0.02	2.9 ± 0.1	0.9 ± 0.7	n.d.
	D,L-4-a-2-mba[d]	0.02 ± 0.02	2.1 ± 0.5	1.0 ± 0.3	1.1 ± 0.4	<0.01	0.01 ± 0.01	2.1 ± 0.6	1.56 ± 0.02	n.d.
	D,L-4-a-3-mba[d]	<0.01	0.31 ± 0.01	0.06 ± 0.01	0.04 ± 0.01	<0.01	0.01 ± 0.01	0.42 ± 0.02	0.07 ± 0.05	n.d.
δ	5-apa	0.31 ± 0.03	2.6 ± 0.1	1.0 ± 0.1	1.8 ± 0.3	<0.01	0.15 ± 0.02	1.8 ± 0.1	2.2 ± 0.1	n.d.
	Sum (nmol/g)	8 ± 1	40 ± 2	14 ± 3	45 ± 15	216 ± 45	11 ± 1	42 ± 3	38 ± 1	102 ± 30

n.d. = value not determined due to trace amino acid abundances and/or lack of standards.

[a]Extracts were analyzed by OPA/NAC derivatization (15 min.) and LC-FD/Q-ToF-MS. For the LC-FD/Q-ToF-MS data, the mono-isotopic masses (m/z 379.13 ± 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 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 3–6 separate measurements (n) with a standard error, $\delta x = \sigma_x \cdot (n-1)^{-1/2}$.

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

[c]3-a-3-mba co-elutes with one of the enantiomers of D,L-4-apa; therefore, upper limits for 3-a-3-mba were estimated by taking the difference in peak areas of the two D,L-4-apa enantiomers.

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

[e]Poor chromatographic resolution of D,L-3-a-2-epa prevented its accurate quantification; therefore, only upper limits are reported.

[f]HPLC-UV fluorescence data from Glavin (2001).

chromatograms were only identified as amino acids if the retention times of the UV fluorescence peaks coincided with the corresponding mass peaks of the OPA/NAC derivatized amino acid standard. We achieved chromatographic separation of several α-H protein amino acids including aspartic and glutamic acids, serine, threonine, alanine, valine, and their enantiomers (Fig. 1). Furthermore, we achieved enantiomeric separation of D- and L-valine, D- and L-isovaline, and D- and L-norvaline and no interferences or co-elutions with other C_5 amino acid isomers and enantiomers (Fig. 2). The individual D- and L-enantiomers of 3-aminopentanoic acid were also clearly separated (Fig. 2), but could not be enantiomerically identified due to the lack of optically pure standards. Several small UV fluorescent peaks that could be amino acids were present in the Murchison and Aguas Zarcas UA 2741 LC chromatograms (Fig. 1), but were not identified with standards. These peaks could include a variety of other primary aliphatic amino acids and hydroxy amino acids that have been identified in the Murchison meteorite (Cronin and Chang 1993; Koga and Naraoka 2017; Glavin et al. 2018). Multiple injections of the standards, procedural blanks, meteorite, and soil extracts using two different LC gradients required that the samples be run on different days, which resulted in retention time differences of the C_5 amino acid peaks eluting in the 21–33 min region of the LC-Q-ToF-MS single ion chromatograms. These retention time differences and can be explained by slight changes in the column conditions due to differences in buffer batches and column equilibration times between injections (Fig. 2) and had no effect on the accurate identification and quantification of the C_5 amino acids in the meteorite and sample extracts because they were compared to standards run on the same day under the same conditions.

All of the identified amino acids and their procedural blank–corrected concentrations and uncertainties are given in Tables 1 and 2. The total amino acid abundances (free + bound) of identified C_2 to C_6 amino acids in 6 M HCl-hydrolyzed hot water extracts of the Aguas Zarcas meteorites ranged from ~85 to 222 nmol/g for UA 2741 and ~438 nmol/g in UA 2746. The total amino acid abundances in the Murchison meteorite water extracts (~132–135 nmol/g, Table 1) were similar to the average value (~153 nmol/g) of the two different UA 2741 fragments we investigated. Only trace levels (0.01–0.09 nmol) of L-aspartic acid, L-glutamic acid, L-serine, glycine, β-alanine, L-alanine, and ε-amino-*n*-caproic acid were measured in the procedural blanks, indicating that very little amino acid contamination of the samples occurred during sample processing (Fig. 1). However, the low amino acid abundances in the procedural blanks do not rule out the possibility of amino acid contamination of the meteorites from the Aguas Zarcas soils after landing, or during collection, storage, and handling of the samples. The elevated abundances of protein amino acids in the Aguas Zarcas meteorite UA 2746 compared to UA 2741 (Tables 1 and 2), which both have similar protein amino acid distributions compared to the Aguas Zarcas soil UA 2745 (Fig. 3), are consistent with both some terrestrial amino acid exposure of the Aguas Zarcas meteorites after their fall and visual observations of plant material in UA 2746. Not surprisingly, the total amino acid abundances in the Aguas Zarcas and Murchison fall site soil extracts were dominated by the protein amino acids and an order of magnitude higher than the meteorites (~1,523–2,062 nmol/g, Table 1).

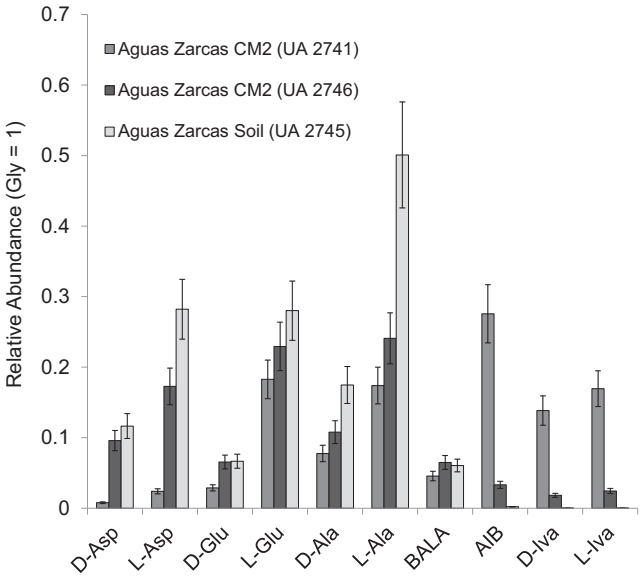

Fig. 3. A comparison of the relative molar abundances of several protein and non-protein amino acids (glycine = 1.0) in the 6 M HCl-hydrolyzed, hot water extracts of the Aguas Zarcas meteorite samples (0.5 g extract of UA 2741 and 0.52 g extract of UA 2746) and soil (0.17 g extract of UA 2745) collected from the Aguas Zarcas recovery site.

A similar distribution of free amino acids was also observed in the 0.08 g extract of Aguas Zarcas UA 2741 representing roughly 57% of the total amino acid abundance, which is higher than the percentage of free amino acids in the 0.08 g extract of the Murchison meteorite (free/total ~29%, Table 1) analyzed in this study, but falls within the range of relative abundances of free amino acids measured in other CM and CR carbonaceous chondrites that range from ~38 to 70% (Glavin et al. 2006, 2010; Pizzarello et al. 2008). It has been shown previously that acid hydrolysis of the water extracts from CI, CM, and CR type carbonaceous chondrites will readily release bound amino acids

(Glavin et al. 2010). These bound amino acids have their amino group chemically protected and are not subject to OPA/NAC derivatization or exist as a precursor to the amino acid and would have a different mass and retention time compared to the OPA/NAC labeled amino acid. The increase in amino acid concentration in the hydrolyzed extracts observed in many carbonaceous chondrites is believed to result from a combination of terrestrial protein amino acid contamination and derivatives and/or acid-labile precursors of non-biological origin that are converted to amino acids through acid hydrolysis. For example, in the Murchison meteorite, most of the acid-labile precursors are low molecular weight derivatives including mono- and dicarboxylic acid amides, hydroxy acid amides, lactams, carboxylactams, N-acetylamino acids, and substituted hydantoins (Cronin 1976; Cooper and Cronin 1995).

The presence of non-protein amino acids in meteorites that are not common on Earth, such as α-AIB and isovaline, has often been used to argue that these amino acids are indigenous to the meteorites and not terrestrial contaminants. Despite some obvious terrestrial protein amino acid contamination of the Aguas Zarcas meteorite fragments studied here, the total abundances of the non-protein amino acids α-AIB and isovaline in the Aguas Zarcas meteorites UA 2741 and UA 2746 were similar (~5–9 nmol/g, Tables 1 and 2). Furthermore, the relative molar abundances of α-AIB and isovaline in the Aguas Zarcas meteorites UA 2741 and UA 2746 greatly exceeded that which was observed in the Aguas Zarcas soil UA 2745 (Fig. 3). The lower relative abundances of α-AIB and isovaline in Aguas Zarcas UA 2746 compared to UA 2741 (Fig. 3) reflects the much higher total abundance of glycine in UA 2746 (Table 1), which is mostly from terrestrial contamination. Only trace levels of α-AIB (~1 nmol/g, Table 1) were detected in the Aguas Zarcas soil UA 2745 and isovaline was not present in the soil above the analytical detection limit (<0.1 nmol/g, Table 2). It should be noted that some fungal peptides can contain these non-protein amino acids (Bruckner et al. 2009), which could be the source of the α-AIB identified in the Aguas Zarcas soil UA 2745. The presence of both α-AIB and D- and L-isovaline at elevated concentrations of ~10–20 nmol/g in the Murchison meteorite extracts, but not in the Murchison soil (Tables 1 and 2), provides additional evidence that these two α-dialkyl amino acids are indigenous to the meteorite.

In addition to isovaline, several other five-carbon (C_5) non-protein amino acids that were not identified in the Aguas Zarcas soil UA 2745 above the 0.01 nmol/g level (Table 2), including D,L- and *allo*-3-amino-2-methylbutanoic acid (3-a-2-mba), 3-amino-3-methylbutanoic acid (3-a-3-mba), D,L-4-aminopentanoic acid (4-apa), D,L-4-amino-2-methylbutanoic acid (4-a-2-mba), D,L-4-amino-3-methylbutanoic acid (4-a-3-mba), and 5-aminopentanoic acid (5-apa), were identified well above procedural blank levels in the Aguas Zarcas and Murchison meteorites (Tables 1 and 2; Fig. 2). All of these C_5 amino acids are terrestrially rare and therefore of likely extraterrestrial origin in these CM2 carbonaceous chondrites. The relative molar abundances of the C_5 amino acid isomers in the CM2 Aguas Zarcas and Murchison meteorites as a function of amine position (α, β, γ, or δ) normalized to the total number of possible C_5 structural isomers, show identical C_5 amino acid distributions within uncertainties (Fig. 4). This finding provides a strong indication that the C_5 amino acids formed in chemically similar parent bodies. The dashed line in Fig. 4 corresponding to a relative abundance of 1 indicates the expected ratio if there was an equal probability of forming all of the C_5 amino acid isomers. Therefore, enhanced and depleted relative C_5 amino acid abundances refer to values that fall above and below the dashed line, respectively. The enhanced relative abundance of the C_5 α-amino acids compared to β-, γ-, and δ-amino acids in the Aguas Zarcas and Murchison meteorites is similar to what is observed in pristine Antarctic CM2 and CR type 2 and 3 carbonaceous chondrites (Fig. 4) and provides evidence that the α-amino acids in these meteorites were mainly formed by Strecker-cyanohydrin synthesis during the parent body aqueous alteration phase. It is also possible that some α-amino acids could have formed by direct polymerization of HCN during aqueous alteration (Matthews 1992; Lerner et al. 1993; Levy et al. 2000) or prior to incorporation into the parent body on interstellar ice grain surfaces exposed to radiation (Bernstein et al. 2002; Muñoz Caro et al. 2002; Elsila et al. 2007). The reaction of HCN, NH_3, and carbonyl compounds (aldehydes and ketones) will lead to the formation of α-amino, α-imino, and α-hydroxy acids (but not β-, γ- and δ-amino acids) in aqueous solution via the Strecker-cyanohydrin pathway; all of these expected Strecker byproducts have been identified in the Murchison meteorite (Peltzer and Bada 1978; Peltzer et al. 1984; Lerner and Cooper 2005). Based on the similarity in α-amino acid compositions in the Aguas Zarcas and Murchison meteorites, we predict that a similar distribution of Strecker reaction products is also present in the Aguas Zarcas meteorite; however, we did not conduct a search for α-imino or α-hydroxy acids in this study.

In contrast to Aguas Zarcas, Murchison, and other CM and CR type 2 and 3 carbonaceous chondrites which are dominated by α-amino acids formed by the Strecker-cyanohydrin pathway, the more aqueously

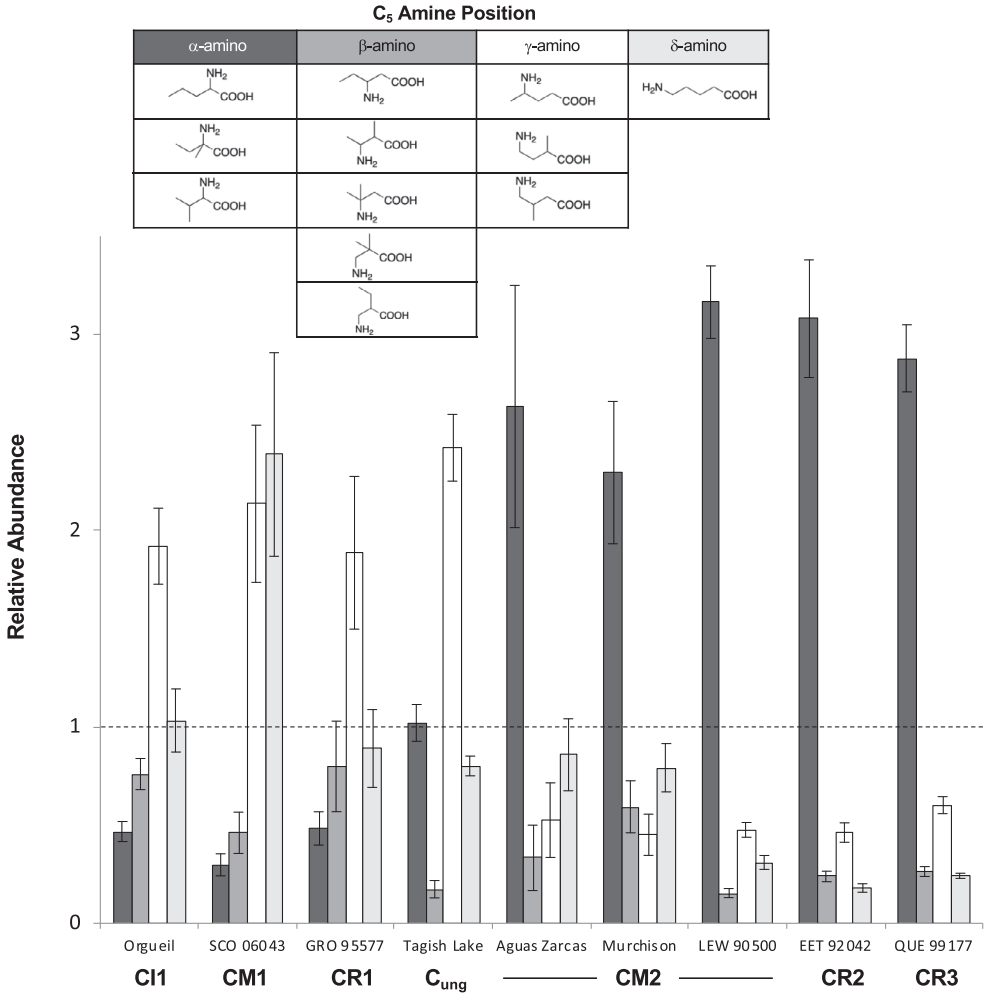

Fig. 4. A comparison of the relative molar abundances of the total C_5 amino acids in CI, CM, CR, and the ungrouped Tagish Lake carbonaceous chondrites as a function of amine position (α-, β-, γ-, and δ-) normalized to the total number of possible structural isomers. Amino acid data from the Aguas Zarcas meteorite (0.5 g extract of UA 2741) and Murchison (1.0 g extract of Chicago Field Museum) were used in the plot. The dashed line corresponds to the expected relative abundance if the amino acids were formed by a completely random synthetic process. The relative abundance data for Orgueil, SCO 06043, GRO 95577, Tagish Lake, LEW 90500, EET 92042, and QUE 99177 taken from Glavin et al. (2010, 2012) are shown for comparison.

altered type 1 CI, CM, and CR chondrites and the Tagish Lake meteorite typically have lower relative abundances of C_5 α-amino acids and elevated abundances of γ- and δ-amino acids (Fig. 4). One possibility is that more extensive parent body aqueous alteration in the type 1 compared to the type 2 and 3 carbonaceous chondrites results in an increase in the rate of hydrolysis of bound amino acid precursors such as lactams or thermal decarboxylation of α-amino dicarboxylic acids yielding elevated levels of γ- and δ-amino acids in these carbonaceous chondrites (Cooper and Cronin 1995; Glavin et al. 2010). Another possible explanation for the high relative abundances of C_5 γ- and δ-amino acids in type 1 chondrites is that these amino acids are more stable to thermal decomposition than the α- and β-amino acids as has been observed for some C_4 amino acids (Li and Brill 2003). In general, the relative abundances of the C_5 β-amino acids in the type 1 chondrites seem to be slightly higher than in the less altered CR type 2 and type 3 chondrites (Fig. 4); however, we see no clear trend in C_5 β-amino acid abundance with degree of alteration in the meteorites analyzed. Overall, the relative abundances of the C_5 amino acids in the Aguas Zarcas and Murchison meteorites suggest that these CM type 2 carbonaceous chondrites experienced a similar degree of aqueous alteration on their respective parent bodies that is intermediate between the less altered CR2.8 carbonaceous chondrites described by Harju et al. (2014) and the highly altered type 1 chondrites. It is

Table 3. Summary of the $\delta^{13}C$ values (‰, VPDB) of amino acids in the 6 M HCl-acid hydrolyzed extracts of the Aguas Zarcas meteorites (UA 2741 and UA 2746) and soil (UA 2745) and the Murchison meteorite.[a]

	Aguas Zarcas			Murchison
	UA 2741	UA 2746	Soil#2 UA 2745	Chicago Field Museum
	0.50 g extract (total)	0.52 g extract (total)	0.62 g extract (total)	1.0 g extract (total)
Amino acids	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰)
D-aspartic acid	n.d.	−15 ± 21	−18 ± 7	n.d.
L-aspartic acid	n.d.	−9 ± 27	−5 ± 7	n.d.
D-glutamic acid	+20 ± 8	−7 ± 13	−14 ± 9	+31 ± 3
L-glutamic acid	−10 ± 4	−12 ± 4	−15 ± 5	+15 ± 3
Glycine	+15 ± 6	+6 ± 9	+5 ± 4	+24 ± 4
D-alanine	+40 ± 3	−7 ± 3	−18 ± 4	+49 ± 5
L-alanine	+16 ± 2	−2 ± 5	−11 ± 3	+38 ± 5
β-alanine	+9 ± 4	−17 ± 3	−22 ± 2	+10 ± 1
AIB	+17 ± 5	+30 ± 12	n.d.	+33 ± 6
D-isovaline	+25 ± 3	+32	n.d.	+18 ± 6
L-isovaline	+32 ± 5	+34	n.d.	+26 ± 7

n.d. = value not determined due to trace amino acid abundances and/or chromatographic interferences.

[a]The errors in the corrected $\delta^{13}C$ values of the amino acids in the samples were determined from the contributions of the errors from the carbon isotope values of both derivatized and underivatized standards and the derivatized samples from three separate measurements. Values shown without an error were derived from a single measurement. $\delta^{13}C$ values for amino acids in the Murchison fall site soil were not determined.

possible that the slight differences in the relative C5 amino acid abundances observed in these CM chondrites is related to differences in their petrologic subtypes (i.e., CM2.X) as described elsewhere (Rubin et al. 2007). Although to date we have not identified the mechanism(s) responsible for the variations seen in the C5 amino acid distributions in the CI, CM, and CR carbonaceous chondrites, the correlation with the degree of parent body aqueous alteration at modest temperature suggests a solution-based explanation.

Amino Acid Carbon Isotopes and L-Enantiomeric Excesses

Carbon isotope measurements were made for the most abundant amino acids in the acid-hydrolyzed, hot water extracts of the Aguas Zarcas and Murchison meteorites and the Aguas Zarcas soil. The GC-MS/IRMS technique employed provides simultaneous compound-specific structural and stable carbon isotopic information from a single GC injection. This approach permitted three replicate analyses of D- and L-aspartic and D- and L-glutamic acids, glycine, D- and L-alanine, and β-alanine in the meteorite and soil extracts and α-AIB, and D- and L-isovaline in the meteorite extracts. Due to low aspartic acid abundances in Aguas Zarcas UA 2741 and Murchison, we were not able to determine the carbon isotope composition of aspartic acid in these meteorites. The $\delta^{13}C$ values of D- and L-aspartic and D- and L-glutamic acids, glycine, D- and L-alanine, and β-alanine in the Aguas Zarcas UA 2746 meteorite ranged from +6‰ for glycine to −17‰ for β-alanine and were all similar (within analytical uncertainties) to the $\delta^{13}C$ values measured for the same amino acids in the Aguas Zarcas soil (Table 3), which is evidence of terrestrial contamination. In contrast, the Aguas Zarcas UA 2741 meteorite showed substantial ^{13}C enrichments in several amino acids including D-glutamic acid, glycine, D- and L-alanine, and β-alanine with $\delta^{13}C$ values ranging from +9‰ to +40‰ (Table 3). These values clearly fall outside of the typical terrestrial range for organic carbon of −6‰ to −40‰ (Bowen 1988) and the carbon isotope values of amino acids in the Aguas Zarcas soil UA 2745 (Table 3), indicating an extraterrestrial component.

The carbon isotopic compositions of the same amino acids in the Murchison meteorite also fall well outside of the terrestrial range and were even more enriched in ^{13}C compared to Aguas Zarcas UA 2741 with $\delta^{13}C$ values ranging from +10‰ to +49‰ (Table 3), which may indicate that this Murchison meteorite sample experienced less terrestrial amino acid contamination than UA 2741. Carbon isotope measurements of the α-dialkyl amino acids α-AIB and isovaline in the Aguas Zarcas and Murchison meteorites were similar given the analytical uncertainties and also enriched in ^{13}C with $\delta^{13}C$ values ranging from +17‰ to +34‰ (Table 3). The carbon isotope values measured for amino acids in the Murchison meteorite sample investigated in this study were all very similar to the $\delta^{13}C$ values that have been reported in previous analyses of Murchison conducted using similar techniques in multiple laboratories (Engel et al. 1990; Pizzarello et al. 2004; Elsila et al. 2012), which provide

additional confidence in the accuracy of the carbon isotope results for the Aguas Zarcas meteorites and Aguas Zarcas soil.

The D/L ratios and corresponding L-enantiomeric excesses (L_{ee} = %L–%D) for all of the chiral amino acids in the acid-hydrolyzed hot water extracts that were resolved by liquid chromatography (aspartic and glutamic acids, serine, alanine, valine, β-amino-*n*-butyric acid [β-ABA], norvaline, and isovaline) are shown in Table 4. The measured D/L ratios of the protein amino acids in the Aguas Zarcas meteorite extracts ranged from ~0.01 to 0.56 with corresponding L_{ee} of ~28% for aspartic acid up to 99% for threonine (Table 4). Similar D/L ratios and L_{ee} were measured for the same protein amino acids in the Aguas Zarcas soil UA 2745 (Table 4), which is consistent with some terrestrial amino acid contamination of the meteorites.

Terrestrial Origin of L-Protein Amino Acid Excesses in Aguas Zarcas

For Aguas Zarcas UA 2741, carbon isotope measurements of amino acids in the meteorite demonstrate that many of the protein amino acids are indigenous to the meteorite since they are enriched in ^{13}C compared to amino acids in the Aguas Zarcas soil and also fall outside of the typical terrestrial range for organic carbon (Table 3). However, both L-glutamic acid and L-alanine in Aguas Zarcas UA 2741 have lower $\delta^{13}C$ values than their respective D-enantiomers, which implies some terrestrial contribution to the L-glutamic acid and L-alanine in the meteorite. As detailed in Table 5, it is possible to calculate a $\delta^{13}C$ value of $-15.8‰$ for the excess L-glutamic acid in Aguas Zarcas UA 2741 based on the measured abundances and $\delta^{13}C$ values of D- and L-glutamic acids by assuming that the indigenous glutamic acid was initially racemic (D/L = 1) and that the original carbon isotope value for L-glutamic acid was the same as D-glutamic acid ($\delta^{13}C = +20‰$). A similar calculation for Aguas Zarcas UA 2746 determined that the additional L-glutamic acid in this meteorite required to lower the $\delta^{13}C$ value from an assumed initial value of $-7‰$ to $-12‰$ must have a $\delta^{13}C$ value of $-14‰$. In both Aguas Zarcas meteorites, the estimated carbon isotope value for the excess L-glutamic acid is identical within error to the measured carbon isotope value of L-glutamic acid ($\delta^{13}C = -15 \pm 5‰$, Table 4) extracted from the Aguas Zarcas soil. This analysis shows that the most parsimonious explanation for the large L-glutamic acid excesses (~56–73%, Table 4) measured in UA 2741 and UA 2746 is mostly terrestrial in origin. Similarly, based on the measured carbon isotope values and alanine abundances, most of the L-alanine excess in the Aguas Zarcas meteorites (L_{ee} ~ 38%, Table 4) can be explained by terrestrial L-alanine contamination from the Aguas Zarcas soil.

Despite the large errors due to low abundances, carbon isotope measurements of D-aspartic acid ($\delta^{13}C = -15 \pm 21‰$) and L-aspartic acid ($\delta^{13}C = -9 \pm 27‰$) in Aguas Zarcas UA 2746 are also similar to the Aguas Zarcas soil aspartic acid carbon isotope values (Table 3) suggesting a likely terrestrial origin for aspartic acid in this meteorite. We were unable to determine the carbon isotope values of other chiral protein amino acids identified in the Aguas Zarcas meteorites including serine, threonine, and valine due to low abundances and poor GC separation; however, the similarity in the D/L ratios of serine and threonine compared to the Aguas Zarcas soil points toward a terrestrial origin of the measured L-serine and L-threonine excesses in the Aguas Zarcas meteorite (Table 4). The D/L ratios of valine in Aguas Zarcas UA 2741 (0.29 ± 0.03) and Aguas Zarcas UA 2746 (0.13 ± 0.06) are elevated relative to a D/L valine ratio of 0.05 ± 0.01 in the Aguas Zarcas soil UA 2745 (Table 4), which may indicate that there is some extraterrestrial valine in these meteorites; however, without any knowledge of the carbon isotopic composition of D- and L-valine in the Aguas Zarcas meteorites and soil, it is difficult to constrain the origin of this protein amino acid.

Non-Terrestrial Origin of L-Glutamic Acid Excesses in Murchison

Amino acid analyses of the Murchison meteorite showed much less evidence for terrestrial contamination compared to the Aguas Zarcas meteorites, although the Murchison meteorite was also recovered from soil enriched in L-protein amino acids and fell 50 years ago (see Murchison Soil#1: Tables 1, 2 and 4). It is possible that differences in direct exposure to the terrestrial environment after impact, recovery and handling, and/or curation conditions of the meteorites were a factor in the extent of terrestrial amino acid contamination of the Aguas Zarcas and Murchison meteorites. Large L-enantiomeric excesses of aspartic acid, glutamic acid, serine, threonine, and valine ranging from 20 to 48% were measured in Murchison, but no L-excesses of alanine were detected in the meteorite (Table 4). Furthermore, carbon isotope measurements of D-alanine ($\delta^{13}C = +49 \pm 5‰$) and L-alanine ($\delta^{13}C = +38 \pm 5‰$) in Murchison show that both enantiomers are heavily enriched in ^{13}C (Table 3), similar to the carbon isotope values of alanine that have been previously reported in Murchison and other CM2 meteorites and well within the extraterrestrial range (Elsila et al. 2012). The discovery of racemic alanine in this Murchison sample

Table 4. Summary of the D/L ratios and L-enantiomeric excesses (L_{ee}) measured for several amino acids in the 6 M HCl-hydrolyzed hot water extracts of the Aguas Zarcas meteorites (UA 2741 and UA 2746) and soil collected from the Aguas Zarcas fall site (UA 2745) and the Murchison meteorite and Murchison fall site soil.[a]

	Aguas Zarcas						Murchison			
	UA 2741 0.50 g extract (total)		UA 2746 0.52 g extract (total)		Soil#2 UA 2745 0.62 g extract (total)		Chicago Field Museum 1.0 g extract (total)		Soil#1[b] 0.17 g extract (total)	
Amino acids	D/L	L_{ee} (%)	D/L	L_{ee} (%)	D/L	L_{ee} (%)	D/L	L_{ee} (%)	D/L	L_{ee} (%)
Aspartic acid	0.32 ± 0.17	52 ± 15	0.56 ± 0.03	28 ± 2	0.42 ± 0.02	41 ± 1	0.56 ± 0.04	28 ± 3	0.23 ± 0.01	63 ± 1
Glutamic acid	0.16 ± 0.01	73 ± 1	0.29 ± 0.01	56 ± 1	0.24 ± 0.02	62 ± 2	0.36 ± 0.02	48 ± 2	0.07 ± 0.06	87 ± 7
							0.41 ± 0.02[c]	42 ± 2[c]		
Serine	0.20 ± 0.18	67 ± 18	0.29 ± 0.05	55 ± 4	0.19 ± 0.01	69 ± 1	0.7 ± 0.2	20 ± 12	<0.07	>87
Threonine	0.007 ± 0.001	99 ± 1	0.013 ± 0.007	98 ± 1	0.04 ± 0.01	92 ± 1	0.53 ± 0.06	31 ± 4	n.d.	n.d.
Alanine	0.46 ± 0.06	37 ± 4	0.45 ± 0.13	38 ± 9	0.35 ± 0.01	48 ± 1	1.0 ± 0.1	0	0.13 ± 0.01	77 ± 1
Valine	0.29 ± 0.03	55 ± 3	0.13 ± 0.06	76 ± 7	0.05 ± 0.01	91 ± 2	0.67 ± 0.03	20 ± 2	0.04 ± 0.03	92 ± 4
β-ABA	1.0 ± 0.1	0	1.0 ± 0.8	0	0.8 ± 0.1	11 ± 8	1.1 ± 0.2	−5 ± 11	n.d.	n.d.
Norvaline	1.0 ± 0.4	0	0.94 ± 0.09	3 ± 4	0.47 ± 0.07	36 ± 4	1.0 ± 0.1	0	n.d.	n.d.
Isovaline	0.8 ± 0.1	11 ± 6	0.74 ± 0.13	15 ± 7	n.d.	n.d.	0.83 ± 0.01	10 ± 1	n.d.	n.d.

n.d. = value not determined due to trace amino acid abundances and/or lack of standards.

[a]The standard errors (δx) for the D/L ratios and L-enantiomeric excesses (L_{ee}) are based on the values and errors from Tables 2 and 3 propagated through the relevant equations with L_{ee} (%) = [(L-D)/(L+D)]*100.

[b]HPLC-UV fluorescence data from Glavin (2001).

[c]Values determined from the average D- and L-amino acid peak areas measured by GC-MS.

Table 5. Summary of the calculations to determine the $\delta^{13}C$ values of the terrestrial contributions to the L-glutamic acid excesses in the Aguas Zarcas and Murchison meteorites and the corrected extraterrestrial D/L glutamic acid ratios in Murchison.

Steps to calculate $\delta^{3}C$ value of glu L_{ee} and corrected D/L ratio and L_{ee}	Aguas Zarcas									Murchison		
	UA 2741 0.50 g extract (total)			UA 2746 0.52 g extract (total)			Soil#2 UA 2745 0.62 g extract (total)			Chicago Field Museum 1.0 g extract (total)		
	nmol/g	$\delta^{13}C$ (‰)	D/L	nmol/g	$\delta^{13}C$ (‰)	D/L	nmol/g	$\delta^{13}C$ (‰)	D/L	nmol/g	$\delta^{13}C$ (‰)	D/L
D-glu (final measured)	0.59	+20	0.16	10.3	−7	0.29	28	−14	0.24	2.7	+31	0.36
L-glu (final measured)	3.7	−10		36	−12		119	−15		7.6	+15	
1. L_{ee} = (L-glu – D-glu)	3.11			25.7			91			4.9		
2. Assume L-glu initial abundance and initial $\delta^{13}C$ value same as D-glu	L-glu = 0.59 D-glu = 0.59	L-glu = +20 D-glu = +20	1	L-glu = 10.3 D-glu = 10.3	L-glu = −7 D-glu = −7	1				L-glu = 2.7 D-glu = 2.7	L-glu = +31 D-glu = +31	1
3. $\delta^{13}C$ value of L-glu excess[a]		−15.8			−14.0						+6.2	
4. Assume two component mixture of L_{ee} in Murchison with extraterrestrial L-glu $\delta^{13}C$ = +31‰ and terrestrial L-glu $\delta^{13}C$ range from Scott et al. (2006)											Extraterrestrial L-glu = +31; Terrestrial L-glu = −0.3 to −60.9	
5. Calculated potential terrestrial L-glu contributions to L_{ee}[b]										L-glu terr. = 3.9 L-glu terr. = 1.3	For L-glu terr. −0.3 For L-glu terr. −60.9	
6. Corrected extraterrestrial L-glu abundances[c]										L-glu corr. = 3.7 L-glu corr. = 6.3	For L-glu terr. −0.3 For L-glu terr. −60.9	
7. Corrected extraterrestrial D/L glu ratios[d]											For L-glu terr. −0.3 For L-glu terr. −60.9	0.73 0.43

[a]$\delta^{13}C$ value of L-glu excess = [(measured $\delta^{13}C$ L-glu) x (measured L-glu abundance) – (initial $\delta^{13}C$ L-glu) x (initial L-glu abundance)]/(L_{ee} = L-glu – D-glu).
[b]Terrestrial L-glu abundance contribution to L_{ee} (T): (terrestrial L-glu $\delta^{13}C$ x T) + (extraterrestrial L-glu $\delta^{13}C$) x (L_{ee} – T) = ($\delta^{13}C$ value of L-glu excess) x (L_{ee}).
[c]Corrected extraterrestrial L-glu abundance = (L-glu final measured) – (calculated L-glu terrestrial).
[d]Corrected extraterrestrial D/L glu ratio = (D-glu final measured)/(L-glu corrected abundance).

was somewhat surprising given that the meteorite fell over 50 yrs ago and could have been exposed to terrestrial L-amino acid contamination. L-alanine is a very common protein amino acid in biology and the second most abundant amino acid in the Murchison soil (D-alanine + L-alanine = 403 nmol/g, Table 1) with an L-alanine excess of 77% (Table 4). Therefore, any terrestrial amino acid contamination of Murchison should have also included L-alanine. Typically, in meteorites that have experienced terrestrial biological contamination after their fall to Earth, the samples do not have racemic mixtures of any common proteinogenic amino acids (Burton et al. 2011, 2014, 2016). Finally, the total abundance of racemic alanine of 16.5 nmol in the 1 g Murchison meteorite extract was higher than all of the other chiral protein amino acids present in the meteorite that have large L-excesses (Table 1). Consequently, these observations cannot be readily explained by biological contamination. A non-biological terrestrial contamination source that consists of only L-aspartic acid, L-glutamic acid, L-serine, L-threonine, and L-valine, but not L-alanine is highly improbable, but cannot be ruled out. Previous amino acid measurements of the same Murchison meteorite fragment yielded the same results (Friedrich et al. 2018); however, carbon isotope measurements needed to firmly establish the origin of these large L-protein amino acid excesses in Murchison were not made in the earlier study.

Carbon isotope measurements of D- and L-glutamic acid, glycine, D- and L-alanine, β-alanine, α-AIB, and D- and L-isovaline in the acid-hydrolyzed, hot water extract of the 1 g Murchison sample were made by GC-MS/IRMS and all of these amino acids were found to be heavily enriched in ^{13}C with $\delta^{13}C$ values ranging from +10 to +49‰ (Table 3), which are all well outside of the typical terrestrial range for organic carbon (Bowen 1988; Scott et al. 2006). Unfortunately, the abundances of D- and L-aspartic acid in the Murchison meteorite extract were insufficient to yield carbon isotope values. The GC-MS/IRMS data for the D- and L-glutamic acid peaks in the Murchison extract are shown in Fig. 5. The retention times and mass spectra for both peaks in the Murchison extract closely match those for the TFAA/IPA derivatives of the D- and L-glutamic acid peaks in the racemic standard (Fig. 5). One unidentified GC-IRMS peak labeled "X" in the racemic standard, the procedural blank, and the Murchison meteorite is an analytical artifact that did not affect accurate quantification of the D- and L-glutamic acid peaks and their carbon isotopic compositions because peak "X" did not co-elute with the target analytes. We found no evidence of additional mass fragments in the mass spectra obtained for the D- and L-glutamic acid peaks in the Murchison extract compared to the mass spectra of the racemic glutamic acid standard that would suggest the presence of any co-eluting or interfering compounds (Fig. 5). The likelihood of co-eluting compound(s) affecting the D/L glutamic acid ratio is further reduced by the fact that the GC-MS measurement of the D/L glutamic acid ratio of 0.41 ± 0.02 in the Murchison extract from the integrated D- and L-glutamic acid peak areas was similar (within error) to an LC-FD/Q-ToF-MS measurement of the D/L glutamic acid ratio of 0.36 ± 0.02 (Table 4) in the same extract, which uses an entirely different amino acid derivatization, separation, and detection method. The measured D/L ratios for glutamic acid in Murchison are not due to the extraction procedure or LC-FD/Q-ToF-MS and GC-MS analytical biases, since we observed no change in the enantiomeric ratio of racemic glutamic acid standards taken through the identical procedure.

The D/L glutamic acid ratio of 0.36 ± 0.02 measured by LC-FD/Q-ToF-MS and 0.41 ± 0.02 measured by GC-MS in Murchison correspond to L-enantiomeric excesses (L_{ee} = L%–D%) of 48 ± 2% and 42 ± 2%, respectively (Table 4). These values are similar to a D/L glutamic acid ratio of ~0.3 (L_{ee} ~55%) measured by GC-MS in another sample of Murchison by Engel and co-workers who also found the D- and L-glutamic acid enantiomers were heavily enriched in ^{15}N ($\delta^{15}N$ = +60‰ for D-glutamic acid and $\delta^{15}N$ = +58‰ for L-glutamic acid) providing strong evidence for an extraterrestrial origin of most of the L-glutamic acid excess in the meteorite (Engel and Nagy 1982; Engel and Macko 1997). A carbon isotope value for L-glutamic acid of $\delta^{13}C$ = +6‰ was also measured in Murchison, but the $\delta^{13}C$ value for D-glutamic acid was not reported (Engel et al. 1990). Carbon isotope measurements of glutamic acid in Murchison measured in this study resulted in $\delta^{13}C$ = +31 ± 3‰ for D-glutamic acid and $\delta^{13}C$ = +15 ± 3‰ for L-glutamic acid. Although both D- and L-glutamic acid have carbon isotope values that are clearly extraterrestrial, the fact that the L-enantiomer is less enriched in ^{13}C than the D-enantiomer may indicate a terrestrial contribution to the measured L-glutamic acid excess. This assumes that there was no carbon isotopic fractionation of glutamic acid during enantiomeric enrichment.

Based on the same assumptions that were used to estimate a $\delta^{13}C$ value of −14 to −16‰ for the excess L-glutamic acid in the Aguas Zarcas meteorites, a similar calculation for Murchison yields $\delta^{13}C$ = +6.2‰ for the excess L-glutamic acid required to reduce the $\delta^{13}C$ value from +31 to +15‰ (Table 5). This $\delta^{13}C$ value of +6.2‰ for the L-glutamic acid excess in Murchison is much more enriched in ^{13}C than the L-glutamic acid excesses in the Aguas Zarcas meteorites and outside the range of stable carbon isotope values of glutamic acid ($\delta^{13}C$ = −0.3 to −60.9‰) that have been measured in a

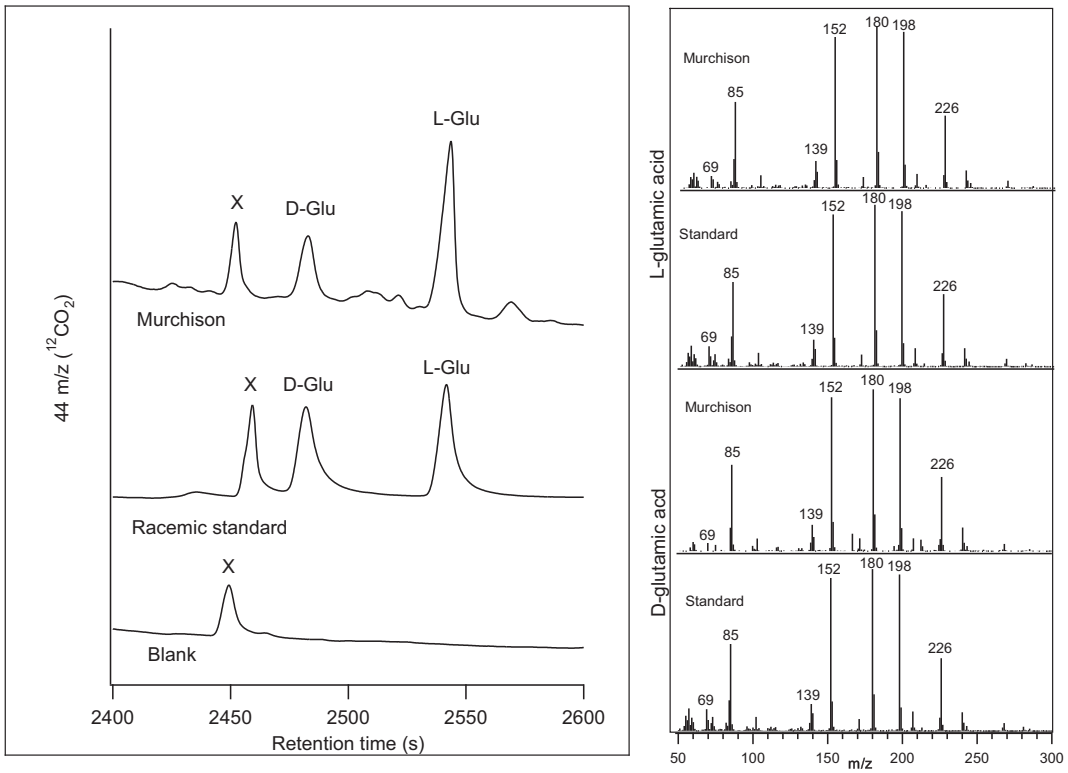

Fig. 5. Gas chromatography separation and mass spectrometry analysis of D- and L-glutamic acid of the TFAA/IPA-derivatized 6 M HCl-hydrolyzed, hot water extract of the Murchison meteorite (1.0 g extract of Chicago Field Museum), a racemic standard, and the blank carried through the same procedure as the meteorite. The traces on the left show the m/z 44 ($^{12}CO_2$) peak produced and measured by GC-IRMS for the peaks assigned to D- and L-glutamic acid. The traces on the right show the simultaneously collected mass spectral fragmentation pattern for these peaks in the Murchison meteorite and standard. Peaks were identified by comparison of retention time and mass spectral fragmentation with the amino acid standard analyzed on the same day. The peak labeled X is an unidentified analytical artifact. The data used for this figure can be found in supporting information.

diverse set of terrestrial microorganisms (Scott et al. 2006). This implies that there must be a non-biological component to the L-glutamic acid excess measured in the Murchison meteorite. Since the carbon isotope value of glutamic acid in the Murchison soil is unknown, we assume a two component mixture of the L-glutamic acid excess in the Murchison meteorite, that is, one component with a terrestrial value covering the known carbon isotope range for biological glutamic acid of $\delta^{13}C = -0.3‰$ to $-60.9‰$ (Scott et al. 2006) and an extraterrestrial L-glutamic acid component with $\delta^{13}C = +31‰$ (same as the D-glutamic acid in the Murchison meteorite). Based on these assumptions, we calculate that between 27% and 80% of the measured L-glutamic acid excess in the Murchison meteorite could be terrestrial in origin (Table 5). Subtracting these potential terrestrial L-glutamic acid contributions from the total L-glutamic acid in the 1 g Murchison meteorite extract, yields corrected extraterrestrial D/L glutamic acid ratios ranging from 0.43 to 0.73 (Table 5) with corresponding L-glutamic acid enantiomeric excesses of 16–40%. These corrected L-glutamic acid excesses in Murchison are lower than the non-corrected L_{ee} of ~55% for glutamic acid reported previously in Murchison (Engel and Nagy 1982) and the Tagish Lake meteorite (Glavin et al. 2012), but are still very significant non-terrestrial L-excesses. Although it is clear from the carbon isotope ratios that there must be a non-terrestrial L-glutamic acid component to the excess in the Murchison meteorite, the exact value of the corrected indigenous L-glutamic acid excess in Murchison estimated to be between 16% and 40% remains uncertain since the $\delta^{13}C$ value of terrestrial L-glutamic acid in the Murchison soil (the most likely source of amino acid contamination in the Murchison meteorite) is not known.

Non-Terrestrial L-Isovaline Excesses in the Aguas Zarcas and Murchison Meteorites

Establishing an extraterrestrial origin for enantiomeric excesses present in non-protein α-dialkyl

amino acids such as isovaline that are rare in the terrestrial biosphere is more straightforward than for the common α-H protein amino acids, since in most cases, terrestrial contamination of the meteorites is not a concern. In addition, as mentioned previously, non-terrestrial L-isovaline excesses have already been discovered in the Murchison meteorite and a variety of other aqueously altered carbonaceous chondrites with L-excesses as high as ~20% (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000; Glavin and Dworkin 2009; Glavin et al. 2010, 2012; Burton et al. 2013). For these reasons, we focused part of this investigation on measuring the enantiomeric ratio and carbon isotopic composition of isovaline in the Aguas Zarcas meteorites and carbon isotopic measurements of D- and L-isovaline in the Chicago Field Museum Murchison sample to confirm the slight L-isovaline excesses that had been found previously in this fragment (Friedrich et al. 2018).

The LC-FD/Q-ToF-MS instrument used in this study was optimized for separation of the C_5 acyclic amino alkanoic acids and the retention times for all possible C_5 amino acid isomers and enantiomers were identified based on the analysis of standards. The LC-FD/Q-ToF-MS chromatograms centered at m/z 379.13 ± 0.02 (the peak width at half maximum) shown in Fig. 2 correspond to the C_5 amino acids in the standard and the acid-hydrolyzed, hot water extracts of a procedural blank, the Murchison meteorite, and the Aguas Zarcas UA 2741 meteorite. Although complete separation of all 23 possible C_5 amino acid isomers and enantiomers could not be achieved under the chromatographic conditions employed, all of the C_5 amino acids were accounted for and we observed no interference or co-elution of the D- and L-enantiomers of isovaline, valine, norvaline, and 3-aminopentanoic acid with other C_5 amino acids. As with a number of rare C_5 amino acids, the D- and L-enantiomers of 3-apa were clearly separated (Fig. 2, peaks labeled 27) from both D- and L-isovaline (Fig. 2, peaks 26 and 28, respectively).

A comparison of the D/L ratios and corresponding L-enantiomeric excesses (L_{ee} = %L–%D) of the C_5 amino acids valine, norvaline, and isovaline in the meteorites and soils is shown in Table 4. Given the carbon isotopic evidence for terrestrial L-glutamic acid and L-alanine contamination in the Aguas Zarcas meteorites from the soil, it is likely that the relatively low D/L valine ratios of 0.29 ± 0.03 in Aguas Zarcas UA 2741 and 0.13 ± 0.06 in Aguas Zarcas UA 2746 is due to a significant terrestrial L-valine contribution from the soil (Table 4). It is interesting to note that the Murchison meteorite has a much higher D/L valine ratio of 0.67 ± 0.03 compared to the Aguas Zarcas meteorites and the Murchison soil, which suggests a possible extraterrestrial origin of the 20 ± 2% L-valine excess in Murchison (Table 4). Unfortunately, isotopic measurements of D- and L-valine could not be made by GC-IRMS to confirm the origin of this L-valine excess given the low valine abundances in Murchison.

In contrast to valine and most of the other α-H protein amino acids detected in the Aguas Zarcas and Murchison meteorites that have relatively large L_{ee} (Table 4), much smaller L_{ee} for the non-protein amino acid isovaline (L_{ee} ~ 10–15%) were observed in these meteorites and norvaline was racemic (D/L ~ 1) within analytical errors (Table 4). Although norvaline was also identified in the Aguas Zarcas soil at trace levels (Table 2), the soil norvaline has an L_{ee} = 36 ± 4% whereas the Aguas Zarcas and Murchison meteorites do not have any L-norvaline excesses within analytical uncertainties (Table 4), indicating that terrestrial norvaline contamination of the meteorites from the soil is highly unlikely. Isovaline was not detected in the Aguas Zarcas or Murchison soil extracts above the 0.1 nmol/g level (Table 2) and is therefore also an unlikely terrestrial contaminant for these meteorites. The Aguas Zarcas meteorites have similar total isovaline abundances (~6.3–9.0 nmol/g, Table 2) with small L-isovaline excesses of 11 ± 6% for UA 2741 and 15 ± 7% for UA 2746 that are identical within errors (Table 4). A similar L-isovaline excess of 10 ± 1% was also measured in Murchison, which is in the same range of L-isovaline enantiomeric excesses (~0–18.5%) that have been previously reported in other samples of Murchison (Pizzarello et al. 2003; Glavin and Dworkin 2009). An extraterrestrial origin of the isovaline and the measured L-excesses in the Aguas Zarcas and Murchison meteorites was confirmed by GC-MS/IRMS measurements that found that both D- and L-isovaline peaks were enriched in ^{13}C relative to typical terrestrial values and similar within analytical uncertainties (Table 3).

The GC-MS/IRMS data for the D- and L-isovaline peaks in the Aguas Zarcas UA 2741 extract are shown in Fig. 5. The retention times and mass spectra for both peaks in the Aguas Zarcas extract closely match those for the TFAA/IPA derivatives of the D- and L-isovaline peaks in the racemic standard and the similarity in the mass spectra of the GC-MS peaks in the standard and in the Aguas Zarcas extract indicates no other compounds were interfering with the D- and L-isovaline carbon isotope measurements (Fig. 6). For Aguas Zarcas UA 2741, a D-isovaline value of $\delta^{13}C$ = +25 ± 3‰ and L-isovaline $\delta^{13}C$ = +32 ± 5‰ were determined from the GC-IRMS peaks and similar $\delta^{13}C$ values of +32 to +34‰ were measured for D- and L-isovaline in Aguas Zarcas UA 2746 from a single measurement (Table 3). The measured

carbon isotope values of D- and L-isovaline in Murchison are indistinguishable within errors (D-isovaline: $\delta^{13}C = +18 \pm 6‰$ and L-isovaline: $\delta^{13}C = +26 \pm 7‰$), similar to the Aguas Zarcas meteorites (Table 3), and are similar to the $\delta^{13}C$ value of +18‰ that has been measured previously for D- and L-isovaline in another fragment of Murchison (Pizzarello et al. 2003).

As noted previously, terrestrial isovaline contamination of these meteorites after falling to Earth is highly unlikely since isovaline was not detected in any of the relevant collection site environments or any of the laboratory procedural blanks. Although some fungal peptide contamination of both D- and L-isovaline in these meteorites cannot be completely ruled out, it is important to note that isovaline is most commonly found in the D-configuration in fungal peptides (Bruckner et al. 2009), which would decrease the measured L-isovaline excesses and also deplete the $\delta^{13}C$ value (Table 5). Nevertheless, it is possible that terrestrial contamination of the meteorites by microorganisms such as fungi could have metabolized ^{13}C-enriched meteoritic organic matter leading to the production of isotopically heavy isovaline and other amino acids with an L-excess. However, many common fungal peptides also contain L-alanine (D/L ~0.06) at similar abundances to isovaline (Elsila et al. 2011); therefore, if any significant fungal peptide contamination of these meteorites had occurred, the D/L alanine ratio should have been affected as well. This was not the case for the Murchison meteorite, which contained racemic alanine and no evidence for significant terrestrial L-alanine contamination (Table 4).

In summary, the lack of evidence for a biological source of the L-isovaline excesses observed in the Aguas Zarcas and Murchison meteorites and the large L-glutamic acid excesses measured in Murchison requires an alternate explanation. One possible mechanism for the origin of the non-terrestrial L-amino acid excesses observed in these carbonaceous chondrites is discussed in detail in the following section.

Origin of Amino Acid Asymmetry and Enrichment During Parent Body Alteration

It has been proposed that the L-enantiomeric excesses of the α-H and α-dialkyl amino acids found in Murchison and other aqueously altered carbonaceous chondrites could be the result of asymmetric photolytic decomposition of the amino acids or their precursors by UV circularly polarized light (UV CPL) in the presolar cloud (Bonner and Rubenstein 1987) prior to incorporation inside their parent asteroids. Polarized photons of synchrotron radiation derived from strong magnetic fields around neutron stars or scattered from interstellar dust in star forming regions have also been suggested as alternative sources of the amino acid asymmetry found in meteorites (Bonner 1991; Bailey et al. 1998; Fukue et al. 2009). Chiral leucine symmetry breaking and enantiomeric enrichment of up to 2.5% could be generated in the laboratory with the destruction of ~75% of the starting solid leucine by asymmetric photolysis with UV CPL (Flores et al. 1977). In other laboratory experiments, similar slight enantiomeric enrichments of ~0.2–2.5% in the protein amino acids alanine and valine and non-protein amino acids norvaline, α-amino-*n*-butyric acid, and 2,3-diaminopropanoic acid have been produced directly from interstellar ice analogs exposed to UV CPL (Takano et al. 2007; de Marcellus et al. 2011; Modica et al. 2014). Importantly, all of the amino acid enantiomeric excesses generated were in the same direction (all L-excesses or all D-excesses) for a given UV light polarization (R-CPL or L-CPL, respectively) and no amino acid asymmetry could be induced with non-polarized UV light (Modica et al. 2014). Isovaline was not detected in any of these ice irradiation experiments, but the generation of small L-isovaline excesses based on its well-characterized behavior under UV CPL seems plausible (Meierhenrich et al. 2010; Meinert et al. 2012). However, in order to produce the largest ≥15% L-isovaline excesses measured for isovaline in Murchison (Pizzarello et al. 2003; Glavin and Dworkin 2009), more than 99% of the compound would need to be destroyed by UV CPL (Flores et al. 1977). Relying on UV polarized radiation destruction alone to explain the even larger ~30–60% L-aspartic acid and L-glutamic acid enantiomeric excesses measured in the Murchison and Tagish Lake meteorites becomes even more problematic. Therefore, UV CPL as the sole mechanism for amino acid enantiomeric enrichment seems unlikely given (1) the relatively high concentrations of isovaline found in the Murchison and Aguas Zarcas meteorites and (2) chemical evidence that isovaline and the other α-amino acids detected in these meteorites formed by Strecker-cyanohydrin synthesis during aqueous alteration inside the CM2 meteorite parent body, and were therefore shielded from any circularly polarized radiation. UV CPL–induced amino acid enantiomeric excesses observed to date tend to be significantly smaller than the measured enantiomeric excesses in meteorites, meaning that if UV CPL was responsible for breaking chiral symmetry, there must have been another mechanism to amplify the small chiral excesses.

A promising mechanism for amplifying amino acid enantiomeric excesses is based on the behavior of chiral molecules during phase transitions, such as from solid–vapor and solid–liquid transitions; the crystallization behavior of amino acids in solution may explain some of

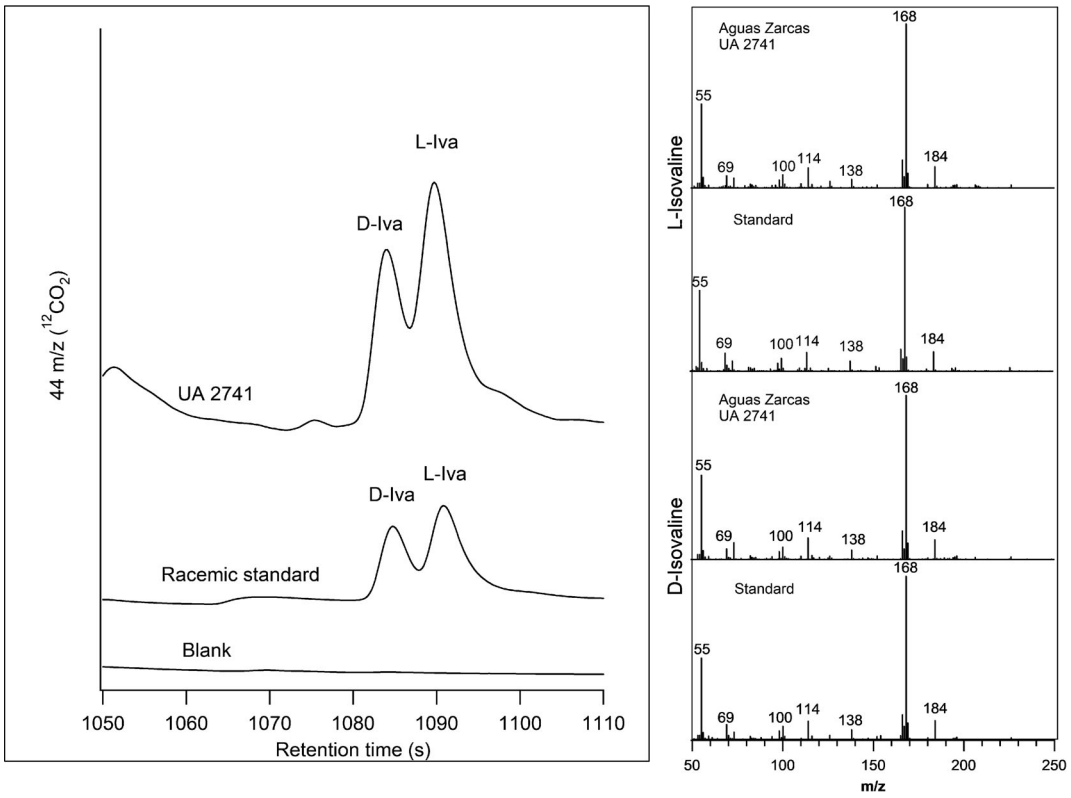

Fig. 6. Gas chromatography separation and mass spectrometry analysis of D- and L-isovaline of the TFAA/IPA-derivatized 6 M HCl-hydrolyzed, hot water extract of the Aguas Zarcas meteorite (0.5 g extract of UA 2741), a racemic standard, and the procedural blank carried through the same procedure as the meteorite. 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 D- and L-isovaline. The traces on the right show the simultaneously collected mass spectral fragmentation pattern for these peaks in the Aguas Zarcas meteorite and standard. The data used for this figure can be found in supporting information.

the differences observed in the amino acid enantiomeric excesses measured in meteorites. For example, Viedma and others have demonstrated that sublimation could be used to preferentially separate an amino acid enantiomer present in excess away from its racemic solid (Perry et al. 2007; Viedma et al. 2011, 2012). A similar phenomenon has also been observed in the solution phase (Viedma 2007; Viedma et al. 2008; Blackmond 2010). Serine, which exhibits a very high eutectic enantiomeric excess of >99% in water at 25 °C, provides a virtually enantiopure solution from a nearly racemic sample under solid–liquid equilibrium conditions (Klussmann et al. 2006). The physical separation of enantiomers can be applied to most of the 20 proteinogenic amino acids, and is based on them forming racemic crystals (crystals made up of equal amounts of D- and L-enantiomers) that have lower solubilities (or vapor pressures) than conglomerate enantiopure solid crystals (crystals made up of all D- or all L-enantiomers) of those same compounds (Klussmann et al. 2006). If one enantiomer was initially present in slight excess over the other inside the meteorite parent body (which may have been the case for amino acids of interstellar origins that were exposed to circularly polarized radiation), then amplification of the enantiomer in excess could occur for conglomerate-forming amino acids via repeated crystallization and continuous racemization during parent body aqueous alteration. However, any initial asymmetry in amino acids that preferentially form solid racemic crystals, such as alanine, would not readily amplify through this mechanism, and in fact over time should be completely erased through racemization under aqueous conditions (Bada 1991). This is because an enantiomeric excess in solution will drive racemization toward a racemic solution phase, causing more racemic crystals (with lower solubility) to precipitate. An illustration of the solid–liquid phase behavior of amino acids that form conglomerates and racemic solid crystals is shown in Fig. 7.

It has also been shown experimentally that aspartic acid, glutamic acid, threonine, and isovaline have very different crystallization behaviors in saturated solutions compared to alanine: alanine preferentially forms racemic crystals (Klussmann et al. 2006), while free aspartic and glutamic acids, threonine, and isovaline

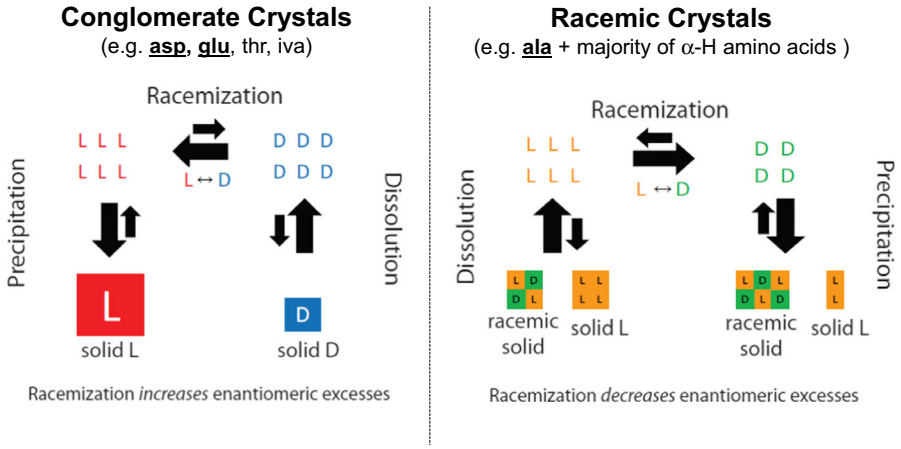

Fig. 7. An illustration of the solid–liquid phase behavior of amino acids that form conglomerate (left) and racemic (right) solid crystals. Amplification of a small initial excess (in this case, the L-enantiomer) for conglomerate forming amino acids such as aspartic and glutamic acid can occur through racemization and precipitation. This figure was published in Primitive Meteorites and Asteroids: Physical, Chemical, and Spectroscopic Observations Paving the Way to Exploration, D. P. Glavin, C. M. O' D. Alexander, J. C. Aponte, J. P. Dworkin, J. E. Elsila, and H. Yabuta, The Origin and Evolution of Organic Matter in Carbonaceous Chondrites and Links to Their Parent Bodies, Page 234, Copyright Elsevier (2018). (Color figure can be viewed at wileyonlinelibrary.com.)

have a tendency to form enantiopure conglomerate crystals (Viedma 2001; Rodrigo et al. 2004; Noorduin et al. 2008; Viedma et al. 2008). Therefore, differences in the solid–liquid phase crystallization behaviors of glutamic acid and alanine may explain why L-glutamic acid and L-isovaline enantiomeric excesses are found in the Murchison meteorite, whereas alanine is racemic (Table 4). We want to make it clear that although we were unable to obtain the necessary carbon isotope data to firmly establish an extraterrestrial origin for the L-excesses measured for other α-H protein amino acids in Murchison, given that there is no evidence for L-alanine contamination in the Murchison fragment investigated in this study, it is possible that the measured L-aspartic acid, L-serine, and L-threonine excesses could also have formed during aqueous alteration on the Murchison meteorite parent body. It is important to state that this amino acid crystallization amplification mechanism cannot explain the large L-alanine excesses of ~33% that have been reported in another sample of Murchison (Engel and Macko 1997). Either the source of the L-alanine excess measured by Engel and Macko (1997) in Murchison was terrestrial in origin or another amplification mechanism led to the L-alanine excess. It is possible that the interaction of these amino acids and their precursors with other organic and inorganic species in the CM meteorite parent body during aqueous alteration would also have an effect on amplification of the L-excesses. This is a line of research that should be explored in greater detail through laboratory crystallization experiments of free amino acids and their acid-hydrolyzable precursors under relevant parent body conditions.

Parent body aqueous alteration may have resulted in the L-isovaline enrichments found in the Aguas Zarcas UA 2741 and UA 2746 meteorite samples and possibly other conglomerate-forming amino acids such as L-aspartic and L-glutamic acids as well (Table 4), although clear terrestrial amino acid contamination of Aguas Zarcas from the landing site soil makes it impossible to establish a non-terrestrial origin for any of the L-protein amino acid excesses in this meteorite. Given similar relative amino acid abundances and magnitudes of the L-isovaline excesses in the Aguas Zarcas and Murchison meteorites, these CM2 carbonaceous chondrites likely experienced similar parent body conditions. Aqueous alteration of the CM meteorites is thought to have been the result of the melting of ice inside the parent asteroid by radioactive heating, largely from the short-lived radionuclides ^{26}Al and ^{60}Fe (McSween et al. 2002). Temperatures during parent body alteration ranging from ~0 °C to 80 °C have been estimated previously for CM2 meteorites over time scales of ~10^2–10^4 years (Zolensky and McSween 1988; Browning et al. 1996; Krot et al. 2006), with recent models suggesting that liquid water could have been present in asteroids for up to millions of years in CM meteorite parent bodies (Cohen and Coker 2000; Palguta et al. 2010). Under these conditions, the racemization rates of the α-H amino acids, aspartic acid, glutamic acid, and alanine, would have been especially rapid (e.g., racemization half-life of aspartic acid in natural samples is ~10^3–10^4 years under aqueous conditions at 25 °C and neutral pH) and considerably faster than their decomposition rates (Bada 1991).

Therefore, small L-excesses of the conglomerate-crystal-forming amino acids aspartic acid and glutamic acid could have become enriched on the CM parent body through a combination of interconversion of their D-enantiomers into L-enantiomers via racemization and subsequent amplification during crystallization.

In contrast to the α-H amino acids, isovaline and other α-dialkyl amino acids are not prone to rapid racemization under aqueous conditions on geological timescales (Bonner et al. 1979b). This makes it more difficult to explain the origin of the L-isovaline enrichments measured in these CM2 meteorites by crystallization during aqueous alteration. Based on laboratory experiments, it is possible that exposure to radiation inside the CM meteorite parent body from natural radioactivity could have led to small amounts (up to ~5%) of racemization of solid isovaline during radiolysis, although radioracemization of isovaline in aqueous solution could have been lower (Bonner et al. 1979a). Assuming that conglomerate crystallization was the dominant mechanism for L-amino acid enantioenrichment during aqueous alteration on the CM meteorite parent body, the slower racemization rates of isovaline and other α-dialkyl amino acids may explain why the L-enantiomeric enrichments for these amino acids are typically lower than most of the α-H amino acids in Murchison.

CONCLUSIONS

Amino acid analyses of two different fragments of the Aguas Zarcas CM2 carbonaceous chondrite have identified a suite of two- to six-carbon amino acids that are derived from both extraterrestrial and terrestrial sources. The elevated abundances of α-amino acids in the Aguas Zarcas meteorites and a relative distribution of five-carbon amino acids that is similar to what has been observed in Murchison and other CM2 carbonaceous chondrites suggest that the extraterrestrial amino acids in the Aguas Zarcas meteorite were formed by Strecker synthesis during parent body alteration on the CM meteorite parent body. Two non-protein amino acids that are rare in biology, α-AIB and isovaline, were identified in the Aguas Zarcas and Murchison meteorites at elevated concentrations ranging from ~5 to 20 nmol/g and are clearly extraterrestrial in origin based on their carbon isotopic compositions that are enriched in ^{13}C relative to terrestrial organic matter. Slight L-isovaline excesses ranging from ~10 to 15% were also detected in both Aguas Zarcas and Murchison meteorites, consistent with what has been observed previously in other aqueously altered carbonaceous chondrites. In the present work, the Murchison meteorite was found to contain much larger enantiomeric excesses of ~15–39% for glutamic acid, but alanine was racemic. Both of these amino acids were confirmed to be extraterrestrial in origin by carbon isotope measurements, which is consistent with previous reports of L-glutamic acid and other α-H protein amino acid excesses in the Murchison and Tagish Lake meteorites. Large L-glutamic acid excesses ranging from ~56 to 73% were measured in the Aguas Zarcas meteorites; however, carbon isotopic analyses of the glutamic acid indicate that the L-excesses are mostly terrestrial in origin.

We surmise that the non-terrestrial L-amino acid enrichments found in some carbonaceous chondrites can be adequately explained by differences in their crystallization behaviors. Nonetheless, future amino acid analyses of pristine samples returned from carbonaceous asteroids and comets and more laboratory experiments to investigate enantioenrichment mechanisms for amino acids (especially the α-dialkyl amino acids) under relevant parent body conditions are still needed to support this hypothesis. Currently, preferential enrichment of UV CPL generated L-amino acid excesses of conglomerate enantiopure crystals during parent body aqueous alteration remains the most plausible asteroid-relevant amplification mechanism for amino acids. The fact that only L-enantiomeric excesses have been observed in amino acids with a single asymmetric carbon in carbonaceous meteorites so far suggests that the origin of life on Earth or elsewhere in our solar system may have been biased toward L-amino acid homochirality from the very beginning. Although amino acid homochirality can be an important signature of biological processes in the search for evidence of life elsewhere, the detection of non-terrestrial L-amino acid excesses in CM2 and other aqueously altered carbonaceous meteorites indicates that non-biological processes could also lead to significant enantioenrichment for some amino acids.

The return of pristine materials from the surface of carbonaceous asteroids and comets to Earth for detailed laboratory organic analyses will be essential to advance our understanding of the origin of chiral amino acid asymmetry in the early solar system given that all meteorites on Earth have been compromised, to some degree, by terrestrial contamination. JAXA's Hayabusa2 mission and NASA's Origins, Spectral Interpretation, Resource Identification, Security, Regolith Explorer (OSIRIS-REx) missions will return samples collected from the surfaces of the carbon-rich asteroids Ryugu and Bennu to Earth in late 2020 and 2023, respectively. These asteroid sample return missions will provide the first opportunities to investigate chiral asymmetries of amino acids and other chiral molecules in pristine solar system materials and

how subsequent parent body processes likely altered their initial enantiomeric ratios.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

Data S1. Excel file containing all of the raw data used to generate the plots shown in Figures 1, 2, 5, and 6.