Compound-specific carbon, nitrogen, and hydrogen isotopic ratios for amino acids in CM and CR chondrites and their use in evaluating potential formation pathways

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Abstract

Stable hydrogen, carbon, and nitrogen isotopic ratios (δD, $\delta^{13}C$, and $\delta^{15}N$) of organic compounds can reveal information about their origin and formation pathways. Several formation mechanisms and environments have been postulated for the amino acids detected in carbonaceous chondrites. As each proposed mechanism utilizes different precursor molecules, the isotopic signatures of the resulting amino acids may indicate the most likely of these pathways.

We have applied gas chromatography with mass spectrometry and combustion isotope ratio mass spectrometry to measure the compound-specific C, N, and H stable isotopic ratios of amino acids from seven CM and CR carbonaceous chondrites: CM1/2 Allan Hills (ALH) 83100, CM2 Murchison, CM2 Lewis Cliff (LEW) 90500, CM2 Lonewolf Nunataks (LON) 94101, CR2 Graves Nunataks (GRA) 95229, CR2 Elephant Moraine (EET) 92042, and CR3 Queen Alexandra Range (QUE) 99177. We compare the isotopic compositions of amino acids in these meteorites with predictions of expected isotopic enrichments from potential formation pathways. We observe trends of decreasing $\delta^{13}C$ and increasing δD with increasing carbon number in the α-H, α-NH_2 amino acids that correspond to predictions made for formation via Strecker-cyanohydrin synthesis. We also observe light $\delta^{13}C$ signatures for β-alanine, which may indicate either formation via Michael addition or via a pathway that forms primarily small, straight-chain, amine-terminal amino acids (*n*-ω-amino acids). Higher deuterium enrichments are observed in α-methyl amino acids, indicating formation of these amino acids or their precursors in cold interstellar or nebular environments. Finally, individual amino acids are more enriched in deuterium in CR chondrites than CM chondrites, reflecting different parent-body chemistry.

Introduction

The organic content of carbonaceous meteorites records information about the synthesis and evolution of organic material in the early solar system. The abundance, isotopic composition, and distribution of these organic compounds depend not only on the original composition and processing of the molecular cloud and solar nebula from which the solar system formed, but also upon subsequent processing on meteorite parent bodies.

The organic inventory of many carbonaceous chondrites includes a variety of amino acids (e.g, Kvenvolden et al., 1970; Cronin and Pizzarello, 1983; Ehrenfreund et al., 2001; Martins et al., 2007; Glavin et al., 2010). Amino acids are of particular interest because they are structurally diverse, nitrogen-containing compounds, most of which are chiral, and their delivery to the early Earth may have contributed to the origin of life and its homochirality (Cronin and Pizzarello, 1997; Glavin and Dworkin, 2009). The indigenous nature of meteoritic amino acids is confirmed by the presence of several compounds that are rare or absent in the terrestrial biosphere (Oró et al., 1971; Cronin and Pizzarello, 1983; Cronin and Chang, 1993; Glavin et al., 2006) and by the presence of nonterrestrial isotopic ratios (Epstein et al., 1987; Pizzarello et al., 1991; Cronin and Chang, 1993; Pizzarello et al., 1994; Glavin et al., 2006; Elsila et al., 2011). Equal abundances of D and L amino acids have also been used to argue for the extraterrestrial origin of amino acids, although extraterrestrial L-excesses of certain amino acids appear possible under certain conditions (Engel and Macko, 1997; Glavin et al., 2012).

Carbonaceous chondrites represent a primitive class of meteorites containing 2 to 5 wt% of carbon and are sub-divided into eight separate groups (CI, CM, CR, CV, CO, CH, CB, and CK) based on differences in elemental composition and mineralogy (Sears and Dodd, 1988). Several of these groups show distinctive patterns of relative abundances and distributions of amino acids (Ehrenfreund et al., 2001; Glavin et al., 2010; Burton et al., 2012a), which may reflect different formation and parent body environments. Over 80 amino acids have been identified in the CM2 Murchison and Murray meteorites (Burton et al., 2012b); this complex mix includes many that are rare or do not occur naturally on the Earth, such as α-aminoisobutyric acid (AIB), isovaline (2-amino-2-methylbutanoic acid), and β-amino-*n*-butyric acid (Cronin and Moore, 1971; Cronin and Chang, 1993). Many more amino alkanoic acids with up to nine carbons have been detected in Murchison, but have not yet been identified (Glavin et al., 2010; Pizzarello and Shock, 2010). The CI1 meteorites Orgueil and Ivuna display a much simpler set of amino acids, dominated by glycine and β-alanine (Ehrenfreund et al., 2001). Antarctic CR2 meteorites contain amino acid abundances that greatly exceed those found in the CM2 meteorites and show a predominance of α-amino acids (Martins et al., 2007; Pizzarello et al., 2008; Glavin and Dworkin, 2009; Pizzarello and Holmes, 2009; Glavin et al., 2010). Thermally altered CV and CO carbonaceous chondrites contain much lower abundances of amino acids dominated by small, straight-chain, terminal-amine compounds (Burton et al., 2012a). Similarities and differences in amino acid abundances and distributions occur even among meteorites of the same group (e.g., CM2 (Glavin et al., 2006) or CR2 (Martins et al., 2007)), suggesting that some meteorites of the same mineralogic and petrologic type originated from chemically distinct parent bodies and/or experienced different degrees of parent body aqueous and thermal alteration, and that these differences affected their amino acid content.

The observed differences in amino acid content suggest a variety of abiotic chemical pathways on meteoritic parent bodies (e.g., Peltzer et al., 1984; Cronin and Chang, 1993; Cooper and Cronin, 1995; Ehrenfreund et al., 2001; Burton et al., 2012a). Several formation pathways have been proposed. The Strecker-cyanohydrin synthesis, in which HCN reacts with NH_3 and an aldehyde or ketone followed by hydrolysis of the α-aminonitrile, is widely accepted as a potential source of α-amino acids produced during aqueous alteration of a meteorite parent body rich in aldehydes and ketones (Peltzer et al., 1984). Michael addition could form β-amino acids through aqueous alteration on a parent body rich in volatile components (Miller, 1957).

Amino acid formation could also predate solar system formation, with synthesis of amino acids or their precursors via gas-phase ion-molecule chemistry in the protosolar nebula or the precursor molecular cloud. Aminomethanol (NH_2CH_2OH) can form in interstellar ices (Bossa et al., 2009), although quantum chemistry calculations (Largo et al., 2004) indicate that the suggested route to glycine involving reaction of $NH_2CH_2OH_2^+$ with formic acid (Kuan et al., 2003) is highly endothermic and that other possible ion-molecule reactions involving neutral carboxylic acids require ions that will have negligible abundances in interstellar clouds. Blagojevich et al. (2003) demonstrated experimentally that glycine and β-alanine could form starting with the reaction of protonated hydroxylamine (NH_2OH) with, respectively, acetic acid and propanoic acid in gas into which the neutral reactant molecules had been evaporated from interstellar ices, such as in hot molecular cores (Herbst and van Dishoeck, 2009). Theoretical calculations indicate that the higher energy isomer ($NH_2OH_2^+$) is most likely to form protonated amino acids, and that the estimated energy barriers would require a hot interstellar environment for these reactions to proceed (Snow et al., 2007; Barrientos et al., 2012). Hydroxylamine could form on cold grains through hydrogenation of NO molecules accreted from the gas (Charnley et al., 2001) or through reaction of NH_2 and OH radicals induced by UV photolysis and heating of interstellar ices (e.g., Tielens et al., 1991; Garrod et al., 2008). Recent experiments have confirmed the viability of these pathways (Zheng and Kaiser, 2010; Congiu et al., 2012). However, a search for NH_2OH in a number of massive star-forming regions failed to detect NH_2OH, and obtained very low upper limits (Pulliam et al., 2012), almost one million times lower than predicted by Garrod et al. (2008). In Orion-KL, Pulliam et al. (2012) obtained their upper limits for the hot core, whereas Kuan et al. (2003) proposed that the glycine molecules observed were present in the cooler Compact Ridge sub-region (*c.f.* Snyder et al., 2005). This makes the NH_2OH non-detections less likely to be due to its high thermal binding energy allowing it to remain bound on the dust, and suggests efficient destruction of NH_2OH could have occurred after the ices were sputtered in a shock wave; such a wind-cloud shock has been proposed as the origin of the Compact Ridge (Blake et al., 1987).

Reactions on ice-covered interstellar dust grains, perhaps via a cyanohydrin-type synthesis or addition of CO_2 to amines are also possible (Bernstein et al., 2002; Muñoz Caro et al., 2002; Woon, 2002; Elsila et al., 2007; Hudson et al., 2009). The Strecker intermediate for glycine formation, aminoacetonitrile (NH_2CH_2CN), has been detected in the interstellar medium (Belloche et al., 2008). If the origin for NH_2CH_2CN proposed by Belloche et al. (2009) is correct, involving association of CH_2NH_2 and CN radicals on grain surfaces, then the amine group and the α-carbon in glycine may be derived from the nitrile upon hydrolysis. The different starting compounds should lead to different isotopic signatures in glycine. Additional hypotheses for the formation of amino acids and their precursors include Fisher-Tropsch Type (FTT) and Haber-Bosch catalytic syntheses (Hayatsu et al., 1971; Yoshino et al., 1971; Pizzarello, 2002; Burton et al., 2012a) or reductive amination of keto acids (Huber and Wächtershäuser, 2003), which have been observed in the Murchison meteorite (Cooper et al., 2005).

Compound-specific isotopic analysis (CSIA) of stable isotope ratios ($^{13}C/^{12}C$, D/H, or $^{15}N/^{14}N$) may reveal differences in the origins of individual amino acids. The isotopic composition of an amino acid derives from both its precursor molecules and its formation pathway, meaning that comparisons of isotopic ratios between compounds and meteorites can provide insight into their formation and alteration histories. Furthermore, specific predictions can be made about the trends in isotopic ratios expected from different formation mechanisms, and these predictions can be compared against meteoritic measurements.

CSIA of amino acids has been carried out in only a handful of meteorites to date. The amino acids of the Murchison meteorite have been studied in the most detail, with measurements of C, N, and H isotopic ratios performed by several research groups (Engel et al., 1990; Engel and Macko, 1997; Pizzarello et al., 2004; Pizzarello and Huang, 2005; Elsila et al., 2011). CSIA of amino acids has also been performed for the Murray (CM2), Orgueil (CI1), GRA 95229 (CR2), LAP 02342 (CR2), and EET 92042 (CR2) carbonaceous chondrites (Ehrenfreund et al., 2001; Pizzarello and Huang, 2005; Martins et al., 2007; Pizzarello et al., 2008; Pizzarello and Holmes, 2009). However, there has been relatively little work comparing C, N, and H isotopes in various amino acids within the same meteorite, with only a handful of amino acids within the Murchison and GRA 95229 meteorites analyzed for all three isotopes. In addition, the analyses of the three isotopes have been performed in different laboratories on different meteorite extracts, making direct comparison of the isotopic data problematic. A range of $\delta^{13}C$ values have been reported in different studies for several amino acids in the Murchison meteorite (Engel et al., 1990; Pizzarello and Cooper, 2001; Pizzarello et al., 2004; Elsila et al., 2011); this range may reflect heterogeneity between meteorite samples or differences in laboratory techniques.

Previous CSIA amino acid studies have revealed some correlations between isotopic composition and amino acid structures that may correspond to possible formation mechanisms. For example, analysis of the Murchison meteorite showed a trend towards decreasing ^{13}C enrichment with increasing chain length for the three-to-five carbon α-amino, α-H monocarboxylic amino acids and for the four- to six-carbon α-amino α-methyl monocarboxylic amino acids (Pizzarello et al., 2004). Higher ^{13}C enrichment was also seen in α-methyl amino acids compared to α-H compounds for the four-to-six carbon amino acids (Pizzarello et al., 2004). The trends may be explained by ^{13}C fractionation in interstellar clouds yielding ^{13}CO as the dominant carrier of ^{13}C nuclei, and creating aldehydes and ketones whose ^{13}C enrichment decreases with increasing carbon number as more ^{13}C-depleted atoms are incorporated into these molecules (Charnley et al., 2004); these interstellar aldehydes and ketones would then react *via* the Strecker-cyanohydrin pathway to form the amino acids. Alternatively, these trends could be the result of Strecker-cyanohydrin reactions of ^{13}C-enriched HCN with less-enriched aldehydes or ketones. However, recent preliminary measurements of $^{13}C/^{12}C$ ratios in interstellar formaldehyde indicate that this molecule is surprisingly enriched in ^{13}C relative to both CO and methanol (Wirström et al., 2011; Wirström et al., 2012b). The $\delta^{13}C$ values of β-amino acids in Murchison were lower than the corresponding α-amino acids and did not show the same correspondence with carbon number, perhaps reflecting a different formation mechanism involving nitriles (Pizzarello et al., 2004).

The $\delta^{15}N$ values of α-methyl amino acids were lower than α-H amino acids in two CR2 chondrites, suggesting an earlier origin in the interstellar medium for the α-methyl amino acids and a later origin in pre-stellar cores for the α-H ones (Pizzarello and Holmes, 2009). The δD value of branched amino acids was reported to be higher than that of straight-chain amino acids in the Murchison and Murray CM2 chondrites (Pizzarello and Huang, 2005) and in the GRA 95229 CR2 chondrite (Pizzarello et al., 2008), with no correlation with chain length. This observation has been used to argue that the branched-chain amino acids may have a more direct relationship than the straight-chain amino acids to the cold environments believed to lead to hydrogen fractionation, while the straight-chain amino acids may have experienced more parent-body processing and exchange with deuterium-depleted water (Pizzarello and Huang, 2005). Although these studies have yielded some interesting correlations, the overall number of amino acids and meteorites studied in all carbon, nitrogen, and hydrogen isotopes has been very limited.

In this work, we report on carbon, hydrogen, and nitrogen CSIA of amino acids in seven different CM and CR carbonaceous chondrites, ranging from petrographic type 1 to 3. The samples include four meteorites for which no CSIA amino acid data have previously been published: the CM2 chondrites LON 94101 and LEW 90500, the CR3 QUE 99177, and the CM1/2 ALH 83100. In contrast to previous analyses, in this study all three isotopic analyses of each meteorite were performed on the same meteoritic sample extract, removing the uncertainty of sample heterogeneity when comparing the three isotopic ratios within a single meteorite. We report the C-, N-, and H-isotopic compositions for amino acids of different structural types and compare the trends observed to those predicted for various formation mechanisms. Our observations both support previous reports and extend the available compound-specific isotopic data and interpretations for meteoritic amino acids.

Materials and Methods

Meteorite samples

The CM2 carbonaceous chondrite Murchison (USNM 6650.2, mass 6.3 g) was provided by the Smithsonian National Museum of Natural History, Washington, D.C. The following Antarctic carbonaceous chondrites were provided by the Antarctic meteorite curator at the NASA Johnson Space Center in Houston, TX: EET 92042 (specific 67, parent 0, mass 0.806 g, CR2); GRA 95229 (specific 87, parent 0, 0.530 g, CR2), QUE 99177 (specific 38, parent 0, 0.515 g, CR3), ALH 83100 (specific 246, parent 26, 4.9 g, CM1/2), LEW 90500 (specific 69, parent 1, 4.1 g, CM2), and LON 94101 (specific 65, parent 6, 8.2 g, CM2).

Extraction and Processing Procedures

All glassware and sample handling tools were rinsed with Millipore Milli-Q Integral (18.2 MΩ, < 4 ppb total organic carbon) ultrapure water, wrapped in aluminum foil and then oxidized in a furnace in air at 500°C overnight. Each meteorite sample was crushed into a fine powder and homogenized using a mortar and pestle in a positive pressure high efficiency particulate air (HEPA) filtered laminar flow hood (AirClean Systems). Individual powdered meteorite samples were extracted with Millipore water at 100°C for 24 h in flame-sealed glass ampoules. For the meteorites with a total mass of <1 g, extraction was performed in 1 mL Millipore water. For the larger meteorites, samples were split into aliquots of ~2 g each and each aliquot was extracted in separate glass ampoules in 1.5 mL each of Millipore water (except for LON 94101, which was extracted in 1 g aliquots with 2.0 mL water). The water supernatants were dried under vacuum and the residues then hydrolyzed under 6 M HCl acid vapor at 150 °C for 3 hours (Glavin et al., 2006). The acid-hydrolyzed, hot-water extracts were desalted using cation-exchange resin (AG50W-X8, 100-200 mesh, hydrogen form, BIO-RAD) and the amino acids recovered by elution with 2 M NH_4OH (prepared from Millipore water and NH_3(g) (AirProducts), *in vacuo*). After desalting, the amino acids in the NH_4OH eluates were dried under vacuum to remove excess ammonia; the residues were then re-dissolved in Millipore water. For meteorites with total sample mass >1 g, aliquots were recombined at this point. The desalted sample extracts were stored in 1 mL of Millipore water at -20°C prior to analysis. Procedural blanks were carried through the extraction and hydrolysis procedure in parallel with each meteorite extraction.

Approximately 1% of each desalted, HCl-hydrolyzed, hot-water extract was analyzed for total amino acid content using a Waters ACQUITY and LCT Premier for ultra-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) coupled with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization. Specific details about the derivatization protocol and LC-FD/ToF-MS conditions used for amino acid analyses are given elsewhere (Glavin and Dworkin, 2009; Glavin et al., 2010). Amino acid abundances and distributions for these meteorites have been published previously (Glavin et al., 2006; Martins et al., 2007; Glavin and Dworkin, 2009), with the exception of LON 94101.The current analyses were compared with the previous results to verify successful extraction and hydrolysis and to determine the amount of each meteorite extract needed for amino acid isotopic measurements; the data from LON 94101 was compared with LON 94102 (Glavin et al., 2010), with which it is presumed to be paired. The extractions performed on large samples with a higher rock-to-water ratio showed lower-than-expected recoveries compared to previous extractions of smaller samples (~60-80% of expected); these recoveries were still sufficient for analysis, and comparison of the large-scale Murchison data with previous analyses showed no evidence of isotopic fractionation.

Isotopic Measurements

Each desalted, acid-hydrolyzed, hot-water extract was allocated as follows: 10% for carbon CSIA, 30% for nitrogen CSIA, and 60% for hydrogen CSIA. Each aliquot was dried under vacuum using a LabConco CentriVap centrifugal concentrator. Samples were esterified with isopropanol and the isopropyl esters reacted with trifluoroacetic anhydride (TFAA) using established methods (e.g., Elsila *et al.* 2009). The TFAA-isopropanol derivatives were dissolved in 5 µL of ethyl acetate (Fisher Chemical, Optima Grade).

The δ^{13}C, δ^{15}N, and δD values of the TFAA-isopropanol derivatized samples were analyzed by gas chromatography coupled with mass spectrometry and isotope ratio mass spectrometry (GC-MS/IRMS), which provides compound-specific structural and stable isotopic information from a single sample injection. The GC-MS/IRMS instrument 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 either a Thermo GC-C III interface, where eluting amino acids are oxidized and reduced to carbon dioxide and nitrogen gas for δ^{13}C and δ^{15}N analyses, or a Thermo GC-TC interface, where amino acids are quantitatively pyrolyzed to hydrogen gas for δD analyses. These gases are passed into a Thermo MAT 253 IRMS for stable isotopic measurement. For δ^{15}N analysis, a liquid nitrogen trap is used to remove the CO_2 from the gas stream prior to entry into the IRMS; this is necessary to eliminate interferences caused by CO (mass-to-charge ratio 28, identical to N_2) created by fragmentation of CO_2 in the IRMS source (Brand et al., 1994).

Derivatized extracts were injected in 1 µL aliquots into the GC; typically, three or four injections of each derivatized extract were made. The GC was outfitted with a 5-m base-deactivated fused silica guard column (Restek, 0.25 mm ID) and four 25-m Chirasil L-Val columns (Varian, 0.25 mm ID) connected using Press-Tight connectors (Restek). The following oven program was used: initial temperature was 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 at 200 °C for 10 min. Six pulses of CO_2 ($\delta^{13}C = -24.23‰$ VPDB) or N_2 ($\delta^{15}N = -0.62$ ‰ AIR) that had been precalibrated against commercial reference gases (Oztech Corporation) were injected into the IRMS for computation of the $\delta^{13}C$ or $\delta^{15}N$ values of the eluting compounds. For hydrogen isotope analysis, high-purity H_2 (δD = -207.180‰ VSMOW, Oztech) was introduced through the dual inlet of the IRMS and used as a reference gas. Analysis of the IRMS data was performed with Thermo Isodat 2.5 software.

Stock solutions of the amino acids of interest were combined to make a standard mixture that was carried through the derivatization process and run daily on the GC-MS/IRMS. A stock solution of L-alanine with a known $\delta^{13}C$ value (-23.33‰, IsoAnalytical) was also derivatized and injected daily as a working standard. The individual, underivatized stock solutions or solid pure standards were also analyzed on a Costech ECS 4010 combustion elemental analyzer (EA) connected to the IRMS; this was necessary to correct for the carbon added during derivatization. The final $\delta^{13}C$ values of the amino acids in the samples and their precision were calculated as described elsewhere (Docherty et al., 2001; O'Brien et al., 2002; Elsila et al., 2009). The $\delta^{15}N$ values of the derivatized amino acids were assumed to be identical to the $\delta^{15}N$ values of the amino acids prior to derivatization, as no nitrogen is added during the TFAA/IPA derivatization process used in this study. The δD values of the carbon-bound hydrogen atoms in each amino acid were calculated through the following equation, which assumes that the hydrogen remaining on the derivatized amine fully exchanges with the isopropanol alcohol hydrogen: $\delta D_{aa} = \left[\delta D_{der.\,aa} - fr_{ip}(\delta D_{ip})\right]/fr_{aa}$, where $\delta D_{der.aa}$ is the measured δD value of the derivatized amino acid, and fr_{ip} and fr_{aa} are the fractional hydrogen abundances of the isopropanol (ip) alkyl portion or the amino acid (aa), respectively. The δD value of the isopropanol was measured as -100‰ ± 2‰ via thermal combustion elemental analysis.

Results

Tables 1 to 3 list the $\delta^{13}C$, $\delta^{15}N$, and δD values for the suite of measurable amino acids in the seven carbonaceous chondrites analyzed. Figure 1 shows a representative GC-IRMS chromatogram from the carbon analysis of EET 92042; measurable amino acids are identified, while other peaks represent compounds that could not be analyzed due to coelutions or low sensitivity. Although each derivatized extract was injected a minimum of three times, low amino acid abundances limited the detection of amino acids in some cases, and the number of measurable detections is also shown in the tables. Differences in detection limits between carbon, nitrogen, and hydrogen CSIA also affected the ability to make amino acid isotope measurements for some meteorites. Mass spectral data was used to verify the absence of coeluting compounds; a small contribution from coelutions in a few peaks is noted in the Tables. Amino acid abundances for these meteorites have been published previously (Glavin et al., 2006; Martins et al., 2007; Glavin and Dworkin, 2009).

Table 4 lists the detected amino acids along with their key structural characteristics. The suite of ten detected amino acids contain from two to six carbons (C_2 to C_6) and include both straight- and branched-chains, both α-H and α-CH_3 substituents, and amines in the α-, β-, γ-, δ-, and ε-positions. The $\delta^{13}C$ and δD values of glycine were measured in all seven meteorites, and $\delta^{15}N$ for glycine was obtained in six of the seven; the number of detections for the other amino acids varied.

Figure 2 shows the isotopic relationships (δD vs. $\delta^{13}C$; $\delta^{15}N$ vs. $\delta^{13}C$, and δD vs. $\delta^{15}N$) for amino acids when more than one isotope was measured in a given meteorite. Areas of the plots in which structurally similar amino acids grouped together are outlined. Observable trends from these figures are discussed in more detail below.

Discussion

Comparison with previous analyses

Table 5 compares our results with previous analyses for amino acids in the Murchison and GRA 95229 chondrites. These carbonaceous chondrites are the only ones for which C, N, and H compound-specific isotopic analyses had previously been published, although each of those previous measurements was performed on different meteoritic extracts and in some cases in different laboratories. In contrast, the data presented in our current study reflect the isotopic signatures of amino acids in a single sample of each chondrite using the same instrument, thus reducing the effects of meteoritic heterogeneity and analytical artifacts on data analysis and interpretation. Our data are generally in agreement with previous reports; a comparison of the data reveals potential heterogeneity in meteorite samples or differences in laboratory techniques. For example, in the Murchison meteorite, the $\delta^{13}C$ values for individual amino acids in different analyses vary greatly, with variations of up to 38‰ seen for the same compound. Glycine has one of the largest ranges of reported values of the amino acids measured in Murchison in $\delta^{13}C$ and $\delta^{15}N$. This variability may be the result of terrestrial contamination by this ubiquitous biological amino acid or greater heterogeneity for this compound among meteorite samples. In contrast, the GRA 95229 chondrite shows greater consistency between analyses, with isovaline showing the most isotopic variability. The observed consistency of isotopic values for amino acids in GRA 95229 may be indicative of less meteoritic heterogeneity in the much smaller GRA 95229 sample (over 100 kg of Murchison was recovered compared to only 130 g of GRA 95229), or from less exposure to terrestrial contamination in Antarctica and a shorter time in curation.

Sources of isotopic fractionation

The $\delta^{13}C$, $\delta^{15}N$, and δD isotopic compositions of amino acids depend on their formation mechanisms, and the isotopic signature of different mechanisms can be predicted to varying degrees. Deuterium fractionation is an indicator of interstellar or presolar origin, with deuterium enrichment occurring in these cold (<30 K) environments (Sandford et al., 2001; Nuth et al., 2006). High D/H ratios thus imply interstellar or presolar formation pathways to meteoritic amino acids or their precursor materials. Reactions with deuterium-depleted water on meteorite parent bodies, estimated to have $\delta D \approx -100‰$ (Robert and Epstein, 1982), would reduce the D/H ratio. Deuterium measurements of amino acids are complicated by potential exchange of labile hydrogen atoms in the laboratory during analytical work-up. Thus, predicted D/H trends are those expected to be exhibited by the "pristine" suite of reaction products and can be considered as a starting point for assessing possible effects of the relative exchange of D and H atoms.

For carbon, a key theoretical prediction is that at temperatures near 10 K, gas-phase ion-molecule reactions act to incorporate almost all ^{13}C nuclei into the stable ^{13}CO species (Langer et al., 1984), leaving a deficiency of ^{13}C available for all other C-containing molecules (e.g. HCN, H_2CO, CH_2CHCN, CH_3NH_2). This chemistry yields $^{13}CO/^{12}CO$ ratios close to the elemental value and $^{13}C/^{12}C$ ratios for the remaining atoms and molecules, those in the so-called "carbon isotope pool", that are typically 3-6 times lower. This is a time-dependent effect with the greatest depletions occurring in dense cloud material after about $\sim 10^5$-10^6 years, within the estimated lifetimes of dense cores (Enoch et al., 2008). The potential for significant partitioning of ^{13}C between CO and other atoms and molecules leads to predictive differences between proposed amino acid formation pathways involving various precursors. It should, however, be noted that this isotopic partitioning has not yet been demonstrated unequivocally for observations of a large suite of interstellar molecules. Indeed, recent measurements indicate that, in some star-forming cores, formaldehyde is more enriched in ^{13}C than CO (Wirström et al., 2012b), a result contrary to all theoretical predictions.

Nitrogen fractionation in ion-molecule chemistry has also been studied in detail (Terzieva and Herbst, 2000). When applied to models of molecular cloud cores, two major repositories of ^{15}N emerge that can become incorporated into the ice phase. Nitrogen in NH_3 can become highly fractionated in cores, where selective depletion of CO over N_2 has occurred on a time-scale of $\sim 10^6$ years (Charnley and Rodgers, 2002). HCN can also become enriched in ^{15}N, but on a much shorter time-scale of $<10^5$ years or less (Rodgers and Charnley, 2008a). Model calculations (Rodgers and Charnley, 2008b) can explain the bulk and "hotspot" $^{15}N/^{14}N$ fractionation found in meteorites and IDPs (e.g., Messenger, 2000; Floss et al., 2004; Busemann et al., 2006; Floss et al., 2006), and the $C^{15}N/C^{14}N$ ratios measured in many comets, as well as the two cometary measurements of $HC^{15}N/HC^{14}N$ (Hutsemékers et al., 2005; Manfroid et al., 2005; Bockelée-Morvan et al., 2008). In the case of NH_3, subsequent, but as yet undetermined, parent-body processing must be invoked to incorporate the amine groups into the organic component of primitive matter.

Potential formation mechanisms and isotopic predictions

We considered four plausible formation pathways for meteoritic amino acids: (1) Strecker-cyanohydrin synthesis (Peltzer et al., 1984); (2) Michael addition to nitriles (Cronin and Chang, 1993; Ehrenfreund et al., 2001); (3) CO_2 addition to amines (Hudson et al., 2009); and (4) reductive amination of keto acids (Huber and Wächtershäuser, 2003). We created predictions for the isotopic composition of amino acids resulting from each of these pathways (Table 6); the reasoning behind these predictions is described below.

The Strecker synthesis is widely accepted as the dominant formation mechanism for α-amino acids in meteorites, occurring in the presence of liquid water on parent bodies as a reaction between HCN, NH_3, and aldehydes or ketones. If these compounds are presumed to be of interstellar origin, then the dominant routes to the aldehyde and ketone precursors in cold environments probably involve CO as a starting point (Charnley and Rodgers, 2008). Assuming that significant ^{13}C isotopic partitioning has occurred between CO and other gaseous precursor species, and that interstellar aldehydes and ketones are derived from this CO, the α carbon in the resulting α-amino acid should be the most enriched in ^{13}C (Charnley et al., 2004). The carboxyl group derives from ^{13}C-depleted HCN, and the alkyl groups derive from the similarly less-enriched "carbon isotope pool". Thus, ^{13}C enrichment should decrease in longer-chained α-amino acids, as the overall fraction of carbon from the alkyl groups increases. The precursor aldehydes may form on grains and the ketones in gas reactions among evaporated grain-formed molecules (e.g. aldehydes and the alcohols formed from them). These compounds could therefore have very high D/H ratios (~10-30%, Ceccarelli et al., 2007), leading to similarly high ratios in the amino acids formed from them. A simple statistical treatment for D and H additions on cold dust (Rodgers and Charnley, 2002) indicates D enrichment that scales combinatorially with the number of ways of incorporating a D atom into the precursor molecule, which also suggests that D/H ratios will increase with increasing number of hydrogen atoms. The nitrogen in amino acids formed via Strecker synthesis derives from NH_3, suggesting an overall enrichment in ^{15}N. The enrichments found in ammonia liberated from meteoritic insoluble organic matter (+50 to +455‰; Pizzarello and Williams, 2012) are comparable to those predicted for bulk interstellar NH_3 ices (Rodgers and Charnley, 2008a) but modest relative to the highest predicted 'monolayer' values (Rodgers and Charnley, 2008b).

β-amino acids can form via Michael addition of NH_3 to an unsaturated nitrile, followed by hydrolysis (Miller, 1957). If the unsaturated nitrile comes from the "carbon isotope pool," then all of the carbons in the resulting β-amino acids should have similarly depleted $^{13}C/^{12}C$ ratios, with no dependence on chain length. As in the case of Strecker synthesis, the nitrogen derives from NH_3 and should contain an overall ^{15}N enrichment. The precursor nitriles are not expected to be as significantly enriched in D as the carbonyl-containing compounds that react in Strecker synthesis. This is because interstellar nitrile deuteration (DCN, DNC, DC_3N, CH_2DCN) takes place in cold, dense gas in which significant freeze-out of molecules (particularly CO) has not yet occurred. In this case, H_2D^+ is the main deuterating ion and D/H ratios of ~ 0.01-0.06 are typical (Hirota et al., 2001). On the other hand, molecules containing the carbonyl group are believed to form on dust grains by H atom additions to CO (e.g., Herbst and van Dishoeck, 2009). Theoretically, D/H ratios in these molecules can become extremely high (~1) in dense cores where most of the CO and other molecules have frozen out (Roberts et al., 2003); this can explain the very high D/H ratios (~0.1-0.9) and multi-deuteration observed in formaldehyde (Bergman et al., 2011) and methanol (Parise et al., 2002). Thus, the β-amino acids produced by this pathway should be less enriched in D than the α-amino acids formed from Strecker synthesis.

The CO_2 addition mechanism involves alkylamines, derived from the potentially ^{13}C-depleted molecular pool, and CO_2 that is easily derived from CO in a variety of grain-surface processes (e.g., d'Hendecourt et al., 1985; Allamandola et al., 1988; Hudson and Moore, 1999; Oba et al., 2010). The chemical formation routes to interstellar methylamine and higher alkylamines are uncertain. However, it has been demonstrated experimentally that methylamine can be the end product in the hydrogenation of HCN and methanimine (CH_2NH) on grains (Theule et al., 2011). In this case the ^{15}N enrichment in glycine would derive from that of HCN, which is predicted and observed to be large (Rodgers and Charnley, 2008a; Milam and Charnley, 2012). Thus one might expect based on observed interstellar $^{15}NH_3/^{14}NH_3$ and $HC^{15}N/HC^{14}N$ ratios (Gerin et al., 2009; Milam and Charnley, 2012) that the ^{15}N enrichments of amino acids formed via this mechanism would be significantly greater compared to those of amino acids putatively derived from ammonia. Although the gaseous nitrile precursors are expected to have modest D/H enrichment, the observation that atomic D/H ratios can be large suggests that alkylamines produced from H and D atom additions to condensed nitriles could also be significantly enriched in D. As the C from CO_2 ends up in the carboxyl group, and the nitriles are probably derived from the ^{13}C-depleted pool, we expect this pathway to also produce amino acids in which increasing chain length corresponds with less overall ^{13}C enrichment.

In reductive amination, the requisite precursor keto acids could be derived from interstellar/nebular grain chemistry from hydrogenation and oxidation of CO; grain reactions involving association of simple functional groups can produce glyoxylic acid, oxalic acid, hydropyruvic acid and pyruvic acid (Kisiel et al., 2007; Kisiel et al., 2009). Thus, in this scenario all the carbons of the resulting α-amino acids should be enriched in ^{13}C to a similar degree. As in the case of Strecker synthesis and Michael addition, the nitrogen derives from NH_3 and should contain an overall ^{15}N enrichment. The keto acids most likely formed from precursors with a high D/H ratio, as in the earlier discussion of D/H ratios for carbonyl-containing molecules, suggesting an increase in D/H with chain length similar to that expected from the Strecker pathway.

The α-H, α-amino acids

Figure 3 illustrates the $\delta^{13}C$ and δD values measured for the C_2 to C_5 amino acids in five of the carbonaceous chondrites; only the D-isomers of the C_3 to C_5 compounds are plotted, but similar trends are observed for the L-isomeric data. Previous literature reported decreasing ^{13}C enrichment with increasing chain length for the three-to-five carbon α-amino α-H amino acids in Murchison; the C_2 amino acid glycine was less enriched than the C_3 alanine (Pizzarello et al., 2004). Our data from the C_2 to C_4 α-amino, α-H amino acids in Murchison shows this same trend (Figure 3). In addition, we see this same correlation in the C_2 to C_5 compounds in the CR2 chondrites GRA 95229 and EET 92042; for the CM2 chondrite LON 94101, the trend is less pronounced for C_2 to C_4, but C_5 is significantly lower. The CR3 chondrite QUE 99177 shows a decrease in $\delta^{13}C$ for D-alanine (C_3) over glycine (C_2), although this difference is small compared to the experimental uncertainties. This overall observation of decreasing carbon enrichment with increasing carbon number supports the prediction made about formation via Strecker-cyanohydrin synthesis (Table 6).

We also observe a trend towards increasing δD values with increasing chain length in these same compounds in the CM2 chondrite LON 94101, the CR2 chondrites GRA 95229 and EET 92042, and the CR3 QUE 99177 (C_2 to C_3 only). This correlation again matches the predictions made for formation via Strecker synthesis (Table 6). This relationship between deuterium enrichment and carbon number has not previously been reported, although a re-examination of the prior analysis of amino acids in the Murray meteorite does reveal a similar trend (Pizzarello and Huang, 2005).

No correlation was observed between $\delta^{15}N$ and chain length for these compounds. All α-H, α-amino acids showed ^{15}N enrichments (Table 2), which is consistent with predictions for the Strecker pathway.

Taken together, the carbon, nitrogen, and deuterium isotopic data from the series of C_2 to C_5 α-H, α-amino acids in the CM2, CR2, and CR3 chondrites analyzed here support the hypothesis that these compounds formed via Strecker synthesis from precursors that had a cold, likely interstellar, chemistry origin.

Isotopic correlations with amine position

The suite of identified amino acids included amino acids with the amine group in the α-, β-, γ-, δ-, and ε-positions. The Strecker synthesis is only capable of forming α-amino acids; other mechanisms must be invoked for the other amine positions. Michael addition of ammonia to α,β-unsaturated nitriles has been proposed for the formation of β-amino acids (Cronin and Chang, 1993; Ehrenfreund et al., 2001). Decarboxylation of α-amino dicarboxylic acids (including those formed by Strecker synthesis) or hydrolysis of lactams (Cooper and Cronin, 1995) can lead to the formation of γ- and δ-amino acids.

Figure 4 shows the $\delta^{13}C$ values for D- and L-alanine (α-amino acids) and β-alanine (a β-amino acid) in six of the seven analyzed meteorites. In all cases, the $\delta^{13}C$ values for D- and L-alanine agreed within experimental uncertainty, while the β-alanine was markedly less enriched in ^{13}C. This lowered ^{13}C content matches the predictions made for formation via Michael addition (Table 6). Michael addition is also predicted to form amino acids that are similarly enriched in ^{15}N to the Strecker-formed compounds. The $\delta^{15}N$ values for β-alanine measured in these meteorites was typically within the range encompassed by D- and L-alanine (Table 2), with the exception of LON 94101, where β-alanine was more enriched in $\delta^{15}N$ than D- and L-alanine. The deuterium enrichment signature of Michael addition is predicted to be lower than that for

Strecker synthesis; our data did not reveal a consistent pattern, however, with β-alanine being more enriched in deuterium than D- and L-alanine in three chondrites, less enriched in one, and with no significant difference in the last. The β-alanine could also form by decarboxylation of aspartic acid; however, no CSIA data for aspartic acid was obtained, which precludes an evaluation of this possible mechanism.

The potential contribution of terrestrial contamination to the $\delta^{13}C$ value of β-alanine must be considered; this possibility has previously been suggested to explain low $\delta^{13}C$ β-alanine measurements (Pizzarello et al., 2004). However, it is difficult to explain contamination of β-alanine without corresponding contamination of other biological amino acids such as L-alanine, which was nearly racemic with D-alanine in the meteorites studied. The strong agreement between $\delta^{13}C$ values for D- and L-alanine also argues against significant terrestrial contamination. In addition, terrestrial β-alanine would be expected to show similar effects on the $\delta^{15}N$ and δD values, and the lack of consistently lower measurements for the $\delta^{15}N$ values supports the idea that no significant contamination is present.

The CM1/2 chondrite ALH 83100 contained low abundances of amino acids, primarily the *n*-ω-amino acids glycine, β-alanine, γ-ABA, δ-amino-*n*-valeric acid, and ε-amino-*n*-caproic acid (EACA), as well as the α-amino, α-dialkyl amino acid α-AIB; this is in agreement with previous analyses of this meteorite (Glavin et al., 2006). The isotopic composition of α-AIB could not be measured in this meteorite because of an unknown co-eluting compound. The *n*-ω-amino acids in ALH 83100 exhibited the lowest $\delta^{13}C$, δD, and $\delta^{15}N$ values in this study, and the β-alanine and γ-ABA measured in other meteorites also had relatively low $\delta^{13}C$ values (Figure 2b). Recent analyses of CV3 and CO3 carbonaceous chondrites and Antarctic ureilites found a suite of *n*-ω-amino acids in low abundance in these thermally altered meteorites (Burton et al., 2012a); elevated levels of *n*-ω-amino acids have also been reported in the Bells and Ivuna carbonaceous chondrites (Monroe and Pizzarello, 2011). The $\delta^{13}C$ value of these compounds was surprisingly light for extraterrestrial amino acids (e.g., $\delta^{13}C$ = -27‰ ± 8‰ for γ-amino-*n*-butyric acid), and it was proposed that both the predominance of *n*-ω-amino acids and this light $\delta^{13}C$ value was a signature of formation via Fischer-Tropsch-type syntheses (Burton et al., 2012a). Although the initial CO gas that reacted in FTT synthesis may have been ^{13}C-enriched, fractionation may occur during the formation of amino acids; such fractionation has been shown for the production of alkanes via FTT reactions (Lancet and Anders, 1970; Yuen et al., 1990) and further investigations into fractionation of amino acids is necessary. The light carbon isotopic composition and the low abundances of *n*-ω-amino acids in ALH 83100 may therefore also reflect the same formation pathway as in the CV3 and CO3 chondrites and the ureilites. Because β-alanine could form through either Michael addition or the same mechanism creating other *n*-ω-amino acids, its light isotopic signature could result from either pathway. In addition, EACA is a known terrestrial contaminant of some Antarctic meteorites, resulting from exposure to Nylon-6 in sample storage bags, which may have influenced the light $\delta^{13}C$ value for this compound (Glavin et al., 2006; Elsila et al., 2009).

Effects of α-position substituents

The α-dialkyl amino acids α-AIB and isovaline differ from the other detected compounds because they possess a methyl group rather than a hydrogen in the alpha position. These compounds were the most highly enriched in deuterium in previous analyses of Murchison (Pizzarello and Huang, 2005) and CR2 carbonaceous chondrites (Pizzarello et al., 2008). Our results confirm this observation; isovaline and α-AIB have the highest δD values of any amino acids in each meteorite (Table 3, Figure 2). As discussed above, this observation may indicate a more direct link between α-dialkyl amino acids and the cold environments believed to lead to hydrogen fractionation. Lower D enrichments in α-H amino acids may indicate exchange of the α-H with deuterium-depleted water on the meteorite parent body.

These α-dialkyl compounds do not show correspondingly high ^{13}C enrichments, with $\delta^{13}C$ values that are in the middle of the range seen in this study. Previous Murchison analyses suggested that α-methyl amino acids were enriched in ^{13}C compared to α-H for the C_4 to C_6 amino acids (Pizzarello et al., 2004). Our data confirm this relationship between the C_4 compounds α-AIB and D-α-ABA in Murchison. In the other chondrites, however, a comparison of α-AIB and D-α-ABA as well as the C_5 compounds isovaline and D-valine reveals that this is not a universal trait. In some cases, the α-methyl amino acid is less enriched in $\delta^{13}C$ than the α-H; in other cases the opposite is true or there is no significant difference between them (Figure 5).

Isovaline is the least ^{15}N-enriched compound within experimental error in the three chondrites in which it was measured; α-AIB is the second-least-enriched in the CR2 chondrite EET 92042, but the most ^{15}N-enriched compound in the CM2 chondrites Murchison ($\delta^{15}N$ = +176‰) and LON 94101 ($\delta^{15}N$ = +158‰). Again, these results support previous reports, including the high $\delta^{15}N$ value for α-AIB in Murchison (Engel and Macko, 1997; Pizzarello and Holmes, 2009). Recent theoretical calculations indicate that the efficiencies of interstellar D and ^{15}N fractionation can be anti-correlated at low-temperatures when the differing rates of ion-molecule fractionation reactions in which the distinct *ortho* and *para* spin states of molecular hydrogen are considered (Wirström et al., 2012a). A high fraction of *ortho*-H_2 acts as a "poison" for deuteration (Pagani et al., 2011) but permits efficient ammonia formation, whereas after spin-exchange ion-molecule reactions convert most H_2 to *para*-H_2, deuteration proceeds but ammonia formation and associated ^{15}N enrichment are suppressed. This effect could therefore explain the anti-correlation between δD and $\delta^{15}N$ enrichments found in isovaline, as well as in meteoritic IOM "hotspots" (Briani et al., 2009), as being due to the effects of a time-dependent H_2 *ortho*/*para* ratio in the fractionation of the precursor molecules in the presolar core. The observation of an anti-correlation between δD and $\delta^{15}N$ for α-AIB in EET 92042 but not in the CM2 chondrites suggests a more complicated mix of potential origins for that compound.

Correlations with petrographic type and carbonaceous chondrite group

Figure 2 allows a comparison of isotopic data both across structural groups of amino acids and between carbonaceous chondrite group and petrographic type. The amino acids in the CM and CR chondrites show a similar range of $\delta^{13}C$ and $\delta^{15}N$ values, with only the CM1/2 chondrite ALH 83100 containing compounds with markedly lower $\delta^{15}N$ enrichments. The CR chondrites possess the amino acids with the highest deuterium enrichments, while the lowest deuterium enrichments of amino acids are found in the CM chondrites. This observation agrees with previous measurements of the CR2 GRA 95229, and may reflect a formation of the CR amino acids in cold, deuterium-enriched environments, as well as subsequent CR parent-body chemistry that did not permit much hydrogen exchange or alteration via deuterium-depleted water (Pizzarello et al., 2008).

The chondrites analyzed here can be arranged in rough order from most altered to least altered based on mineralogical and isotopic data as follows (Zolensky and McSween, 1988; Kallemeyn et al., 1994; Zolensky et al., 1997): ALH 83100 > Murchison ≈ LEW 90500 ≈ LON 94101 > GRA 95229 ≈ EET 92042 > QUE 99177. Extent of alteration does not appear to strictly correlate with isotopic enrichment; the least altered CR3 QUE 99177 contains amino acids that rank among the most and least enriched in ^{13}C, ^{15}N, and D (Figure 2a and b). The most altered carbonaceous chondrite studied here, CM1/2 ALH 83100, showed the overall lowest D and ^{13}C enrichments. The amino acids in this meteorite were primarily *n*-ω-amino acids; as described above, these compounds showed low enrichments in D and ^{13}C in all meteorites analyzed. Thus, it is not clear if the low levels of enrichment in ALH 83100 reflect alteration properties that affected isotopic composition or simply reflect the different suite of amino acids, which presumably formed via a different pathway.

The δ^{13}C and δD ratios were measured for glycine in all seven chondrites and δ^{15}N in six of the seven, making it a convenient amino acid to use for examining effects of chondrite group and degree of parent body alteration. Figure 6 shows the isotopic compositions for glycine. The glycine in the CR chondrites is significantly more enriched in deuterium than in the CM chondrites; this higher δD value in CR chondrites is seen for every individual amino acid measured (Table 3). The glycine is higher in ^{15}N in CR chondrites than in the CMs; this is common but not universal for the other amino acids (Table 2). The δ^{13}C value for glycine shows no significant differences between CM and CR chondrites; this is true for most amino acids studied (Table 1), with the possible exception of γ-ABA, which is more enriched in ^{13}C in CM2 chondrites than in CR2 chondrites.

Within the CM chondrites, the δ^{13}C and δ^{15}N values vary, but the variation does not correlate with extent of alteration. The δD value of glycine in all four CM chondrites is roughly equal, perhaps reflecting an origin from the same precursor molecules or reactions with the same deuterium-depleted water on the CM parent body. In the CR chondrites, the least altered CR3 QUE 99177 possesses the highest deuterium enrichment; the lower values in the CR2 chondrites may reflect reactions with deuterium-depleted water on the parent body. The CR3 chondrite QUE 99177 also shows the highest δ^{15}N enrichment and one of the highest δ^{13}C values (within experimental error), again reflecting less overall alteration.

The bulk isotopic compositions of insoluble organic matter (IOM) in carbonaceous chondrites have been extensively studied (Alexander et al., 2007) and a comparison of bulk IOM with compound-specific amino acid analyses shows several differences. When plotting isotopic compositions of the IOM, carbonaceous chondrite groups tend to form discrete clusters; CR chondrites are markedly more enriched in ^{15}N and D and slightly less enriched in ^{13}C than CM chondrites (Alexander et al., 2007). Although CR chondrites do contain the amino acids with the highest δ^{15}N and δD values, the chondrite groups do not cluster together, and the isotopic compositions of CR and CM chondrites are interspersed when plotted (Figure 2). The clustering of the bulk IOM measurements was interpreted as perhaps reflecting a common precursor composed of isotopically distinct components whose relative stabilities were sensitive to parent body processing conditions (Alexander et al., 2007). The compound-specific data suggests that the amino acids in the different chondrites may have originated from common precursors and through common formation mechanisms, creating similar isotopic signatures. The overall deuterium enrichment of the amino acids in the CR chondrites may reflect differences in parent-body chemistry and alteration reactions after formation; because those reactions did not similarly universally affect the ^{13}C or ^{15}N enrichment of individual amino acids, it is likely that the relevant reactions involved deuterium-depleted water.

Summary

The purpose of this study was to extend and improve the available compound-specific isotopic measurements of amino acids in carbonaceous chondrites to encompass a range of CM and CR chondrites of varying petrographic types, including several chondrites for which no amino acid isotopic data were previously available, as well as to compare trends in measured isotopic compositions with theoretical predictions made for different amino acid formation pathways. The analysis of carbon, nitrogen, and hydrogen stable isotopic compositions on a single extract of each meteorite also eliminated potential effects of meteoritic heterogeneity or differences in laboratory techniques on the comparison of these different isotopic ratios within a given meteorite. The results of this work support and extend observations made previously, and lead to the following observations and conclusions:

1) Strecker-cyanohydrin synthesis of α-H, α-amino acids should result in decreasing ^{13}C enrichment and increasing deuterium enrichment with increasing chain length. We observe this signature in all of the carbonaceous chondrites studied for which concentration of those amino acids was sufficient to make isotopic measurements.
2) The C_3 β-amino acid, β-alanine, was consistently less enriched in ^{13}C than the corresponding C_3 α-amino acid, alanine. Similarly, other short-chain, amine-terminal amino acids were also less enriched in all three isotopic ratios. The β-alanine signature may reflect formation via Michael addition, or a separate formation mechanism leading to *n*-ω-amino acids may cause the lighter isotopic signature.
3) The amino acids containing an α-methyl group had consistently higher deuterium enrichment than corresponding α-hydrogen amino acids, with no consistent $\delta^{13}C$ correlation. Isovaline was also consistently less enriched in ^{15}N than other amino acids. The δD and $\delta^{15}N$ trends may be due to the formation of precursor molecules in cold interstellar or presolar environments where the spin-state of hydrogen molecules played a key role in the fractionation chemistry.
4) Individual amino acids in the CR chondrites are consistently higher in deuterium than in the CM chondrites, while there was no significant difference in ^{13}C enrichment. This may reflect differences in reactions between amino acids and water on their respective parent bodies.

The compound-specific isotopic data highlights differences in formation mechanisms, precursors, and environments between different structural classes of amino acids and different carbonaceous chondrite groups and petrographic types. Amino acid distributions and abundances have been shown to vary in other carbonaceous chondrite groups beyond the CM and CR samples studied here; further compound-specific isotopic analyses, in particular N and H isotopic measurements, may help illuminate the origin and evolutionary history of amino acids in the other carbonaceous chondrite groups as well.

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Table 1. δ^{13}C (‰ VPDB) values for amino acids in the analyzed meteorites.[a]

Amino Acid	ALH 83100 (CM1/2)	Murchison (CM2)	LEW 90500 (CM2)	LON 94101 (CM2)	GRA 95229 (CR2)	EET 92042 (CR2)	QUE 99177 (CR3)
Glycine	11 (2)	13 ± 3 (4)	47 ± 10 (3)	38 ± 3 (3)	35 ± 9 (4)	26 ± 3 (3)	42 ± 12 (3)
D-alanine	[b]	38 ± 10 (4)[c]	37 ±9 (3)[c]	43 ± 2 (3)	40 ± 3 (4)[c]	29 ± 2 (4)	38 ± 10 (2)[c]
L-alanine	[b]	40 ± 9 (4)	40 ± 6 (3)	44 ± 1 (3)	38 ± 2 (4)	34 ± 4 (4)	39 ± 4 (3)
β-alanine	0 ± 5 (3)	10 ± 6 (4)	21 ± 3 (3)	20 ± 6 (3)	8 ± 20 (3)	18 ± 9 (4)	-1 ± 6 (3)
α-aminoisobutyric acid	[b]	38 ± 4 (4)	[b]	11 ± 3 (3)	24 ± 1(2)	25 ± 1 (4)	20 ± 9 (2)
D- α-aminobutyric acid	[b]	18 ± 5 (4)	[b]	44 ± 5 (3)	20 ± 3 (4)	20 ± 2 (3)	[b]
L- α-aminobutyric acid	[b]	[b]	[b]	[b]	10 ± 14 (3)	22 ± 3 (3)	-8 ± 4 (2)
γ-aminobutyric acid	-22 ± 4 (3)	[b]	17 ± 10 (3)	19 ± 3 (3)	-18 ± 11 (4)	5 ± 3 (4)	-10 ± 4 (3)
D-valine	[b]	[b]	[b]	22 ± 3 (3)	18 ± 3(3)	16 ± 10 (3)	[b]
L-valine	[b]	[b]	[b]	[b]	13 ± 7 (3)	21 ± 5 (3)	3 ± 12 (2)
Isovaline	[b]	39 ± 2 (4)	[b]	33 ± 1 (3)	16 ± 8 (2)	21 ± 2 (4)	7 (1)
δ-amino-*n*-valeric acid	-2 ± 4 (2)	[b]	[b]	[b]	[b]	[b]	[b]
ε-amino-*n*-caproic acid	-18 ± 3 (3)	[b]	[b]	-12 ± 9 (3)	[b]	[b]	[b]

[a] Errors shown are standard deviations; number of measurements is shown in parentheses.

[b] Measurement not made due to insufficient abundance or chromatographic interferences.

[c] Includes small contribution from unidentified coeluting peak.

Table 2. δ^{15}N (‰ AIR) values for amino acids in the analyzed meteorites.[a]

Amino Acid	ALH83100 (CM1/2)	Murchison (CM2)	LEW 90500 (CM2)	LON 94101 (CM2)	GRA 95229 (CR2)	EET92042 (CR2)	QUE 99177 (CR3)
Glycine	[b]	80 ± 2 (3)	114 ± 15 (3)	91 ± 3 (2)	139 ± 1 (3)	140 ± 6 (4)	147 ± 3 (3)
D-alanine	[b]	99 ± 10 (3)	[b]	120± 5 (2)	208 ± 10 (3) [c]	115 ± 5 (4)	326 ± 9 (3) [c]
L-alanine	[b]	162 ± 15 (3)	[b]	111 ± 7 (2)	127 ± 3 (3)	187 ±11 (4) [c]	141 ± 21 (3)
β-alanine	75 ± 1 (2)	92 ± 2 (3)	120 ± 35 (3)	164 ± 7 (2)	155 ± 6 (3)	154 ± 23 (4)	156 ± 13 (3)
α-aminoisobutyric acid	[b]	176 ± 2 (3)	[b]	158 ± 11 (2)	[b]	77 ± 3 (4)	[b]
D- α-aminobutyric acid	[b]	[b]	[b]	86 ± 11 (2)	193 ± 22 (3)	142 ± 17 (4)	[b]
L- α-aminobutyric acid	[b]	[b]	[b]	89 ± 18 (2)	140 ± 5 (3)	152 ± 8 (4)	[b]
γ-aminobutyric acid	17 ± 3 (2)	[b]	[b]	[b]	93 ± 9 (3)	118 ± 6 (4)	70 ± 13 (3)
D-valine	[b]	[b]	[b]	[b]	145 ± 5 (3)	[b]	[b]
L-valine	[b]	[b]	[b]	[b]	127 ± 4 (3)	[b]	[b]
Isovaline	[b]	68 ± 3 (3)	[b]	[b]	102 ± 14 (3)	48 ± 9 (4)	[b]
δ-amino-*n*-valeric acid	[b]	[b]	[b]	[b]	[b]	[b]	[b]
ε-amino-*n*-caproic acid	12 ± 3 (2)	[b]	[b]	[b]	[b]	[b]	[b]

[a] Errors shown are standard deviations; number of measurements is shown in parentheses.

[b] Measurement not made due to insufficient abundance or chromatographic interferences.

[c] Includes small contribution from unidentified coeluting peak.

Table 3. δD (‰ VSMOW) values for amino acids in the analyzed meteorites.[a]

Amino Acid	ALH83100 (CM1/2)	Murchison (CM2)	LEW 90500 (CM2)	LON 94101 (CM2)	GRA 95229 (CR2)	EET92042 (CR2)	QUE 99177 (CR3)
Glycine	355 ± 49 (3)	341 ± 186 (3)	307± 157 (3)	366 ± 71 (3)	866 ± 60 (3)	1070 ± 82 (6)	1241 ± 216 (4)
D-alanine	[b]	[b]	[b]	725 ± 25 (3)	1382 ± 226 (3)	1693 ± 90 (6)	2204 ± 53 (4)[c]
L-alanine	[b]	[b]	[b]	765 ± 74 (3)	1528 ± 113 (3)	1564 ± 80 (6)	2311 ± 493 (4)
β-alanine	[b]	529 ± 57 (3)	[b]	915 ± 54 (3)	2286 ± 367 (3)	3462 ± 70 (6)	2253 ± 112 (4)
α-aminoisobutyric acid	410 ± 116 (3)	3027 ± 295 (3)	[b]	2362 ± 76 (3)	4303 ± 1189 (3)	7065 ± 390 (6)	2791 ± 770 (3)
D- α-aminobutyric acid	[b]	[b]	[b]	1212 ± 31 (3)	1920 ± 204 (3)	2769 ± 557 (6)	[b]
L- α-aminobutyric acid	[b]	[b]	[b]	[b]	2099 ± 263 (3)	3409 ± 232 (6)	1945 ± 59 (3)
γ-aminobutyric acid	58 ± 6 (3)	[b]	[b]	[b]	[b]	2018 ± 105 (6)	736 ± 39 (4)
D-valine	[b]	[b]	[b]	1216 ± 82 (3)	2165 ± 307 (3)	[b]	[b]
L-valine	[b]	[b]	[b]	[b]	2086 ± 345 (3)	3307 ± 283 (6)	1822 ± 95 (3)
Isovaline	[b]	2904 ± 396 (3)	[b]	2081 ± 42 (3)	3813 ± 253 (3)	6017 ± 395 (6)	4956 ± 57 (3)
δ-amino-*n*-valeric acid	[b]	[b]	[b]	[b]	[b]	[b]	[b]
ε-amino-*n*-caproic acid	[b]	[b]	[b]	[b]	[b]	[b]	[b]

[a] Errors shown are standard deviations; number of measurements is shown in parentheses.

[b] Measurement not made due to insufficient abundance or chromatographic interferences.

[c] Includes small contribution from unidentified coeluting peak.

Table 4. Analyzed amino acids and their structural characteristics.

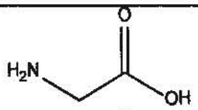
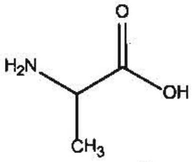
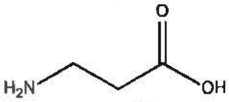
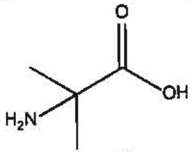
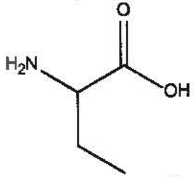
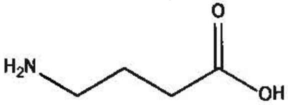
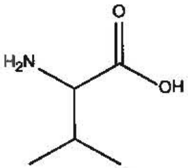
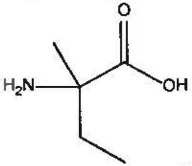
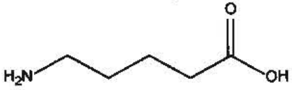
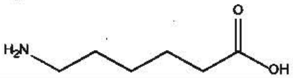
Name	Structure	Carbon number	Amine position	Alpha substituent
Glycine (Gly)		2	α	H
Alanine (Ala)		3	α	H
β-alanine (β-Ala)		3	β	H
α-aminoisobutyric acid (α-AIB)		4	α	CH_3
α-aminobutyric acid (α-ABA)		4	α	H
γ-aminobutyric acid (γ-ABA)		4	γ	H
Valine (Val)		5	α	H
Isovaline (Iva)		5	α	CH_3
δ-amino-*n*-valeric acid		5	δ	H
ε-amino-*n*-caproic acid		6	ε	H

Table 5. Comparison of data from this study with previous measurements of the Murchison and GRA 95229 meteorites.

Murchison

Amino acid	$\delta^{13}C$	$\delta^{15}N$[c]	δD[d]
Gly	**13**, 22[a] ,41[b]	**80**, 37	**341**, nr
D-Ala	**38**, 30[a], 52[b]	**99**, 60	**nd**, nr
L-Ala	**40**, 27[a], 38[b]	**162**, 57	**nd**, nr
β-Ala	**10**, 5[b]	**92**, 61	**529**, 429
D-α-ABA	**18**, 29[b]	**nd**, nr	**nd**, nr
α-AIB	**38**, 5[a], 43[b]	**176**, 184	**3027**, 3058
D,L-Iva	**39**, 17[a], 22[b]	**68**, 66	**2094**, 3419

GRA 95229

Amino acid	$\delta^{13}C$[e]	$\delta^{15}N$[f]	δD[g]
Gly	**35**, 34	**139**, 131	**866**, 868
D-Ala	**40**, 42	**208**, 126	**1382**, 1182
L-Ala	**38**, 41	**127**, 126	**1528**, 1159
L-α-ABA	**nd**, nr	**140**, 122	**3409**, 2890
AIB	**24**	**nd**, 97	**4303**, 7245
D,L-Iva	**16**, 50.5	**102**, 77	**3813**, 5807

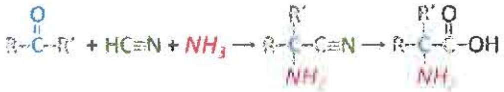
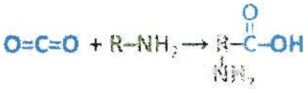
Measurements in bold are from this study

nd. Not detected.

nr. Not reported.

[a]Engel et al., 1990; [b]Pizzarello et al., 2004; [c]Engel and Macko, 1997; [d]Pizzarello and Huang 2005; [e]Martins et al, 2007; [f]Pizzarello and Holmes, 2009; [g]Pizzarello et al., 2008

Table 6. Proposed formation mechanisms and predictions

Mechanism	Predictions			
	Amine	$\delta^{13}C$	$\delta^{15}N$	δD
I. Cyanohydrin (Strecker) 	α	Lower enrichment in longer chains	Enriched	Higher enrichment with more H atoms
II. Michael Addition 	Mostly β (no α)	Lower enrichment, independent of length	Enriched	Less enriched than Strecker
III. CO$_2$ Addition 	Any	Lower enrichment in longer chains	Potentially higher than other mechanisms	Enriched
IV. Reductive Amination 	Any mono-alkyl	Higher enrichment, independent of length	Enriched	Higher enrichment with more H atoms

Blue/bold represents material from ^{13}C-enriched CO; green represents material derived from the "carbon isotope pool". Ammonia-derived nitrogen is shown in red/italics.

Figure 1. GC-MS/IRMS chromatogram of the derivatized, acid-hydrolyzed, hot-water extract of EET 92042. The trace shows the m/z 44 ($^{12}CO_2$ peak) produced and measured during carbon compound-specific isotope analysis. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of coelutions or insufficient sensitivity.

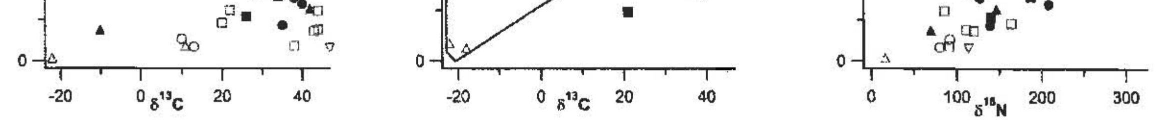


Figure 2. Isotopic data for the amino acids in the seven analyzed carbonaceous chondrites. Outlined areas highlight subsets of structurally similar compounds.

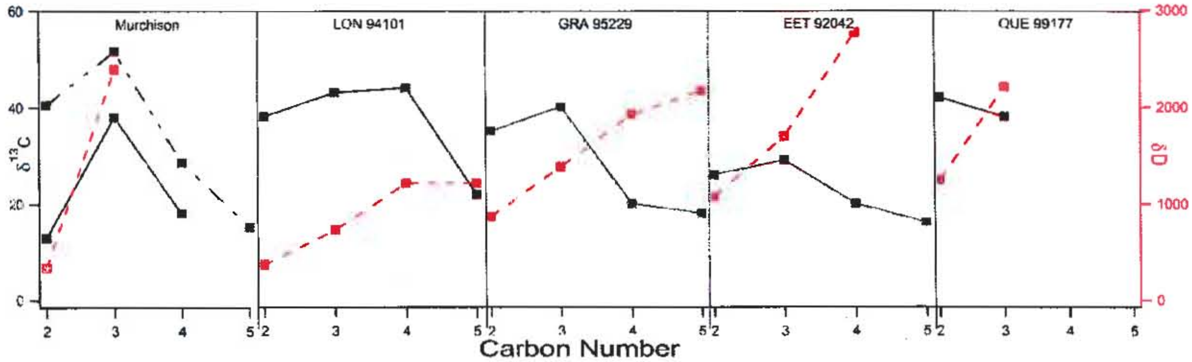


Figure 3. Carbon and deuterium isotopic data for two-to-five-carbon α-amino, α-H amino acids in five carbonaceous chondrites. The black solid line and left axis show the $\delta^{13}C$ values; the dashed line and right axis show the δD values. The amino acids are: glycine (C_2), D-alanine (C_3), D-α-amino-*n*-butyric acid (C_4), D-valine (C_5). The dotted line in the Murchison panel represents data from Pizzarello et al., 2004. No δD data was obtained for the C_3, C_4 or C_5 α-amino, α-H amino acids in Murchison.

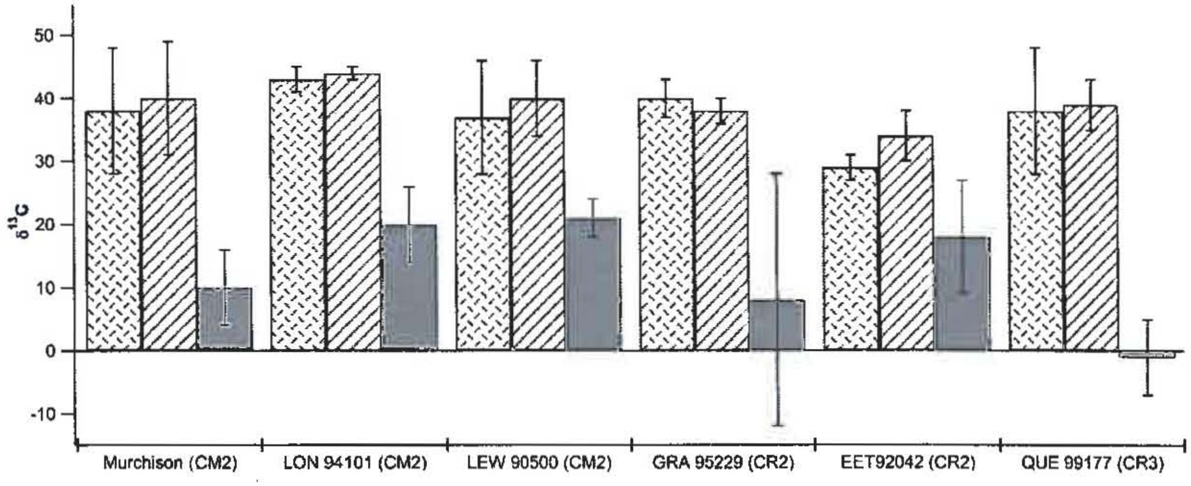


Figure 4. $\delta^{13}C$ values for D-alanine (checked), L-alanine (striped), and β-alanine (solid) in six carbonaceous chondrites. Error bars represent standard deviations (see Table 1). β-alanine is consistently less enriched in ^{13}C, perhaps reflecting a different formation pathway.

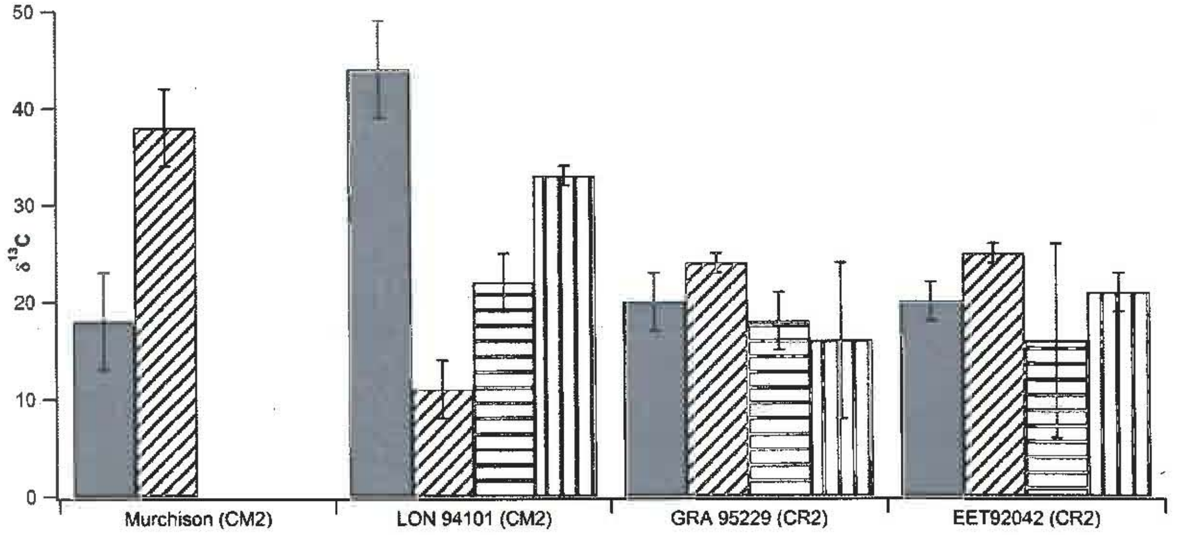


Figure 5. $\delta^{13}C$ values for the four-carbon amino acids D-α-ABA (dark gray) and α-AIB (diagonal stripes) and the five-carbon amino acids D-valine (horizontal stripes) and isovaline (vertical stripes). Error bars represent standard deviations (see Table 1). There is no clear correlation between the alpha substituent and ^{13}C enrichment.

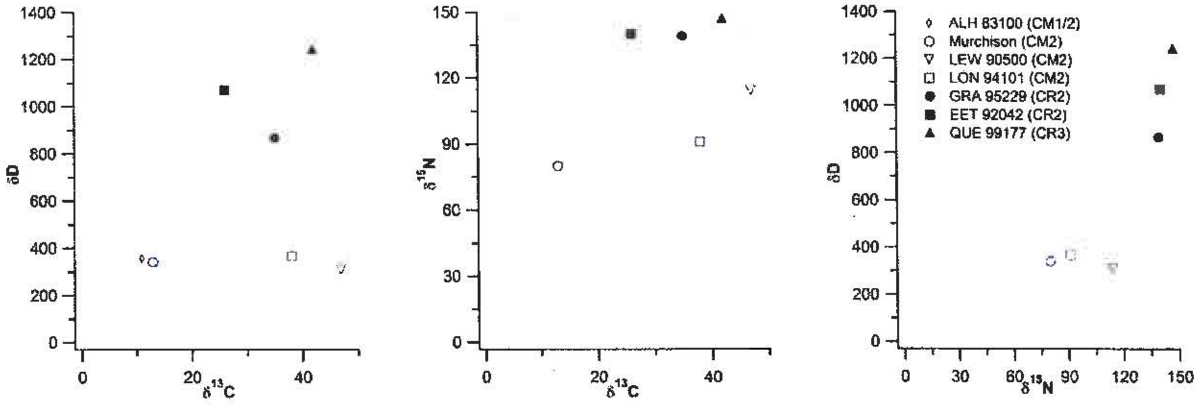


Figure 6. Isotopic data for glycine in the seven analyzed carbonaceous chondrites. Nitrogen data was not obtained for ALH 83100.