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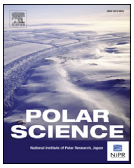

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The effects of parent-body hydrothermal heating on amino acid abundances in CI-like chondrites

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Abstract

We determined the amino acid abundances and enantiomeric compositions of the Antarctic CI1 carbonaceous chondrites Yamato (Y)-86029 and Y-980115, as well as the Ivuna and Orgueil CI1 carbonaceous chondrites by liquid chromatography with fluorescence detection and time-of-flight mass spectrometry. Y-86029 and Y-980115 both show evidence of parent-body heating (500−600 °C) in addition to aqueous alteration, while Ivuna and Orgueil only show evidence for aqueous alteration. In contrast to Ivuna and Orgueil, which each contain ~70 nmol/g of amino acids in acid-hydrolyzed, water extracts, both heated Yamato CI meteorites contain only low levels of amino acids that were primarily L-enantiomers of proteinogenic amino acids, indicating that they are likely to be terrestrial in origin. Because indigenous amino acids have been found in meteorites that have experienced metamorphic temperatures of >1000 °C with only minimal aqueous alteration, heating alone is not sufficient to explain the lack of amino acids in Y-86029 and Y-980115. Rather, our data suggest that the combination of heating and aqueous alteration has a profound destructive effect on amino acids in meteorites. This finding has implications for the origins of amino acids and other molecules in the early evolution of our solar system.
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Keywords: Meteorite; Amino acid; CI chondrite; Aqueous alteration; Thermal metamorphism

1. Introduction

The presence of organic molecules in primitive stony meteorites is well-known, and analyses of these compounds have provided numerous insights into chemical processes occurring early in the evolution of our solar system (Botta and Bada, 2002; Pizzarello et al., 2006; Pizzarello and Shock, 2010 and references therein). Amino acids serve as a useful indicator of parent body chemistry due to their structural diversity, presence in a wide range of meteorites, and the availability of sensitive methods for their analysis. Recent work has focused on identifying relationships between meteorite parent body composition, alteration history, and amino acid abundances in an effort to further refine our understanding of the prebiotic chemistry that may have helped jump-start life on Earth. One such relationship is that

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meteorites that experienced significant thermal metamorphism on their parent bodies contain only low levels of extraterrestrial amino acids (Burton et al., 2011; Callahan et al., 2013; Glavin et al., 2010a). In contrast, a second relationship is meteorites that experienced low temperature parent body aqueous alteration are generally rich in amino acids (Botta et al., 2002; Burton et al., 2013; Glavin et al., 2010b). Among aqueously altered carbonaceous meteorites, there is an inverse correlation between extent of alteration and amino acid abundance, such that type 2 and 3 carbonaceous chondrites are generally more abundant in amino acids than type 1 (Glavin et al., 2010b; Pizzarello et al., 2012). Several fragments of the Sutter's Mill meteorite, a CM2 carbonaceous chondrite that experienced thermal metamorphism at temperatures up to 400 °C in addition to aqueous alteration, were recently found to be nearly devoid of non-terrestrial amino acids (Burton et al., in press; Jenniskens et al., 2012), a surprising result because CM2 chondrites have been long known to contain abundant amino acids of extraterrestrial origin (e.g., Cronin and Moore, 1971; Glavin et al., 2006; Kotra et al., 1979; Kvenvolden et al., 1970). Laboratory studies have shown that amino acids can be rapidly decomposed under hydrothermal conditions, particularly in the presence of minerals (Islam et al., 2003; McCollom, 2013), suggesting the combination of heating and aqueous alteration could have led to the destruction of any indigenous amino acids in the Sutter's Mill meteorite. To assess how widespread this phenomenon might be in other carbonaceous meteorite groups, we analyzed two CI carbonaceous chondrites found in the Yamato region of Antarctica that have also experienced hydrothermal conditions.

Ivuna-like carbonaceous chondrites (CI chondrites) arguably contain the most primitive materials in our solar system based on the observation that their bulk elemental composition very closely matches that of the solar photosphere (Anders and Grevesse, 1989; Lodders, 2003). CI chondrites have experienced extensive aqueous alteration, with all known samples classified as alteration type 1. Amino acid data have only been published for two CI carbonaceous chondrites, Ivuna and Orgueil; these two meteorites have similar total amino acid abundances of ~70 nmol/g (Ehrenfreund et al., 2001; Glavin et al., 2010b). Both of these meteorites experienced parent-body aqueous alteration at temperatures <150 °C (Bullock et al., 2005; Clayton and Mayeda, 1999). A number of CI-like chondrites have been identified that experienced hydrothermal conditions at temperatures between 500 and 600 °C, including Yamato 86029 (Y-86029) and Yamato 980115 (Y-980115), making possible a comparison of the amino acid contents of low-temperature and high-temperature CI chondrites (Harries and Langenhorst, 2011; Nakamura, 2005; Tonui et al., 2014, 2002, 2003). In the present work, we have determined the amino acid contents of Y-86029 and Y-980115 as well as samples of Ivuna and Orgueil using ultra-high performance liquid chromatography with UV-fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS). The results of this analysis are presented here.

2. Materials and methods

2.1. Chemicals and reagents

To clean all sample-handling tools, ceramics, and glassware of organic residue, they were rinsed with Millipore Direct Q3 UV (18.2 MΩ, <3 parts-per-billion [ppb] total organic carbon) ultrapure water (hereafter water), wrapped in aluminum foil, and heated in air at 500 °C for 18–24 h. This process allows for the escape and combustion of organic material from the heated items. The borate derivatization buffer was prepared from solid sodium tetraborate (Sigma Ultra 99.5–100% purity) that was pyrolyzed in air at 500 °C for 3 h to remove any organic contaminants prior to dissolution in water. Details on the sources and preparation of amino acid standards are available in Glavin and Dworkin (2009); all other solutions were prepared as described by Glavin et al. (2006).

2.2. CI chondrite samples and controls

The samples of Y-86029 (110 mg) and Y-980115 (211 mg) were allocated by the National Institute of Polar Research (NIPR). Ivuna (92 mg) was allocated by the Natural History Museum of London. Meteorites were crushed into a powder using a clean mortar and pestle in a Class 100 Labconco laminar flow hood under HEPA-filtered positive pressure. Procedural reagent blanks and samples of powdered serpentine (127 mg) were processed in parallel as controls. In addition, a non-hydrolyzed extract of the Orgueil meteorite (265 mg) from the Musée National of Paris that was processed by Glavin and Dworkin (2009) and stored at −86 °C was also analyzed.

2.3. Extraction procedures and analytical techniques

Meteorite samples and controls were individually flame-sealed in glass ampoules with 1 mL water and placed in an oven set at 100 °C for 24 h. After extraction, the tubes were cooled and centrifuged for 5 min at 5000 rpm for 5 min in a Hanil Fleta 5 centrifuge to separate solid particulate from water supernatant. Half of the water extract was dried *in vacuo* (Labconco Centrivap) and subjected to acid hydrolysis under 6 M HCl vapor at 150 °C for 3 h to liberate amino acids in bound or precursor forms (Glavin et al., 2006). The remaining non-hydrolyzed extract (which contains free, unbound amino acids) and the acid-hydrolyzed extract (which contains both free amino acids and those liberated from bound precursors) were dried *in vacuo* and re-dissolved in 1 mL of water. To remove metal ions and other species that could interfere with the derivatization reaction, both the acid-hydrolyzed and non-hydrolyzed extracts were desalted with cation exchange resin (BIO-RAD, AG50W-X8, 100–200 mesh, hydrogen form). To permit estimation of desalting and derivatization recoveries, a racemic DL-norleucine standard was added to the meteorite extracts prior to loading on the desalting columns. The amino acids were eluted with a 2 M aqueous solution of ammonia prepared from gaseous 99.99% NH_3 (Air Products), dried again, and re-dissolved in 0.1 mL water for analysis. The desalted sample extracts were derivatized with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) chiral fluorescent label for 1 or 15 min as previously described (Glavin et al., 2006). OPA/NAC amino acid derivatives were immediately analyzed by ultrahigh-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) using a Waters Acquity UPLC and a Waters Acquity FD connected in series to a Waters LCT Premier ToF-MS. OPA/NAC derivatives were separated using a Waters BEH C18 column (2.1 × 50 mm, 1.7 μm particle size) followed by a Waters BEH phenyl column (2.1 × 150 mm; 1.7 μm particle size), with chromatographic conditions tuned for general amino acid separation or five-carbon amino acid separation (Glavin et al., 2010b). As in related studies, meteorite and control samples were identified by correlating sample compounds with known standards using the masses of the OPA/NAC amino acid derivatives at the expected chromatographic retention times.

3. Results and discussion

The distribution and enantiomeric composition of several simple two-carbon to six-carbon aliphatic amino acids in hydrolyzed and non-hydrolyzed extracts of the CI chondrites Y-86029, Y-980115 and Ivuna were determined (representative chromatograms are given in Fig. 1), as well as the non-hydrolyzed extract of the Orgueil meteorite. The free and total amino acid abundances for all meteorites analyzed here are in Table 1.

3.1. Amino acid analyses: Ivuna and Orgueil

The individual amino acid abundances reported here are within a factor of two of what was previously reported for the Ivuna and Orgueil meteorites (Ehrenfreund et al., 2001). The differences are easily rationalized since this analysis included high-resolution mass spectrometry that permitted the recognition of co-eluting fluorescent compounds; the improved chromatographic separation allowed the determination of abundances of additional amino acids that were not possible previously; and there is well established heterogeneity in amino acid abundances between different fragments of the same meteorite (e.g., Pizzarello and Shock, 2010).

Although several of the amino acids found in meteorites are also common in terrestrial biology, the amino acids in Ivuna and Orgueil appear to be predominantly indigenous. There are several indicators to help evaluate if amino acids are predominantly indigenous or largely the result of terrestrial contamination. One particularly valuable indicator is the ratio of D-amino acids to their biologically-preferred L counterparts (Table 2). For Ivuna and Orgueil, the D/L ratios for aspartic acid and alanine are ~0.9 or greater (Table 2), consistent with ratios observed in abiotic amino acid syntheses and much higher than observed for these protein amino acids found in terrestrial samples, which typically have D/L values less than 0.3 (e.g., Lomstein et al., 2006). The D/L ratio of valine was somewhat lower in these meteorites (Table 2), suggesting the presence of terrestrial L-valine in the sample. In addition, there appears to have been some terrestrial contamination of L-serine in Ivuna, as the D/L ratio for serine is very low (Table 2). Low levels of L-serine are often introduced during cation exchange chromatography, and L-serine is known to be a contaminant arising during sample handling such as from fingerprints (de Puit et al., 2013; Walton and Curry, 1991), and the low overall levels of serine are consistent with its introduction as a trace contaminant. Glycine is a common proteinogenic amino acid, but is also a major product of abiotic amino acid syntheses e.g., Miller (1953). Because it is achiral, however, D/L ratios cannot be used to differentiate between a terrestrial or extraterrestrial origin. Previous analyses of amino acids in terrestrial samples have shown that glycine is typically present in nearly equal abundance as other

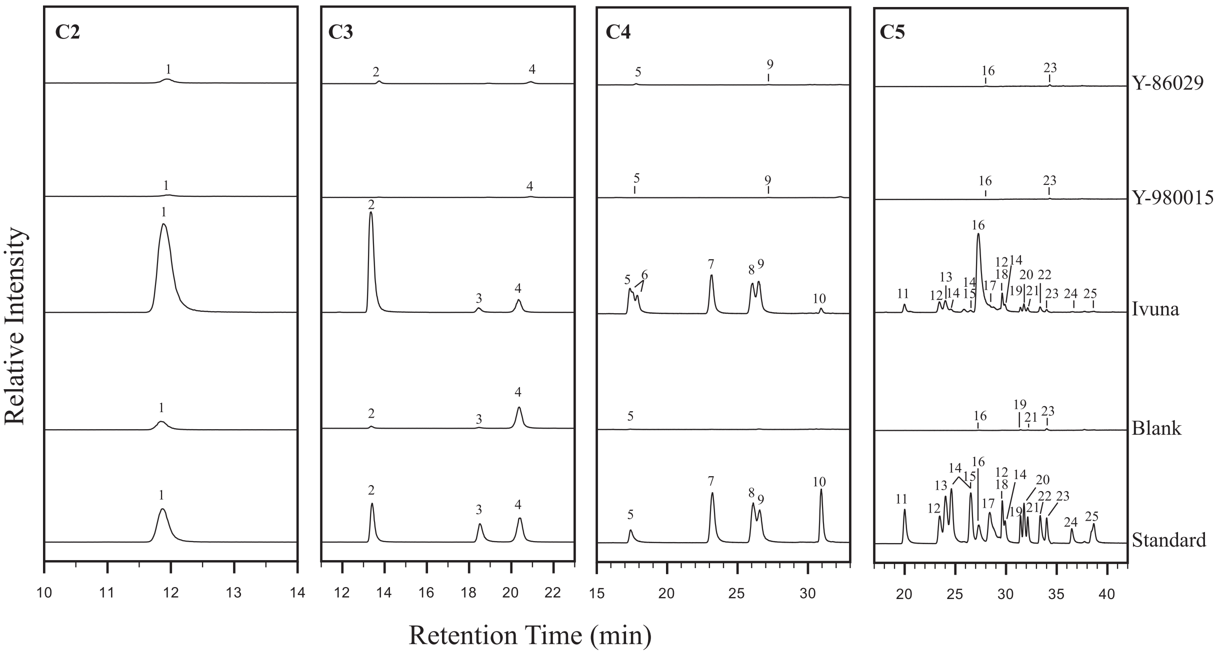

Fig. 1. Representative liquid chromatography-mass spectrometry chromatograms for the acid-hydrolyzed meteorite samples analyzed in this study. Single-ion chromatograms are shown for the C2, C3, C4, and C5-carbon primary, aliphatic, acyclic amino acids (derivatized positive ionization mass-to-charge ratios of 337.0859, 351.1015, 365.1171, and 379.1328, respectively). The masses plotted represent a ~0.07 Da window (the peak width at half maximum) centered around the corresponding theoretical monoisotopic masses of the mono-protonated positive ions of C2 to C5 OPA/NAC amino acid derivatives and are all set to the same scale. Similar chromatograms were obtained for the non-hydrolyzed fractions. The chromatographic conditions were as follows: column temperature, 30 °C; flow rate, 150 μL min^{-1}1; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol). The following gradient was used: time in minutes (%B): 0 (0), 35 (55), 45 (100). To improve separation of the five-carbon amino acids, a different gradient was used: solvent A (50 mm ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); time in minutes (%B): 0 (15), 25 (20), 25.1 (35), 44.5 (40), 45 (100). Peak numbering is as follows: (1) glycine; (2) β-alanine; (3) D-alanine; (4) L-alanine; (5) γ-aminobutyric acid; (6) D,L-β-aminoisobutyric acid; (7) D-β-aminobutyric acid; (8) L-β-aminobutyric acid; (9) α-aminoisobutyric acid; (10) D,L-α-aminobutyric acid; (11) 3-amino-2,2-dimethylpropanoic acid; (12) D,L-4-aminopentanoic acid; (13) D,L-4-amino-3-methylbutanoic acid; (14) D,L- and allo-3-amino-2-methylbutanoic acid; (15) D,L-3-amino-2-ethylpropanoic acid; (16) δ-amino-*n*-valeric acid; (17) D,L-4-amino-2-methylbutanoic acid; (18) 3-amino-3-methylbutanoic acid; (19) D-isovaline; (20) D-3-aminopentanoic acid; (21) L-isovaline; (22) L-3-aminopentanoic acid; (23) L-valine; (24) D-valine; (25) D,L-norvaline; The standard trace is provided for reference, though the standard for D + L-β-aminoisobutyric acid (peak 6) was run separately.

proteinogenic amino acids such as L-glutamic acid, L-aspartic acid, and L-alanine (Burton et al., 2011), and the average abundance of glycine to serine in the more than 500,000 entries in the Swiss-Prot Protein Knowledge database is 1.08:1 (http://web.expasy.org/docs/relnotes/relstat.html; accessed June 5, 2014). The observation that glycine is 5–50-fold more abundant than these amino acids in Ivuna and Orgueil strongly suggests that it did not come from terrestrial contamination, and most of the glycine (or its precursor) is indigenous to the meteorites. In addition, a previous carbon isotopic measurement of glycine in the Orgueil meteorite yielded a δ^{13}C value of +22‰ (Ehrenfreund et al. 2001), a finding that clearly indicates an extraterrestrial origin for this amino acid.

The total amino acid abundance of 74 ± 8 nmol/g for Ivuna, very closely matches what we reported previously in the Orgueil meteorite (71 nmol/g; Glavin et al., 2010b). Both Ivuna and Orgueil contain a number of amino acids that are not found in proteins, and consequently are less commonly found on Earth. The abundances of these molecules relative to the proteinogenic amino acids are strong indicators that they are extraterrestrial in origin. The nearly 3:1 ratio of β-alanine to glycine observed in Ivuna matches that reported previously for Orgueil (Table 1). β-alanine-to-glycine ratios greater than 1 were also observed for type 1 CM and CR chondrites, indicating a possible correlation between parent body alteration and the relative abundance of β-alanine in CI, CM, and CR meteorites (Glavin et al., 2010b). Additional non-proteinogenic amino acids in Ivuna and Orgueil include the four-carbon amino acids γ-amino-*n*-butyric acid, α-aminoisobutyric acid (AIB), D- and L-β-aminoisobutyric acid, D- and L-α-amino-*n*-butyric acid and D- and L-β-amino-*n*-butyric acid. The most notable difference between the two meteorites is in their abundances of δ-amino-*n*-valeric acid, which is present in much higher abundance in Ivuna than in Orgueil. Ivuna also contains elevated levels of γ-amino-*n*-butyric acid when compared with Orgueil. The amino acids β-alanine, γ-amino-*n*-butyric acid and δ-amino-*n*-valeric acid were previously found to be present in high relative abundances in metamorphosed ureilites, CV and CO chondrites (Burton et al., 2012a), though the parent body conditions on those meteorites differed significantly from the conditions on the Ivuna and Orgueil parent body(ies).

The Ivuna and Orgueil meteorites also contain diverse suites of five-carbon amino acids, many of which are not found in biology. Of particular note among the five-carbon amino acids is isovaline, which has only limited use in biology (Elsila et al., 2011), and has been found in L-excesses of extraterrestrial origin in many aqueously altered carbonaceous chondrites, including the CI Orgueil (Glavin and Dworkin, 2009; Pizzarello and Cronin, 2000), CM, CR and metal-rich CH and CB carbonaceous chondrites (Burton et al., 2013; Glavin et al., 2010b). Within each of the four replicate measurements we made, the L-isovaline enantiomer was present in higher abundance, giving an average L-isovaline excess of 6.6% ± 3.9% for Ivuna. This value is lower than the 15.2% ± 4.0% previously reported for isovaline in Orgueil (Glavin and Dworkin, 2009). In the case of Ivuna, however, the accuracy of the isovaline measurements is limited by the smaller sample size studied and lower isovaline abundance compared to Orgueil.

The indigenous nature of the amino acids in Ivuna and Orgueil could be more firmly established by performing compound-specific stable isotope measurements, as amino acids found in meteorites that experienced low-temperature aqueous alteration tend to be enriched in ^{13}C, D, and ^{15}N compared to those formed by terrestrial biology (Elsila et al., 2012). These measurements require at least 1 nmol of a given compound for δ^{13}C measurements, or ~130 mg of Ivuna for glycine and β-alanine (assuming 70% amino acid recoveries), which is more than we have access to presently (D-serine and isovaline would require 10 and 4.5 g, respectively). Carbon isotopic measurements of both glycine and β-alanine in Orgueil have been reported previously (Ehrenfreund et al., 2001). Even larger amounts of sample would be required for δD and δ^{15}N measurements of glycine and β-alanine in these meteorites (~400 and 800 mg, respectively).

3.2. Amino acid analyses: Y-86029 and Y-980115

The amino acid abundances and distributions in extracts of Y-86029 and Y-980115 are markedly different from those in Orgueil and Ivuna (Fig. 2). First, Y-86029 and Y-980115 contain ~25-fold lower concentration of amino acids, ~3 nmol/g (Table 1). Second, the amino acids in Y-86029 and Y-980115 are dominated by proteinogenic amino acids, many with very low D/L ratios indicative of terrestrial contamination (Table 2). Third, the ratios of glycine to L-serine in Y-86029 (1.3:1) and Y-980115 (0.83:1) are much closer to the proteinogenic ratios of ~1.1:1 than the >20:1 values observed in Ivuna and Orgueil. Fourth, the β-alanine to glycine ratios for both Y-86029 and Y-980115 are well below one. And fifth, Y-86029 and Y-980115 are nearly devoid of four-carbon and five-carbon amino acids that are fairly abundant in Orgueil and Ivuna. These differences strongly suggest that most, if not all of the amino acids in Y-86029 and Y-980115 are the result of terrestrial contamination. Of the two meteorites, we note that Y-980115 has higher D/L ratios for several proteinogenic amino acids, making it the more likely of the two to contain indigenous amino acids.

Because amino acids of extraterrestrial origin are now known to be common among aqueously altered carbonaceous chondrites, meteorites that are devoid of these compounds can provide constraints on parent body conditions that are compatible with amino acid synthesis and/or survival. Differences in meteorite parent-body conditions are likely to be particularly relevant. In this case, the most compelling difference between the amino acid-rich CIs, Ivuna and Orgueil, and the amino acid-depleted CIs, Y-86029 and Y-980115, is the degree of heating that the latter two meteorites experienced. More specifically, Ivuna and Orgueil likely never experienced temperatures above 150 °C (Bullock et al., 2005; Clayton and Mayeda, 1999; Zolensky et al., 1993), whereas Y-86029 and Y-980115 have experienced temperatures up to 600 °C (Harries and Langenhorst, 2011; Nakamura, 2005; Tonui et al., 2014, 2002, 2003). These elevated temperatures, particularly in the presence of water, have been shown to be destructive to amino acids. For example, theoretical calculations have shown that for many α-amino acids, activation energies for decarboxylation are reduced by ~50% in the presence of water (Li and Brill, 2003a). Experimentally, amino acids were shown to decompose rapidly in aqueous solutions at temperatures of 240 °C (Bada et al., 1995; Miller and Bada, 1988), well below the temperatures these meteorites experienced. More recently, McCollom (2013) showed that temperatures above 150 °C lead to rapid degradation of alkyl-α-amino acids in the presence of water and certain minerals, and argued that temperatures below 100 °C are far more conducive to amino acid stability under the experimental conditions

Table 1
Summary of the total (free + bound) abundances in nmol/g of the two- to six-carbon amino acids searched for in the acid-hydrolyzed, hot-water extracts of CI carbonaceous chondrites.[a]

Amino acid	Orgueil[b]		Ivuna		Y-86029		Y-980115	
	Free	Total	Free	Total	Free	Total	Free	Total
D-aspartic acid	0.22 ± 0.05	0.41 ± 0.23	0.26 ± 0.11	0.56 ± 0.03	0.04 ± 0.02	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
L-aspartic acid	0.67 ± 0.48	0.41 ± 0.21	0.36 ± 0.09	0.63 ± 0.04	0.05 ± 0.01	0.14 ± 0.07	0.04 ± 0.03	0.03 ± 0.01
D-glutamic acid	0.10 ± 0.07	0.32 ± 0.11	0.05 ± 0.01	0.18 ± 0.03	0.02 ± 0.01	0.01 ± 0.01	0.01	0.01
L-glutamic acid	0.02 ± 0.01	0.56 ± 0.15	0.03 ± 0.02	0.19 ± 0.01	0.10 ± 0.05	0.13 ± 0.02	0.02	0.02 ± 0.01
D-serine	0.03 ± 0.01	<0.01	0.09 ± 0.03	0.05 ± 0.01	<0.01	0.03 ± 0.01	0.01	<0.01
L-serine	0.18 ± 0.06	<0.01	0.15 ± 0.08	0.51 ± 0.03	0.12 ± 0.02	0.59 ± 0.07	0.27 ± 0.12	0.30 ± 0.04
Glycine (1)	4.0 ± 1.3	11.5 ± 6.0	5.5 ± 0.7	10.7 ± 0.8	0.51 ± 0.05	0.79 ± 0.05	0.27 ± 0.05	0.25 ± 0.12
β-alanine (2)	16.4 ± 3.3	30.6 ± 7.6	24.5 ± 2.2	29.2 ± 8.1	0.36 ± 0.04	0.36 ± 0.04	0.12 ± 0.04	0.19 ± 0.02
D-alanine (3)	0.46 ± 0.11	0.90 ± 0.19	0.96 ± 0.22	2.3 ± 0.5	0.07 ± 0.01	0.07 ± 0.01	0.04 ± 0.02	0.15 ± 0.01
L-alanine (4)	0.67 ± 0.22	1.1 ± 0.25	2.3 ± 1.4	2.5 ± 1.8	0.10 ± 0.04	0.10 ± 0.04	0.13 ± 0.09	0.51 ± 0.01
γ-aminobutyric acid (5)	1.1 ± 0.5	2.7 ± 1.3	1.3 ± 0.4	3.9 ± 1.0	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.02	0.15 ± 0.03
D-β-aminobutyric acid (7)	1.7 ± 0.4	2.1 ± 1.1	2.3 ± 0.2	2.2 ± 0.1	<0.01	0.01	<0.01	<0.01
L-β-aminobutyric acid (8)	1.8 ± 0.5	1.8 ± 0.6	2.1 ± 0.2	2.1 ± 0.2	<0.01	0.01	<0.01	<0.01
α-aminoisobutyric acid (9)	3.2 ± 1.6	3.3 ± 1.4	2.6 ± 0.3	2.6 ± 0.3	0.03 ± 0.02	0.02 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
D,L-β-aminoisobutyric acid[c] (6)	d[g]	d[g]	0.6 ± 0.1	2.6 ± 0.2	<0.01	<0.01	<0.01	<0.01
D,L-α-aminobutyric acid[c] (10)	0.36 ± 0.30	0.69 ± 0.48	0.17 ± 0.01	0.4 ± 0.02	<0.01	<0.01	<0.01	0.01
D-valine (24)	<0.01	0.19 ± 0.05	0.02 ± 0.01	0.05 ± 0.01	<0.01	<0.01	<0.01	<0.01
L-valine (23)	0.04 ± 0.01	0.48 ± 0.02	0.03 ± 0.01	0.06 ± 0.01	0.02 ± 0.01	0.14 ± 0.03	0.01	0.02 ± 0.01
D,L-norvaline[c] (25)	0.02 ± 0.01	0.23 ± 0.02	0.05 ± 0.01	0.06 ± 0.01	<0.01	<0.01	<0.01	<0.01
D-isovaline (19)	0.10 ± 0.01	0.31 ± 0.03	0.15 ± 0.02	0.19 ± 0.02	<0.01	<0.01	<0.01	<0.01
L-isovaline (21)	0.10 ± 0.01	0.42 ± 0.02	0.10 ± 0.01	0.22 ± 0.04	<0.01	<0.01	<0.01	<0.01
D-3-aminopentanoic acid (20)	0.18 ± 0.01	1.6 ± 0.1	0.20 ± 0.01	0.22 ± 0.02	<0.01	<0.01	<0.01	<0.01
L-3-aminopentanoic acid (22)	0.18 ± 0.01		0.17 ± 0.01	0.22 ± 0.01	<0.01	<0.01	<0.01	<0.01
D,L- and *allo*-3-amino-2-methylbutanoic acid[d] (14)	0.22 ± 0.01	0.55 ± 0.03	0.28 ± 0.02	0.39 ± 0.04	<0.01	<0.01	<0.01	<0.01
3-amino-3-methylbutanoic acid[e] (18)	<0.35	<0.26	<0.14	<0.68	<0.01	<0.01	<0.01	<0.01
3-amino-2,2-dimethylpropanoic acid (11)	0.13 ± 0.01	0.59 ± 0.03	0.18 ± 0.01	0.27 ± 0.01	<0.01	<0.01	<0.01	0.01
D,l-3-amino-2-ethylpropanoic acid[c] (15)	0.04 ± 0.01	1.5 ± 0.1	0.06 ± 0.01	0.05 ± 0.01	<0.01	<0.01	<0.01	<0.01
D,L-4-aminopentanoic acid[d] (12)	0.32 ± 0.03	2.4 ± 0.2	0.34 ± 0.03	0.92 ± 0.03	<0.01	<0.01	<0.01	<0.01
D,L-4-amino-2-methylbutanoic acid (17)	0.06 ± 0.01	1.5 ± 0.1	0.01	0.75 ± 0.03	<0.01	<0.01	<0.01	<0.01
D,L-4-amino-3-methylbutanoic acid (13)	0.17 ± 0.01	2.8 ± 0.1	0.26 ± 0.02	0.98 ± 0.08	<0.01	<0.01	<0.01	<0.01
δ-aminovaleric acid (16)	0.10 ± 0.01	1.2 ± 0.2	0.39 ± 0.01	8.1 ± 0.3	<0.01	0.04 ± 0.01	<0.01	0.04 ± 0.01
ε-aminocaproic acid	0.09 ± 0.01	0.82 ± 0.79	n.d.	n.d.	0.05 ± 0.02	0.39 ± 0.02	0.08 ± 0.03	0.95 ± 0.50
Total[f]	36 ± 4	71 ± 10	48 ± 3	74 ± 8	1.5 ± 0.1	3.2 ± 0.1	1.1 ± 0.2	2.7 ± 0.5
%free	51%		65%		47%		41%	

[a] All values are reported in nmol/g on a bulk sample basis. Extracts were analyzed by OPA/NAC derivatization (15 min) and UPLC separation with UV fluorescence and time of flight mass spectrometry (ToF-MS) detection. For the LC-ToF-MS data, the mono-isotopic masses of each protonated OPA/NAC amino acid derivative ($M + H^+$) was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The uncertainties (δx) are based on the standard deviation of the average value of at least 3 separate measurements (n) with a standard error, $\delta x = \sigma x \cdot (n - 1)^{-1/2}$.

[b] Total amino acid data for Orgueil are from Glavin and Dworkin (2009).

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

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

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

[f] Total (free + bound) amino acid abundances are the sum of all amino acids included in the table.

[g] β-aminoisobutyric acid was detected but not quantified in the Orgueil hydrolyzed and unhydrolyzed samples.

Table 2

D/L enantiomeric ratios of proteinogenic amino acids found in the acid-hydrolyzed CI carbonaceous chondrite hot water extracts.

Amino acid	Orgueil[a]	Ivuna	Y86029	Y980115
Aspartic acid	0.98 ± 0.75	0.90 ± 0.08	0.16 ± 0.13	0.67 ± 0.38
Glutamic acid	0.57 ± 0.24	1.0 ± 0.15	0.11 ± 0.06	0.74 ± 0.05
Serine	nd	0.10 ± 0.02	0.05 ± 0.02	~0.01
Alanine	0.85 ± 0.27	0.92 ± 0.69	0.15 ± 0.06	0.29 ± 0.02
Valine	0.39 ± 0.10	0.71 ± 0.18	<0.01	<0.05

Uncertainties are based on standard error propagation of the absolute errors of the D- and L-amino acid abundances shown in Table 1.

[a] Amino acid data for Orgueil are from Glavin and Dworkin (2009).

employed. It has been shown that maintaining the hydrogen fugacity of hydrothermal systems can stabilize amino acids (Kohara et al., 1997; Lee et al., 2014), though the lack of amino acids observed in Y-86029 and Y-980115 suggest that this mechanism was not viable or sufficient in these meteorite parent bodies.

Multiple studies have shown that non-α-amino acids that are capable of lactam formation (intramolecular cyclization between the amine and carboxylic acid group) such as γ-amino-*n*-butyric acid and δ-amino-*n*-valeric acid are more resistant to thermal degradation at temperatures up to 400 °C (Islam et al., 2001, 2003; Li and Brill, 2003b). This enhanced stability may explain the elevated levels of these amino acids in aqueously altered meteorites that experienced mild to moderate thermal metamorphism (Burton et al., 2012b; Cooper and Cronin, 1995). The low abundances of γ-amino-*n*-butyric acid and δ-amino-*n*-valeric acid in Y-86029 and Y-980115 suggest that either minimal amino acid synthesis took

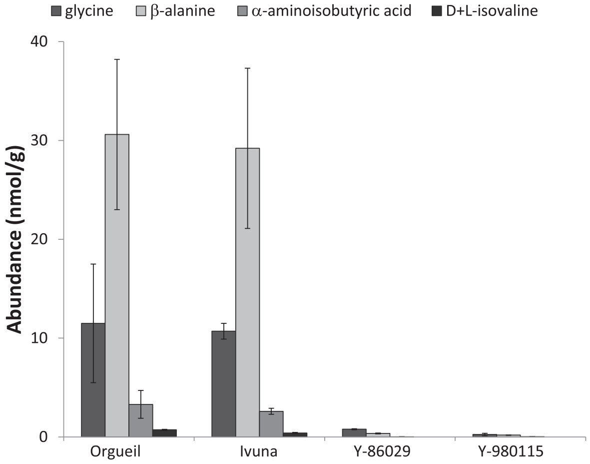

Fig. 2. A comparison of the abundances of selected amino acids among the CI chondrites Orgueil, Ivuna, Y-86029 and Y-980115. The amino acids glycine, β-alanine, α-aminoisobutyric acid and isovaline have been observed in many meteorites, and their extraterrestrial origin has been inferred in several cases through stable isotopic ratio measurements. Abundance data are from Table 1, and error bars reflect the calculated standard errors.

place on their parent bodies or that the temperature and duration of heating on these parent bodies was sufficient to result in near-complete destruction. In either case, the combination of aqueous alteration and heating that the parent bodies of Y-86029 and Y-980115 experienced appears to have been sufficient to effectively sterilize these meteorites of extraterrestrial amino acids, constraining the upper limit for the survivability of amino acids in hydrated meteorites to between 150 and 600 °C; this is consistent with our previous analyses of the Sutter's Mill metamorphosed CM2 chondrites (Burton et al., in press; Jenniskens et al., 2012).

4. Conclusion

Parent-body processes have a profound effect on the amino acid inventories of carbonaceous chondrites. Meteorites from parent bodies that experienced aqueous alteration tend to have greater abundances of amino acids than meteorites from thermally metamorphosed parent bodies. Considering the amino acid abundances of the Sutter's Mill meteorites and the heated Antarctic CI chondrites analyzed here, it is now apparent that the combination of extensive aqueous alteration *and* heating is incompatible with amino acid synthesis and/or survival. This finding provides an important constraint on the range of impactors capable of delivering amino acids to the prebiotic Earth.

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