

## Abundant extraterrestrial amino acids in the primitive CM carbonaceous chondrite Asuka 12236

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**Abstract**—The Asuka (A)-12236 meteorite has recently been classified as a CM carbonaceous chondrite of petrologic type 3.0/2.9 and is among the most primitive CM meteorites studied to date. Here, we report the concentrations, relative distributions, and enantiomeric ratios of amino acids in water extracts of the A-12236 meteorite and another primitive CM chondrite Elephant Moraine (EET) 96029 (CM2.7) determined by ultra-high-performance liquid chromatography time-of-flight mass spectrometry. EET 96029 was highly depleted in amino acids and dominated by glycine, while a wide diversity of two- to six-carbon aliphatic primary amino acids were identified in A-12236, which had a total amino acid abundance of  $360 \pm 18 \text{ nmol g}^{-1}$ , with most amino acids present without hydrolysis (free). The amino acid concentrations of A-12236 were double those previously measured in the CM2.7 Paris meteorite, consistent with A-12236 being a highly primitive and unheated CM chondrite. The high relative abundance of  $\alpha$ -amino acids in A-12236 is consistent with formation by a Strecker-cyanohydrin dominated synthesis during a limited early aqueous alteration phase on the CM meteorite parent body. The presence of predominantly free glycine, a near racemic mixture of alanine (D/L  $\sim 0.93$ – $0.96$ ), and elevated abundances of several terrestrially rare non-protein amino acids including  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB) and racemic isovaline indicate that these amino acids in A-12236 are extraterrestrial in origin. Given a lack of evidence for biological amino acid contamination in A-12236, it is possible that some of the L-enantiomeric excesses ( $L_{ee} \sim 34$ – $64\%$ ) of the protein amino acids, aspartic and glutamic acids and serine, are indigenous to the meteorite; however, isotopic measurements are needed for confirmation. In contrast to more aqueously altered CMs of petrologic types  $\leq 2.5$ , no L-isovaline excesses were detected in A-12236. This observation strengthens the hypothesis that extensive parent body aqueous activity is required to produce or amplify the large L-isovaline excesses that cannot be explained solely by exposure to circularly polarized radiation or other chiral symmetry breaking mechanisms prior to incorporation into the asteroid parent body.

### INTRODUCTION

Meteorites provide an important record of the physical and chemical processes that occurred in the

early solar system and represent some of the oldest solid materials currently available for laboratory analyses. The delivery of organic matter by extraterrestrial material to the early Earth could have been an important source of organic carbon that would have made a wide range of complex prebiotic molecules

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available for the emergence of life (Anders 1989; Chyba and Sagan 1992). In particular, the carbonaceous chondrites are a very primitive class of meteorite that have a carbon-rich matrix containing ~2–5 wt% carbon, the majority of which is from organic matter (Kerridge 1985; Sephton 2002; Pearson et al. 2006; Alexander et al. 2012). More than 50% of the organic carbon in these meteorites is in the form of an insoluble kerogen-like macromolecule that is structurally complex (Sephton et al. 2000; Cody and Alexander 2005; Alexander et al. 2007), while the solvent extractable organic matter represents a much smaller fraction of the organic carbon (up to ~0.1%) and is in the form of a wide variety of different compound classes that include amino acids, carboxylic acids, hydroxy acids, amines, alcohols, aldehydes and ketones, N-heterocycles, polyols, aliphatic and aromatic hydrocarbons, sugars, and others (Glavin et al. 2018, 2020a; Furukawa et al. 2019). The soluble organic component of some carbonaceous chondrites can also be highly complex, as shown by ultra-high-resolution molecular analyses of the CM2 Murchison meteorite that revealed tens of thousands of unique molecular compositions and likely millions of distinct chemical structures (Schmitt-Kopplin et al. 2010), the vast majority of which have not yet been identified.

Carbonaceous chondrites are divided into eight different groups (CI, CM, CR, CH, CB, CO, CV, and CK) and then further differentiated within these groups by a petrologic subtype number ranging between 1 and 6. This number indicates the relative degree of hydrothermal alteration in their parent bodies based on differences in their mineralogy and elemental and isotopic compositions, with numbers decreasing from 3 to 1 indicating increasing aqueous alteration, and numbers increasing from 3 to 6 indicating increasing thermal metamorphism (Van Schmus and Wood 1967; Weisberg et al. 2006; Rubin et al. 2007; Alexander et al. 2013; Harju et al. 2014; Krot et al. 2014; Howard et al. 2015). There are also several carbonaceous chondrites, such as the C2 Tagish Lake meteorite, that are rare and have not yet been assigned to a specific group ( $C_{\text{ung}}$ ). An additional petrologic type classification scheme ranging from 1.0 (most aqueously altered) to 3.0 (no petrologic evidence for aqueous alteration) has been assigned to several CI, CM, and CR chondrites and C2 ungrouped meteorites based on the amount of hydrogen in the meteorite present in the forms of  $H_2O$  and OH and the fraction of phyllosilicate minerals (Alexander et al. 2013; Howard et al. 2015). The degree of parent body hydrothermal alteration has been shown to have a major influence on the measured abundances and molecular distributions of the soluble organic component in CI, CM, and CR carbonaceous

chondrites, particularly for amino acids (Martins et al. 2007a; Glavin et al. 2010). Amino acids have continued to be a primary focus of many soluble organic analyses of carbonaceous chondrites because (1) these molecules are essential components of life (as the monomers of proteins), (2) they have structural diversity (multiple possible isomers) that can be used to help constrain formation mechanisms and parent body conditions, and (3) most amino acids identified in carbonaceous chondrites are chiral, a property that can be used to distinguish between amino acids of extraterrestrial and terrestrial origins.

To date, 96 different amino acids have been *named* in the Murchison meteorite (a moderately aqueously altered CM2 carbonaceous chondrite) with total amino acid abundances ranging from ~110 to 300 nmol  $g^{-1}$  (Shimoyama and Ogasawara 2002; Glavin et al. 2010, 2018, 2020b; Koga and Naraoka 2017), and hundreds of more amino acids detected that have yet to be explicitly identified and quantified (Glavin et al. 2010). The amino acids that have been identified in Murchison include a mixture of two- to seven-carbon cyclic and acyclic amino and diamino alkanic and alkanedioic acids of nearly complete structural diversity, many of which are rare or absent in the terrestrial biosphere (Cronin and Pizzarello 1983, 1986; Cronin and Chang 1993; Botta and Bada 2002; Sephton 2002; Meierhenrich et al. 2004; Glavin et al. 2010). Amino acids have also been identified in many other CM chondrites including the most aqueously altered CM type 1 carbonaceous chondrites Scott Glacier (SCO) 06043 and Meteorite Hills (MET) 01070, which have very low total amino acid concentrations of 3.6 and 5.6 nmol  $g^{-1}$ , respectively (Glavin et al. 2010). In contrast to these CM1s, higher amino acid abundances were found in the much less aqueously altered CM type 2 chondrites Paris (Martins et al. 2015) and the Yamato (Y)-791198 meteorite that had a total amino acid concentration of ~715 nmol  $g^{-1}$ , the highest concentration of amino acids reported in any CM chondrite (Shimoyama et al. 1985; Shimoyama and Ogasawara 2002).

The CR carbonaceous chondrites constitute one of the most primitive meteorite groups and are believed to contain the most primitive insoluble organic matter (IOM) of any carbonaceous chondrite group (Cody and Alexander 2005), although, just like the CM chondrites, the CR chondrites also show petrologic evidence for varying degrees of aqueous alteration (Zolensky et al. 1993; Wasson and Rubin 2009; Harju et al. 2014). Like the CMs, the degree of aqueous alteration has a major influence on the measured amino acid abundances in CR chondrites. The most aqueously altered CR1 Grosvenor Mountains (GRO) 95577 has a very low total amino acid concentration of 13 nmol  $g^{-1}$  (Glavin et al. 2010), whereas the least altered CR2 chondrites,

Queen Alexandra Range (QUE) 99177, Elephant Moraine (EET) 92042, and Graves Nunataks (GRA) 95229 have much higher amino acid concentrations ranging from ~800 to 3100 nmol g<sup>-1</sup> (Martins et al. 2007a; Pizzarello et al. 2008; Glavin and Dworkin 2009; Glavin et al. 2010). Interestingly, these primitive CR2 chondrites also show much less amino acid complexity and structural diversity than the more altered CM2 Murchison meteorite, with no evidence of any amino acids containing more than six carbons (Glavin et al. 2010). At the same time, the highest amino acid concentrations are generally found in the least aqueously altered CM2 and CR2 chondrites. However, one notable exception is the CM2 Paris meteorite that has a relatively low total amino acid concentration of ~180 nmol g<sup>-1</sup> (Martins et al. 2015), compared to the CM2 Y-791198 chondrite and the primitive CR2 chondrites, despite the petrologic classification of Paris as one of the least aqueously and thermally altered CM chondrites (Marrocchi et al. 2014).

One of the most significant meteorite discoveries of relevance to prebiotic chemistry and our understanding of the origin of biological homochirality (i.e., the strong preference for L-amino acids in proteins and D-sugars in nucleic acids) was the finding of several non-racemic  $\alpha$ -dialkyl amino acids in the CM2 chondrites Murchison and Murray, with L-isovaline excesses of up to 18.5% in Murchison (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000; Pizzarello et al. 2003; Glavin and Dworkin 2009; Glavin et al. 2010). These results have been difficult to explain, since the abiotic formation of isovaline and other  $\alpha$ -dialkyl amino acids (e.g., by Strecker-cyanohydrin synthesis) on the CM parent body should produce equal (racemic) mixtures of D- and L-enantiomers (Wolman et al. 1972). However, slight to significant L-isovaline excesses of up to 20.5% have now been reported in a wide range of meteorites across multiple carbonaceous chondrite groups (CI, CM, CR, CB, CH, and the C<sub>ung</sub> Tagish Lake), with a general correlation between the extent of aqueous alteration and the magnitude of the L-excess (Glavin and Dworkin 2009; Glavin et al. 2010, 2012; Burton et al. 2013; Burton and Berger 2018). Even larger non-terrestrial L-excesses up to ~60% in several common  $\alpha$ -hydrogen protein amino acids including L-aspartic acid, L-alanine, and L-glutamic acids have also been found in the CM2 Murchison (Engel and Macko 1997; Glavin et al. 2020b) and C2 Tagish Lake meteorites (Glavin et al. 2012). In contrast, no significant L-isovaline excesses were found in the weakly altered CM2 Paris meteorite (Martins et al. 2015) and no L-excesses of extraterrestrial origin have been confirmed for any amino acids with a single asymmetric carbon (i.e., not a diastereomer) in the primitive CR2 chondrites QUE

99177, EET 92042, and GRA 95229 (Martins et al. 2007a; Pizzarello et al. 2008; Glavin et al. 2010). These findings support the hypothesis that amino acid exposure to liquid water-based chemistry during hydrothermal alteration in these carbonaceous chondrite parent bodies played a significant role in the amplification of some L-amino acids over their D-enantiomers. Multiple mechanisms for amino acid symmetry breaking under interstellar conditions and amplification of enantiomeric excesses to explain the observations in meteorites have been proposed and are discussed in detail elsewhere (Kondepudi et al. 1990; Soai et al. 1995; Kawasaki et al. 2006; Klussmann et al. 2006a; Fletcher et al. 2007; Pizzarello and Groy 2011; MacDermott 2012; Glavin et al. 2020a, 2020b). To date, no statistically significant D-enantiomeric excesses for amino acids with a single asymmetric carbon have been reported in any meteorite. Continued analyses of the distributions and enantiomeric compositions of chiral amino acids in the most primitive, unaltered carbonaceous chondrites are very important for understanding the origin of chiral amino acid asymmetry, the mechanism(s) for enantioenrichment, and the apparent bias toward L-amino acids in the early solar system.

The A-12236 CM meteorite was recovered from the Nansen Ice Field in Antarctica by a joint Belgium and Japan (JARE, Japanese Antarctic Research Expedition) team in 2012 (Yamaguchi et al. 2018) and its weathering classification has been evaluated to be grade A (minor rustiness; rust haloes on metal particles and rust stains along fractures are minor). The A-12236 meteorite provides a rare opportunity to investigate the amino acid composition of a highly primitive CM carbonaceous chondrite that did not experience significant parent body alteration or terrestrial weathering in Antarctica. Petrographic and compositional measurements of A-12236, as well as two other Asuka CM meteorites A-12085 and A-12169 discovered in the same region in Antarctica, indicate that all three meteorites are highly primitive CM chondrites that did not experience significant thermal metamorphism or aqueous alteration on the parent body (Yamaguchi et al. 2018; Kimura et al. 2019a, 2019b), and may be even more primitive than the Paris meteorite, previously cited as the least-altered CM chondrite (Marrocchi et al. 2014; Martins et al. 2015). Based on an apparent lack, or trace amounts, of phyllosilicates and carbonates in A-12236, A-12085, and A-12169 (Kimura et al. 2019a, 2019b) and relatively high abundances of presolar silicate grains and elevated  $\delta$ D and  $\delta^{15}$ N values in A-12236 compared to most other CM chondrites (Nittler et al. 2020), these Asuka meteorites are believed to be the most primitive CM

chondrites identified to date with petrologic types ranging from 2.8 to 3.0 (Kimura et al. 2019a; Nittler et al. 2020). Elephant Moraine (EET) 96029 is another mildly aqueously altered CM chondrite collected in Antarctica that has been designated a petrologic type 2.7 based on the Rubin et al. (2007) alteration scale (Lee et al. 2016) with minor to moderate rustiness (weathering grade A/B). However, EET 96029, unlike A-12236, experienced significant heating to ~400–600 °C from impact shock or solar radiation after aqueous alteration on its CM parent body (Lee et al. 2016).

Here, we report measurements of the amino acid content of the hot water extracts of the primitive CM chondrites A-12236 and EET 96029 made with *o*-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization combined with ultraperformance liquid chromatography with UV fluorescence and time-of-flight mass spectrometry detection (hereafter, LC-FD/ToF-MS). To our knowledge, this is the first amino acid analyses of these primitive CM carbonaceous chondrites. We compare the A-12236 and EET 96029 results to previously published amino acid data from several other carbonaceous chondrites that experienced a wide range of parent body aqueous alteration conditions based on their petrologic type assignments as described in Table 1. These comparisons are important to further understand the effects of parent body hydrothermal alteration on the formation and destruction of amino acids in the early solar system and the conditions that led to the generation of L-amino acid excesses prior to the origin of life. Amino acid analyses are also of particular importance to establish potential parent body and chemical links between primitive carbonaceous chondrites and samples from the carbonaceous asteroids 162173 Ryugu and 101955 Bennu that will be returned by the Hayabusa2 and OSIRIS-REx missions in late 2020 and 2023, respectively (Tachibana et al. 2014; Lauretta et al. 2017).

## MATERIALS AND METHODS

### Chemicals and Reagents

All glassware, ceramics, foil for mass measurements, and sample handling tools used in sample processing were rinsed with ultrapure water (Millipore Milli-Q Integral 10 UV 18.2 M $\Omega$ , <3 ppb total organic carbon), wrapped in aluminum foil, and then heated in a furnace at 500 °C in air overnight. Most of the chemicals and reagents were purchased from Sigma-Aldrich. For all non-C<sub>5</sub> amino acids, a stock solution (1  $\times$  10<sup>-6</sup> M) was prepared by mixing individual amino acid standards (97–99% purity) in ultrapure water. All chiral amino

acid standards were purchased as racemic mixtures (D=L), except for D- and L-threonine (Sigma-Aldrich, >98% purity, *allo*-free) and D- and L-isovaline (Acros Organics, >99% purity) that were prepared as racemic mixtures by adding the appropriate masses of each compound in ultrapure water to the standard mixture. The sources of the other C<sub>5</sub> amino acid standards used are detailed elsewhere (Glavin and Dworkin 2009).

Acid vapor hydrolysis used 6 M double distilled HCl (dd HCl). Cation-exchange resin (AG50W-X8, 100–200 mesh, hydrogen form, BIO-RAD) was used for removal of salts and interfering ions from samples. During the desalting protocol, 1.5 M dd HCl, 2 M sodium hydroxide (NaOH), and 2 M ammonium hydroxide (NH<sub>4</sub>OH) were used. The 2 M NaOH was produced by dissolution of 32 g of NaOH in ultrapure water and the 2 M NH<sub>4</sub>OH was prepared from ultrapure water and ammonia gas (Air Products) *in vacuo*. Pre-column derivatization of samples prior to LC-FD/ToF-MS analyses involved the use of 0.1 M sodium borate, *o*-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC), and 0.1 M hydrazine hydrate. Sodium borate was generated by heating solid sodium borate decahydrate (Sigma-Aldrich, ACS reagent,  $\geq$ 99.5% purity) at 500 °C in air for 3 h prior to dissolution in ultrapure water. The OPA/NAC derivatization reagent was prepared by mixing 300  $\mu$ L of 0.1 M OPA (0.1 g OPA dissolved in 7.5 mL methanol, Optima Grade) with 30  $\mu$ L of 0.5 M NAC (0.408 g NAC dissolved in 5 mL ultrapure water) and 670  $\mu$ L of 0.1 M sodium borate. The 0.1 M hydrazine (NH<sub>2</sub>NH<sub>2</sub>) hydrate solution was prepared ammonia-free by triple vacuum distillation of anhydrous hydrazine (98% purity) over slush chloroform and subsequent dilution in ultrapure water.

### Meteorite Description and Processing Procedures

Single fragments without visible fusion crust of A-12236 (split 71, mass = 241.9 mg) allocated by the National Institute of Polar Research (NIPR: Tokyo, Japan) and EET 96029 (specific 71, parent 68, total mass = 4.2 g) provided by the Antarctic meteorite curator at the NASA Johnson Space Center (Houston, TX USA) were each transferred to a clean piece of aluminum foil and weighed using an analytical balance. The meteorite chips were then transferred to separate clean ceramic mortars and crushed to powders using a pestle inside a positive pressure ISO 5 HEPA-filtered laminar flow hood housed in an ISO 8 white room at NASA Goddard Space Flight Center. An aliquot of each powdered meteorite (A-12236 mass = 0.0493 g; EET 96029 mass = 0.013 g) was transferred from the mortar to individual clean glass ampoules for amino acid extraction.

Table 1. Meteorite names, groups, and petrologic type assignments using several aqueous alteration metrics, and evidence for heating for the carbonaceous chondrites studied and/or discussed in this paper.

Meteorite name	Group	H in OH/H <sub>2</sub> O <sup>a</sup>	Phyllosilicate fraction <sup>b</sup>	Petrology <sup>c</sup>	Heated <sup>d</sup>
Orgueil	CI	1.1	1.0 <sup>f</sup>	2.0 <sup>i</sup>	No
Ivuna	CI	1.1	1.0 <sup>f</sup>	2.0 <sup>i</sup>	No
Y-86029	CI	–	–	2.0 <sup>i</sup>	Yes <sup>m</sup>
Y-980115	CI	–	–	2.0 <sup>i</sup>	Yes <sup>m</sup>
SCO 06043	CM	1.2	1.2	2.0 <sup>j</sup>	No
MET 01070	CM	1.2	1.2	2.0	No
Sutter's Mill SM2	CM	–	–	2.0/2.1 <sup>n</sup>	Yes <sup>n</sup>
Mukundpura	CM	–	–	2.0 <sup>o</sup>	No
GRO 95577	CR	1.3	1.3	2.0	No
Mighei	CM	1.6	1.4	2.3 <sup>j</sup>	No
LEW 90500	CM	1.6	1.4	2.3/2.4 <sup>j</sup>	No
Y-791198	CM	1.5	1.6	2.4	No
Murray	CM	1.5	1.5	2.4/2.5	No
Murchison	CM	1.6	1.5	2.5	No
LON 94102	CM	1.8	1.3	2.6 <sup>j</sup>	No
Tagish Lake 5b	C <sub>ung</sub>	1.9 <sup>e</sup>	>1.6 <sup>g</sup>	–	No
Tagish Lake 10a	C <sub>ung</sub>	–	>1.6 <sup>g</sup>	–	No
Tagish Lake 11h	C <sub>ung</sub>	–	>1.6 <sup>g</sup>	–	No
EET 96029	CM	–	1.6 <sup>h</sup>	2.7 <sup>h</sup>	Yes <sup>h</sup>
Paris	CM	–	–	2.7 <sup>k</sup>	No
A-12085	CM	–	–	2.8 <sup>l</sup>	No
A-12236	CM	3.0 <sup>p</sup>	–	2.9 <sup>l</sup>	No
A-12169	CM	–	–	3.0 <sup>l</sup>	No
GRA 95229	CR	2.5	2.8	2.7	No
QUE 99177	CR	2.4	2.8	2.8	No
EET 92042	CR	2.5	–	2.8	No
MET 00462	CR	2.6	2.6	2.8	No

<sup>a</sup>After Alexander et al. (2013), unless otherwise indicated.

<sup>b</sup>After Howard et al. (2015), unless otherwise indicated.

<sup>c</sup>After Rubin et al. (2007) and Harju et al. (2014), unless otherwise indicated.

<sup>d</sup>Heated to >150 °C after Alexander et al. (2012, 2013) and Quirico et al. (2018), unless otherwise indicated.

<sup>e</sup>Estimated from the bulk analysis of Alexander et al. (2014).

<sup>f</sup>Estimated from the data of Bland et al. (2004) and King et al. (2015).

<sup>g</sup>Gilmour et al. (2019).

<sup>h</sup>Lee et al. (2016).

<sup>i</sup>Assuming that the Rubin et al. (2007) scale also applies to CIs.

<sup>j</sup>Estimated using correlations between petrologic type and bulk H and N isotopes from Alexander et al. (2013).

<sup>k</sup>Marrocchi et al. (2014).

<sup>l</sup>Kimura et al. (2019a, 2019b).

<sup>m</sup>King et al. (2019) and Tonui et al. (2014).

<sup>n</sup>Jenniskens et al. (2012).

<sup>o</sup>Rudraswami et al. (2019).

<sup>p</sup>Nittler et al. (2020).

The individual aliquots of the A-12236 and EET 96029 meteorite powders were flame-sealed in the glass ampoules with 1 mL of ultrapure water and extracted at 100 °C for 24 h. After heating, the sealed ampoules were removed from the oven, cooled to room temperature, and then opened. Half of the water supernatants were transferred to separate tubes, dried under vacuum, and then the water-extracted residues were subjected to a 6 M HCl vapor hydrolysis procedure at 150 °C for 3 h to determine total acid-

hydrolyzable (free + bound) amino acid abundances and enantiomeric compositions as previously described (Glavin et al. 2006). The HCl acid-hydrolyzed, hot water extracts were then desalted by using cation-exchange chromatography (BIO-RAD Poly-Prep<sup>®</sup> ion exchange columns prepacked with 2 mL AG50W-X8 resin, 100–200 mesh, hydrogen form). After elution of the anionic species with water, the amino acids were obtained by elution with 7 mL aqueous 2M NH<sub>4</sub>OH. The NH<sub>4</sub>OH eluates were each dried under vacuum,

resuspended in 100  $\mu\text{L}$  Millipore ultrapure water, transferred to clean glass autosampler vials, and stored at  $-20\text{ }^{\circ}\text{C}$  prior to analyses. The remaining non-hydrolyzed water extracts of the meteorites were taken through the identical desalting procedure in parallel with the acid-hydrolyzed extracts to determine the abundances and enantiomeric compositions of free amino acids. As a control, a procedural water blank was also taken through the identical extraction procedure as the meteorites and processed in parallel. Based on previous analyses of amino acid standards taken through the entire extraction, acid hydrolysis, and desalting procedure, there is no evidence of significant decomposition, racemization, or thermal degradation of the amino acids (Glavin et al. 2010).

### LC-FD/ToF-MS Amino Acid Analysis

The amino acid concentrations, relative distributions, and enantiomeric ratios in the water extracts were determined by LC-FD/ToF-MS. Prior to analysis, 10  $\mu\text{L}$  of each meteorite extract, procedural blank, or standard was added to 20  $\mu\text{L}$  of 0.1 M sodium borate buffer and dried under vacuum. The dried residues were resuspended in 20  $\mu\text{L}$  Millipore ultrapure water at room temperature and then derivatized by adding 5  $\mu\text{L}$  of OPA/NAC. The OPA/NAC reaction was quenched after 15 min with 75  $\mu\text{L}$  of 0.1 M hydrazine hydrate and 10  $\mu\text{L}$  of the derivatized extract immediately then injected into a Waters ACQUITY UPLC with a fluorescence detector and Waters LCT Premier ToF-MS operated in positive electrospray ionization mode for analysis of the OPA/NAC amino acid derivatives. The details of the ToF-MS settings and the amino acid quantification methods used for the Asuka 12236 meteorite analyses are described elsewhere (Glavin et al. 2006). We made three separate injections and LC-FD/ToF-MS analyses of the OPA/NAC derivatized extract which was stored in a freezer set at  $-86\text{ }^{\circ}\text{C}$  in between injections. Each derivatized extract was analyzed using our standard tandem LC column conditions for initial two- to ten-carbon ( $\text{C}_2\text{--}\text{C}_{10}$ ) amino acid separation and characterization (Glavin et al. 2010). The  $\text{C}_2\text{--}\text{C}_6$  amino acids were chromatographically resolved by using a Waters BEH C18 column ( $2.1 \times 50\text{ mm}$ ,  $1.7\text{ }\mu\text{m}$  bead) and a Waters BEH phenyl column ( $2.1 \times 150\text{ mm}$ ,  $1.7\text{ }\mu\text{m}$  bead) in series. The conditions for separation of the OPA/NAC amino acid derivatives at  $30\text{ }^{\circ}\text{C}$  were as follows: flow rate, 150  $\mu\text{L}/\text{min}$ ; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (0), 35 (55), 45 (100). The following day, another 10  $\mu\text{L}$  aliquot of the same desalted extract was derivatized with OPA/NAC as previously described and three separate

injections were analyzed using the same columns, but with a different gradient optimized for the separation of the valine, isovaline, and norvaline enantiomers from other  $\text{C}_5$  amino acid isomers and enantiomers. The gradient was, time in minutes (%B): 0 (15), 25 (20), 25.06 (35), 44.5 (40), 45 (100). The amino acids in the EET 96029 meteorite acid-hydrolyzed water extract and its corresponding procedural blank were measured separately under different analytical conditions using a Waters ACQUITY UPLC with a fluorescence detector and Waters Xevo G2-XS quadrupole time-of-flight mass spectrometer operated in positive ion mode as described elsewhere (Glavin et al. 2020b).

Amino acid concentrations ( $\text{nmol g}^{-1}$ ) by bulk sample weight and their enantiomeric ratios in the A-12236 and EET 96029 meteorites were determined by comparison of the peak areas generated from the UV fluorescence chromatograms (LC-FD,  $\lambda_{\text{ex}} = 340\text{ nm}$ ,  $\lambda_{\text{em}} = 450\text{ nm}$ ) of their OPA/NAC amino acid derivatives to the corresponding peak areas of standards run under the same chromatographic conditions on the same day. In addition to identifying the major fluorescent peaks present in the meteorite and procedural blank LC-FD chromatograms by retention time, we also searched for peaks in the ToF-MS chromatograms corresponding to  $\text{C}_2$  to  $\text{C}_{10}$  amino acids by plotting the accurate mass to within 10 ppm of the theoretical  $m/z$  value of each OPA/NAC amino acid derivative over the elution time. For comparison to A-12236 and EET 96029, previously published amino acid concentrations and enantiomeric ratio data from the Murchison meteorite (Glavin et al. 2020b) and an interior chip of the Paris meteorite (Martins et al. 2015) are also discussed in this paper.

## RESULTS AND DISCUSSION

### Amino Acid Chromatographic Separation and Identification

Representative LC-FD chromatograms of the acid-hydrolyzed, hot water extracts of the A-12236 meteorite, a procedural blank, and an amino acid standard mixture are shown in Fig. 1. Amino acid identification was confirmed by comparison of the retention times of both UV fluorescence chromatogram and associated single ion mass chromatogram peaks in the meteorite and procedural blank data, to the corresponding peaks observed in amino acid standard UV fluorescence and mass chromatograms. Several peaks labeled with an “X” in the UV fluorescence chromatograms for the A-12236 meteorite and the procedural blank are unidentified primary amine compounds from either the chemical workup or analytical artifacts that did not interfere with

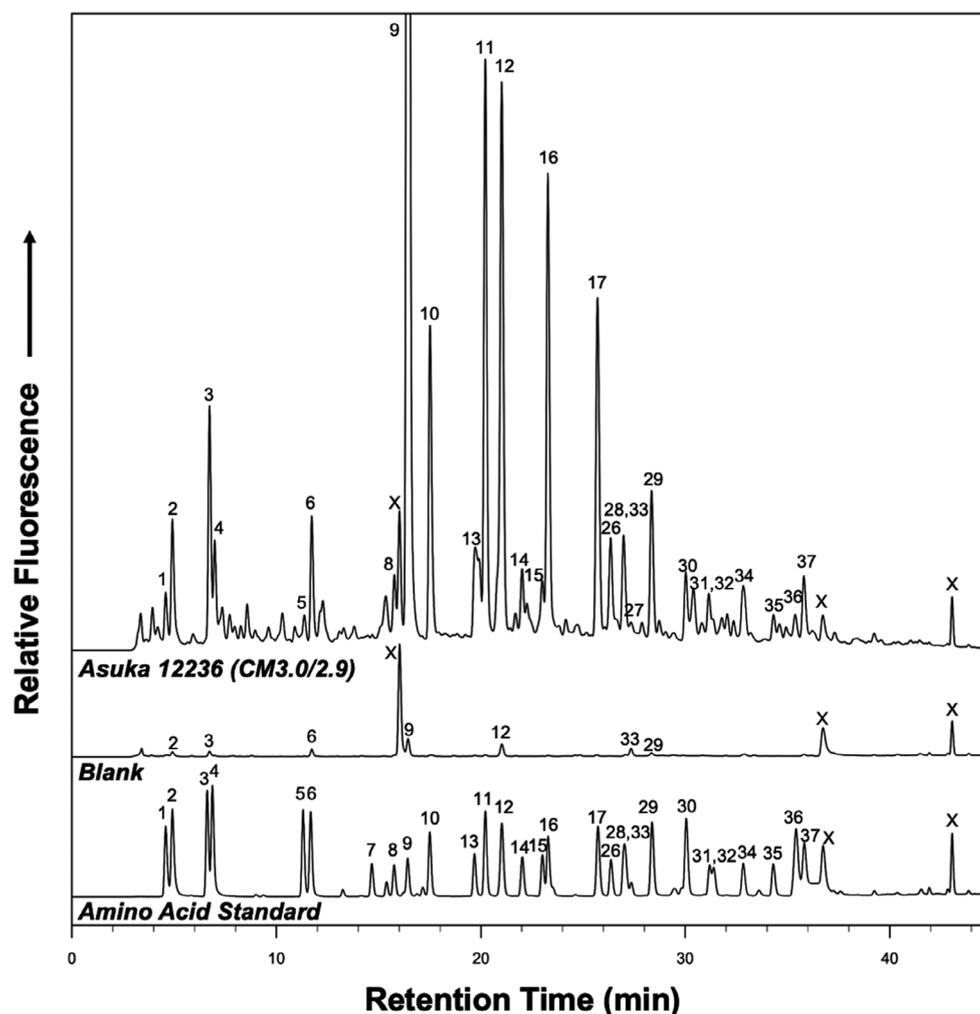


Fig. 1. The 0–42.5 min region of the UPLC-FD chromatograms (no significant peaks were observed beyond this retention time range). OPA/NAC derivatization (15 min) of amino acids in the standard and of the 6 M HCl-hydrolyzed, hot water extracts of the procedural blank and the Asuka 12236 meteorite are shown. Similar chromatograms were also obtained for EET 96029 and the raw data are included for all analyses in the supporting information. Peaks were identified by comparison of the procedural blank or sample UV fluorescence retention times and  $m/z$  values to those peaks in the amino acid standard analyzed on the same day and are designated by peak number as follows: (1) D-aspartic acid; (2) L-aspartic acid; (3) L-glutamic acid; (4) D-glutamic acid; (5) D-serine; (6) L-serine; (7) D-threonine; (8) L-threonine; (9) glycine; (10)  $\beta$ -alanine; (11) D-alanine; (12) L-alanine; (13)  $\gamma$ -amino-*n*-butyric acid + D,L- $\beta$ -aminoisobutyric acid; (14) D- $\beta$ -amino-*n*-butyric acid; (15) L- $\beta$ -amino-*n*-butyric acid; (16)  $\alpha$ -aminoisobutyric acid; (17) D,L- $\alpha$ -amino-*n*-butyric acid; (26) D-isovaline or D-2-amino-2-methylbutanoic acid (D-2-a-2-mba); (27) D, L-3-aminopentanoic acid (D,L-3-apa); (28) L-isovaline or L-2-amino-2-methylbutanoic acid (L-2-a-2-mba); (29) L-valine or L-2-amino-3-methylbutanoic acid (L-2-a-3mba); (30) D-valine or D-2-amino-3-methylbutanoic acid (D-2-a-3-mba); (31) D-norvaline or D-2-aminopentanoic acid (D-2-apa); (32) L-norvaline or L-2-aminopentanoic acid (L-2-apa); (33)  $\epsilon$ -amino-*n*-caproic acid (EACA); (34) D-isoleucine; (35) L-isoleucine; (36) D-leucine; and (37) L-leucine. The peaks labeled X are desalting or OPA/NAC derivatization artifacts that were not identified. The data used for this figure can be found in supporting information.

amino acid identification and quantification (Fig. 1). We achieved LC chromatographic separation of several amino acids including aspartic and glutamic acids, serine, alanine, valine,  $\beta$ -amino-*n*-butyric acid, isovaline, and norvaline and their enantiomers with no known interferences or co-elutions with other amino acid isomers with carbon numbers up to C<sub>5</sub> (Fig. 2; Fig. S1 in supporting information).

The individual D- and L-enantiomers of 3-aminopentanoic acid were also clearly separated (peaks numbered 27, Fig. 2), but could not be enantiomerically identified due to a lack of optically pure standards. Several other small UV fluorescent peaks are also present in the A-12236 meteorite LC-FD chromatogram (Fig. 1), but were not identified with standards. These peaks must all contain a primary amino group in order

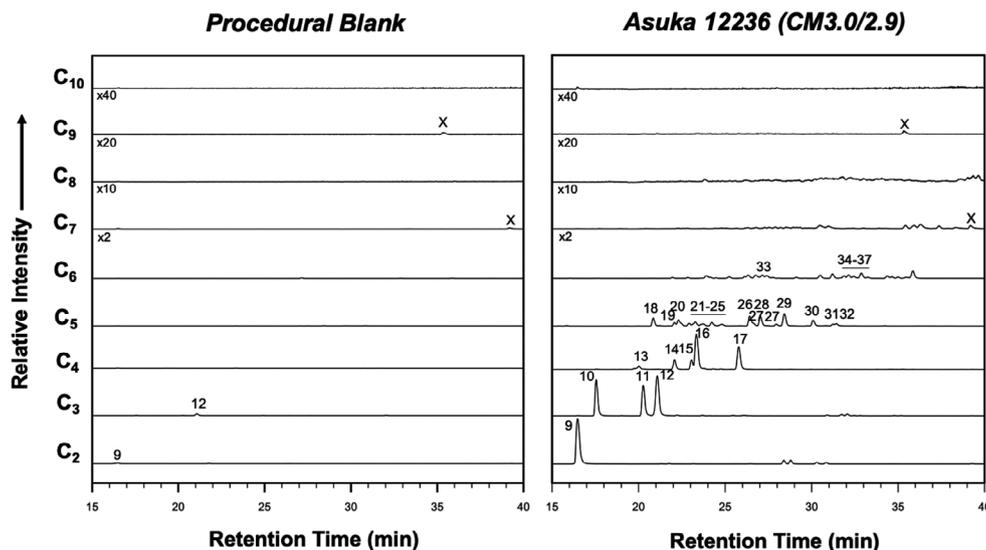


Fig. 2. The 15–40 min region of the LC-ToF-MS single ion mass chromatograms ( $C_2$ :  $m/z = 337.09$ ;  $C_3$ :  $m/z = 351.10$ ;  $C_4$ :  $m/z = 365.12$ ;  $C_5$ :  $m/z = 379.13$ ;  $C_6$ :  $m/z = 393.15$ ;  $C_7$ :  $m/z = 407.16$ ;  $C_8$ :  $m/z = 421.18$ ;  $C_9$ :  $m/z = 435.20$ ; and  $C_{10}$ :  $m/z = 449.21$ ) in positive electrospray ionization mode. OPA/NAC derivatization (15 min) of amino acids in the 6M HCl-hydrolyzed, hot water extracts of the procedural blank and the Asuka 12236 meteorite are shown. Peaks were identified by comparison of the procedural blank or sample retention times and corresponding  $m/z$  values to those in amino acid standards run on the same day and are designated by peak number as follows: (9) glycine; (10)  $\beta$ -alanine; (11) D-alanine; (12) L-alanine; (13)  $\gamma$ -amino-*n*-butyric acid + D,L- $\beta$ -aminoisobutyric acid; (14) D- $\beta$ -amino-*n*-butyric acid; (15) L- $\beta$ -amino-*n*-butyric acid; (16)  $\alpha$ -aminoisobutyric acid; (17) D,L- $\alpha$ -amino-*n*-butyric acid; (18) 3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa); (19) D,L-4-aminopentanoic acid (D,L-4-apa); (20) D,L-4-amino-3-methylbutanoic acid (D,L-4-a-3-mba); (21) D,L- and *allo*-3-amino-2-methylbutanoic acid (D,L- and *allo*-3-a-2mba); (22) D,L-3-amino-2-ethylpropanoic acid (D,L-3-a-2-epa); (23) 5-aminopentanoic acid (5-apa); (24) D,L-4-amino-2-methylbutanoic acid (D,L-4-a-2-mba); (25) 3-amino-3-methylbutanoic acid (3-a-3-mba); (26) D-isovaline or D-2-amino-2-methylbutanoic acid (D-2-a-2-mba); (27) D,L-3-aminopentanoic acid (D,L-3-apa); (28) L-isovaline or L-2-amino-2-methylbutanoic acid (L-2-a-2-mba); (29) L-valine or L-2-amino-3-methylbutanoic acid (L-2-a-3mba); (30) D-valine or D-2-amino-3-methylbutanoic acid (D-2-a-3-mba); (31) D-norvaline or D-2-aminopentanoic acid (D-2-apa); (32) L-norvaline or L-2-aminopentanoic acid (L-2-apa); (33)  $\epsilon$ -amino-*n*-caproic acid (EACA); (34) D-isoleucine; (35) L-isoleucine; (36) D-leucine; and (37) L-leucine. The peaks labeled X are desalting or non-fluorescent mass artifacts that were not identified. The data used for this figure can be found in supporting information.

to react with the OPA/NAC reagent (OPA/NAC will not react with compounds that have secondary or tertiary amino groups) to make a fluorescent derivative and could include a variety of other primary aliphatic amines, amino acids, diamino acids, and hydroxy amino acids that have been identified in Murchison and other CM chondrites (Cronin and Chang 1993; Meierhenrich et al. 2004; Aponte et al. 2014; Koga and Naraoka 2017; Glavin et al. 2018).

Mass peaks corresponding to the OPA/NAC derivatives of species with primary amino groups in A-12236 with up to eight carbons ( $C_8$ ) were detected above procedural blank levels in the single ion LC-ToF-MS chromatograms (Fig. 2; Fig. S1); however, the low peak intensities, poor LC chromatographic resolution of the  $C_6$  and larger amino acids, and a lack of commercially available standards prevented their accurate identification and quantification. The  $C_6$  amino acids D- and L-isoleucine and D- and L-leucine were also identified above background levels in the A-12236

meteorite extract by UV fluorescence and mass with retention times that match standards; however, accurate quantification of isoleucine and leucine was not possible due to unidentified co-eluting  $C_6$  amino acid isomers in both the UV and single ion chromatograms (peaks 34–37, Figs. 1 and 2). A variety of  $C_6$  and  $C_7$  cyclic and acyclic primary  $\alpha$ -amino alkanonic and alkanedioic acids have been identified by GC-MS in the Murchison meteorite (Cronin et al. 1981; Cronin and Pizzarello 1986, 1997; Cronin and Chang 1993; Pizzarello and Cronin 2000) and OPA/NAC derivatives of primary amino-containing species with up to 10 carbons have been detected in Murchison, but their specific molecular identifications remain unknown (Glavin et al. 2010). Given the LC analytical challenges associated with the separation of higher molecular weight amino acids ( $>C_5$ ) and their many possible isomers, future GC-MS measurements of larger mass extracts of the A-12236 meteorite as well as amino acid standards may be required to identify the higher molecular weight ( $\geq C_6$ )

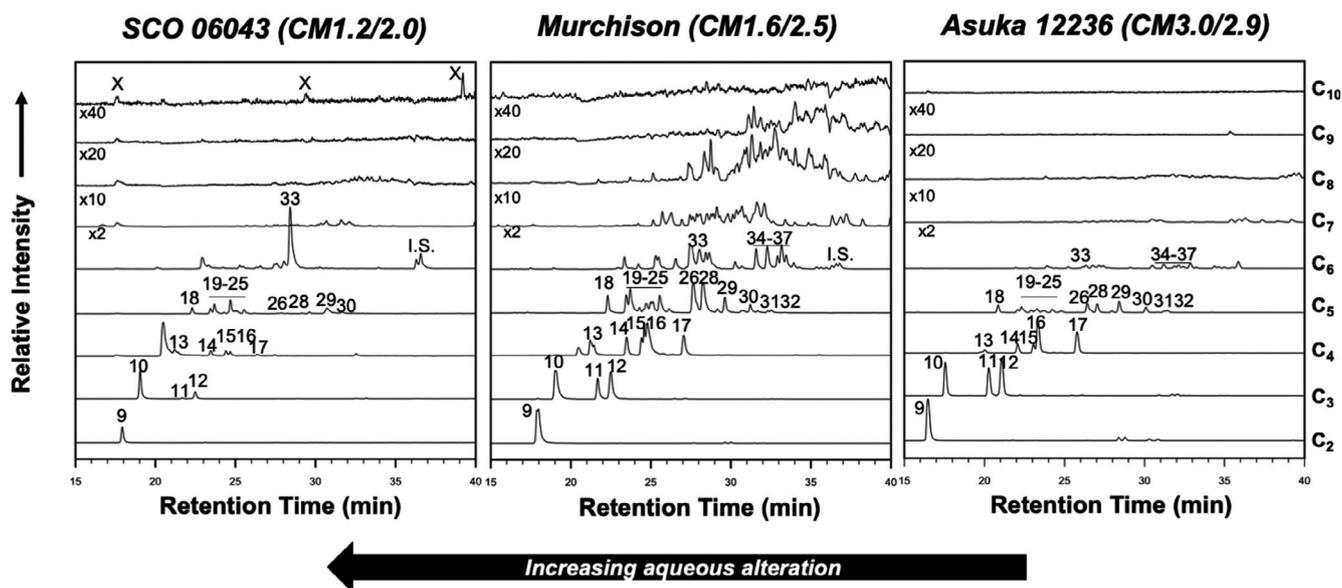


Fig. 3. A comparison of the 15–40 min regions of the LC-ToF-MS single ion mass chromatograms ( $C_2$ :  $m/z = 337.09$ ;  $C_3$ :  $m/z = 351.10$ ;  $C_4$ :  $m/z = 365.12$ ;  $C_5$ :  $m/z = 379.13$ ;  $C_6$ :  $m/z = 393.15$ ;  $C_7$ :  $m/z = 407.16$ ;  $C_8$ :  $m/z = 421.18$ ;  $C_9$ :  $m/z = 435.20$ ; and  $C_{10}$ :  $m/z = 449.21$ ) in positive electrospray ionization mode after OPA/NAC derivatization (15 min) of primary amino-containing compounds in the 6M HCl-hydrolyzed, hot water extracts of the Asuka 12236, Murchison, and SCO 06043 are shown. The data shown for Murchison and SCO 06043 are from Glavin et al. (2010). The arrow indicates increasing aqueous alteration inferred from the meteorite petrologic type assignments as described in Table 1. Peaks were identified by comparison of the sample retention time and corresponding  $m/z$  values to those in amino acid standards run on the same day and are designated by peak number as follows: (9) glycine; (10)  $\beta$ -alanine; (11) D-alanine; (12) L-alanine; (13)  $\gamma$ -amino-*n*-butyric acid + D,L- $\beta$ -aminoisobutyric acid; (14) D- $\beta$ -amino-*n*-butyric acid; (15) L- $\beta$ -amino-*n*-butyric acid; (16)  $\alpha$ -aminoisobutyric acid; (17) D,L- $\alpha$ -amino-*n*-butyric acid; (18) 3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa); (19) D,L-4-aminopentanoic acid (D,L-4-apa); (20) D,L-4-amino-3-methylbutanoic acid (D,L-4-a-3-mba); (21) D,L- and *allo*-3-amino-2-methylbutanoic acid (D,L- and *allo*-3-a-2-mba); (22) D,L-3-amino-2-ethylpropanoic acid (D,L-3-a-2-epa); (23) 5-aminopentanoic acid (5-apa); (24) D,L-4-amino-2-methylbutanoic acid (D,L-4-a-2-mba); (25) 3-amino-3-methylbutanoic acid (3-a-3-mba); (26) D-isovaline or D-2-amino-2-methylbutanoic acid (D-2-a-2-mba); (27) D,L-3-aminopentanoic acid (D,L-3-apa); (28) L-isovaline or L-2-amino-2-methylbutanoic acid (L-2-a-2-mba); (29) L-valine or L-2-amino-3-methylbutanoic acid (L-2-a-3-mba); (30) D-valine or D-2-amino-3-methylbutanoic acid (D-2-a-3-mba); (31) D-norvaline or D-2-aminopentanoic acid (D-2-apa); (32) L-norvaline or L-2-aminopentanoic acid (L-2-apa); (33)  $\epsilon$ -amino-*n*-caproic acid (EACA); (34) D-isoleucine; (35) L-isoleucine; (36) D-leucine; (37) L-leucine; and (I.S.) internal D,L-norleucine standard. The peaks labeled X are desalting or non-fluorescent mass artifacts that were not identified. The data used for this figure can be found in supporting information.

amino acid peaks shown in Figs. 2 and 3 as demonstrated previously for Murchison (e.g., Cronin et al. 1981; Cronin and Pizzarello 1986). In contrast to A-12236, only three small peaks above blank levels corresponding to glycine,  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), and  $\epsilon$ -amino-*n*-caproic acid were identified and quantified by UV and accurate mass measurements in the acid-hydrolyzed water extract of EET 96029 (Table 2).

### Free and Total Amino Acid Concentrations

We identified and quantified all of the  $C_2$ – $C_5$  acyclic, primary aliphatic, monoamino alkanolic acids, and the  $C_6$  amino acid  $\epsilon$ -amino-*n*-caproic acid (EACA) detected in the A-12236 and EET 96029 meteorite water extracts. The procedural blank-corrected concentrations of all of these species that were detected above

background levels are reported in Table 2. The sum of the individual concentrations of identified *free*  $C_2$ – $C_6$  amino acids in the non-hydrolyzed A-12236 water extract was  $300 \pm 9 \text{ nmol g}^{-1}$  while the sum of the *total* (= free + bound) amino acids in the 6M HCl-hydrolyzed hot water extract of the A-12236 meteorite was  $360 \pm 18 \text{ nmol g}^{-1}$  (Table 2). Only trace concentrations of glycine ( $1.7 \pm 0.1 \text{ nmol g}^{-1}$ ),  $\alpha$ -AIB ( $0.006 \pm 0.001 \text{ nmol g}^{-1}$ ), and  $\epsilon$ -amino-*n*-caproic acid ( $0.025 \pm 0.001 \text{ nmol g}^{-1}$ ) were present in the EET 96029 acid-hydrolyzed water extract (Table 2). Considering that amino acids begin to thermally decompose by deamination and decarboxylation at temperatures above  $150 \text{ }^\circ\text{C}$  (Rodante 1992; McCollom 2013), the paucity of amino acids in the mildly aqueously altered CM2.7 EET 96029 meteorite was not surprising since this meteorite was heated to  $\sim 400$ – $600 \text{ }^\circ\text{C}$  by impact shock or solar radiation on the parent

Table 2. Summary of the average concentrations (nmol g<sup>-1</sup>) of the two- to six-carbon amino acids in the non-hydrolyzed (free) and acid-hydrolyzed (total) water extracts of the CM meteorites Asuka 12236 and Murchison and the acid-hydrolyzed (total) water extract of EET 96029 by LC-FD/ToF-MS<sup>a</sup>. For comparison, free and total amino acids concentrations reported in the CM Paris meteorite by GC-MS are also shown. Total mass extracted given under meteorite name and petrologic type.

Amino acids	Asuka 12236 (CM3.0/2.9)		Murchison (CM1.6/2.5)		Paris (CM2.7)		EET 96029 (CM2.7)
	50 mg extract (This study)		80 mg extract Glavin et al. (2020)		200 mg extract Martins et al. (2015)		13 mg extract (This study)
	free	total	free	total	free	total	total
<b>Dicarboxylic Amino Acids</b>							
D-aspartic acid	1.7 ± 0.2	2.4 ± 0.1	0.06 ± 0.01	0.59 ± 0.02	0.67 ± 0.03	1.01 ± 0.04	< 0.01
L-aspartic acid	1.8 ± 0.1	4.9 ± 0.2	0.27 ± 0.02	3.0 ± 0.1	0.90 ± 0.05	1.50 ± 0.04	< 0.01
D-glutamic acid	0.63 ± 0.07	3.1 ± 0.2	0.17 ± 0.01	1.03 ± 0.03	4.1 ± 0.3	5.6 ± 0.4	< 0.01
L-glutamic acid	0.9 ± 0.1	8.4 ± 0.5	0.29 ± 0.01	6.3 ± 0.1	4.9 ± 0.3	6.7 ± 0.5	< 0.01
<b>Hydroxy Amino Acids</b>							
D-serine	1.23 ± 0.05	1.1 ± 0.2	0.04 ± 0.01	0.13 ± 0.03	n.r.	n.r.	< 0.01
L-serine	2.78 ± 0.07	5.0 ± 0.2	0.53 ± 0.02	3.5 ± 0.1	n.r.	n.r.	< 0.01
D-threonine	n.d.	n.d.	< 0.01	0.02 ± 0.01	n.r.	n.r.	n.d.
L-threonine	n.d.	n.d.	0.08 ± 0.05	2.21 ± 0.05	n.r.	n.r.	n.d.
<b>C<sub>2</sub> Amino Acid</b>							
Glycine	155 ± 3	160 ± 5	6.7 ± 0.4	40 ± 3	45 ± 2	110 ± 5	1.7 ± 0.1
<b>C<sub>3</sub> Amino Acids</b>							
β-alanine	13.1 ± 0.6	21 ± 1	3.3 ± 0.1	6.0 ± 0.2	7.0 ± 0.3	14 ± 2	< 0.01
D-alanine	25 ± 1	28 ± 2	0.94 ± 0.06	2.2 ± 0.1	3.3 ± 0.1	8.0 ± 0.4	< 0.01
L-alanine	26 ± 1	30 ± 2	0.98 ± 0.06	3.0 ± 0.2	4.9 ± 0.5	10.8 ± 0.5	< 0.01
<b>C<sub>4</sub> Amino Acids</b>							
D,L-α-amino- <i>n</i> -butyric acid	15 ± 1 <sup>c</sup>	16 ± 2 <sup>c</sup>	0.65 ± 0.01 <sup>c</sup>	2.0 ± 0.4 <sup>c</sup>	1.17 ± 0.04 <sup>d</sup>	2.97 ± 0.07 <sup>d</sup>	< 0.01
D-β-amino- <i>n</i> -butyric acid	3.35 ± 0.07	4.5 ± 0.1	1.13 ± 0.05	1.8 ± 0.1	< 0.01	< 0.01	< 0.01
L-β-amino- <i>n</i> -butyric acid	3.2 ± 0.1	4.4 ± 0.1	1.08 ± 0.04	1.6 ± 0.1	< 0.01	< 0.01	< 0.01
α-aminoisobutyric acid	17.0 ± 0.2	17.9 ± 0.4	10.8 ± 0.3	11.4 ± 0.5	0.84 ± 0.06	3.0 ± 0.1	0.006 ± 0.001
D,L-β-aminoisobutyric acid <sup>c</sup>	n.d.	n.d.	n.d.	n.d.	< 0.01	< 0.01	< 0.01
γ-amino- <i>n</i> -butyric acid	2.0 ± 0.1 <sup>b</sup>	12.1 ± 0.6 <sup>b</sup>	0.7 ± 0.1 <sup>b</sup>	2.4 ± 0.6 <sup>b</sup>	1.2 ± 0.1	1.8 ± 0.2	< 0.01
<b>C<sub>5</sub> Amino Acids</b>							
D-norvaline (D-2-apa)	2.42 ± 0.05	2.7 ± 0.2	< 0.01	0.1 ± 0.1	< 0.3	1.32 ± 0.03	< 0.01
L-norvaline (L-2-apa)	2.48 ± 0.05	2.5 ± 0.1	< 0.03	0.10 ± 0.03	< 0.4	1.52 ± 0.05	< 0.01
D-isovaline (D-2-a-2-mba)	3.9 ± 0.3	4.2 ± 0.3	3.5 ± 0.2	10.0 ± 0.5	0.22 ± 0.02 <sup>c</sup>	1.9 ± 0.1	< 0.01
L-isovaline (L-2-a-2-mba)	4.1 ± 0.2	4.0 ± 0.2	4.5 ± 0.2	11.8 ± 0.7		1.9 ± 0.1	< 0.01
D-valine (D-2-a-3-mba)	5.1 ± 0.1	5.6 ± 0.9	0.09 ± 0.01	0.55 ± 0.02	1.86 ± 0.07	4.9 ± 0.1	< 0.01
L-valine (L-2-a-3-mba)	5.7 ± 0.2	6.8 ± 0.4	0.10 ± 0.01	2.8 ± 0.1	1.9 ± 0.2	5.2 ± 0.2	< 0.01
D,L-3-apa <sup>d</sup>	1.8 ± 0.1	1.8 ± 0.2	0.53 ± 0.02	2.7 ± 0.1	n.r.	n.r.	n.d.
D,L- and allo-3-a-2-mba <sup>d</sup>	1.40 ± 0.04	1.4 ± 0.2	0.04 ± 0.01	0.29 ± 0.04	n.r.	n.r.	n.d.
3-a-3-mba	0.92 ± 0.04	0.8 ± 0.1	1.2 ± 0.1	4.76 ± 0.04	n.r.	n.r.	n.d.
3-a-2,2-dmpa	0.98 ± 0.05	2.48 ± 0.03	0.30 ± 0.02	1.9 ± 0.1	n.r.	n.r.	n.d.
D,L-3-a-2-epa <sup>c</sup>	< 0.3 <sup>c</sup>	< 0.3 <sup>c</sup>	< 0.3 <sup>c</sup>	< 0.3 <sup>c</sup>	n.r.	n.r.	n.d.
D,L-4-apa <sup>c</sup>	0.46 ± 0.07	1.46 ± 0.05	0.30 ± 0.02	2.9 ± 0.1	n.r.	n.r.	n.d.
D,L-4-a-2-mba <sup>c</sup>	n.d.	2.6 ± 0.2	0.01 ± 0.01	2.1 ± 0.6	n.r.	n.r.	n.d.
D,L-4-a-3-mba <sup>c</sup>	0.05 ± 0.01	0.28 ± 0.02	0.01 ± 0.01	0.42 ± 0.02	n.r.	n.r.	n.d.
5-apa	0.64 ± 0.04	2.7 ± 0.3	0.15 ± 0.02	1.8 ± 0.1	n.r.	n.r.	n.d.
<b>C<sub>6</sub> Amino Acids</b>							
ε-amino- <i>n</i> -caproic acid (EACA)	1.16 ± 0.05	2.00 ± 0.04	0.14 ± 0.03	2.2 ± 0.6	< 0.01	< 0.01	0.025 ± 0.001
D,L-isoleucine	n.d.	n.d.	n.d.	n.d.	n.r.	n.r.	n.d.
D,L-leucine	n.d.	n.d.	n.d.	n.d.	< 0.01	< 0.01	n.d.
<b>Sum (nmol g<sup>-1</sup>)</b>	<b>300 ± 9</b>	<b>360 ± 18</b>	<b>39 ± 2</b>	<b>132 ± 8</b>	<b>78 ± 4</b>	<b>182 ± 10</b>	<b>1.7 ± 0.1</b>

n.d. = amino acids identified, but concentration not determined due to interfering peaks or other analytical issues; n.r. = concentration not reported.

<sup>a</sup>Sample 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 ( $M + H^+$ ) were used for quantification. Amino acid concentrations were determined from both UV fluorescence and single ion mass peak areas and 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 reported uncertainties ( $\delta x$ ) are based on the standard deviation of the average value of three to six separate measurements ( $n$ ) with a standard error,  $\delta x = \sigma_x \cdot (n)^{-1/2}$  and take into account peak resolution quality.

<sup>b</sup>The amino acids γ-ABA and β-AIB could not be separated under the chromatographic conditions; therefore, the reported abundances represent the sum of both amino acids.

<sup>c</sup>Enantiomers could not be separated under the chromatographic conditions.

<sup>d</sup>Enantiomers could be separated, but not identified individually due to the lack of optically pure standards.

<sup>e</sup>Poor chromatographic resolution prevented accurate quantification; therefore, only upper limits are reported.

body (Lee et al. 2016; Quirico et al. 2018). The low yields of amino acids extracted from EET 96029 is also consistent with amino acid analyses of other carbonaceous chondrites that were exposed to both aqueous alteration and heating such as the thermally altered CI1 chondrites Yamato 86029 and Yamato 980115 and the thermally altered CM2 Sutter's Mill meteorite (Burton et al. 2014a, 2014b; Chan et al. 2016).

The total amino acid concentration of  $\sim 360 \text{ nmol g}^{-1}$  measured in the A-12236 extract must be considered a lower limit since most of the  $C_6$  amino acids and all of the potential  $C_7$  and  $C_8$  amino acids were excluded from the sum in Table 2. However, contributions to the total amino acid concentration of A-12236 by potential  $C_7$  and  $C_8$  amino acids are likely to be small based on the intensity of the corresponding mass peaks that are a factor of 2 and 10 times lower, respectively, than the  $C_6$  amino acids (Figs. 2 and 3). A-12236 contained both higher overall total amino acid concentrations and a higher percentage of amino acids present without hydrolysis ( $\sim 83\%$  free on average) compared to the Murchison (total =  $132 \pm 8 \text{ nmol g}^{-1}$ ;  $\sim 30\%$  free amino acids) and Paris (total =  $182 \pm 10 \text{ nmol g}^{-1}$ ;  $\sim 43\%$  free) meteorites (Table 2). The high overall percentage of free versus total amino acids in A-12236 of  $\sim 83\%$  is unusual compared to most CI, CM, and CR carbonaceous chondrites that range from  $\sim 30$  to  $70\%$  free (Shimoyama and Ogasawara 2002; Botta et al. 2007; Pizzarello et al. 2008; Glavin et al. 2010, 2020b). Especially notable is that more than  $96\%$  of the total glycine ( $160 \pm 5 \text{ nmol g}^{-1}$ , Table 2) in the A-12236 meteorite water extract is present without hydrolysis ( $155 \pm 3 \text{ nmol g}^{-1}$ , Table 2), which, to our knowledge, is the largest fraction of free glycine reported for any CI, CM, or CR carbonaceous chondrite analyzed to date. High relative concentrations of free glycine (and the  $C_3$ – $C_6$  straight chain, amine terminal,  $n$ - $\omega$ -amino acids) of up to  $100\%$  have also been reported in some CV3 and CO3 carbonaceous chondrites (Burton et al. 2012). However, unlike A-12236, which was not heated, the concentrations of free glycine in the CV3 and CO3 chondrites are much lower ( $\sim 0.04$  to  $2 \text{ nmol g}^{-1}$ ) and may have formed from Fischer–Tropsch type (FTT) gas phase reactions of  $N_2$ , CO, and  $H_2$  as the meteorites cooled down from elevated temperatures inside the parent body (Burton et al. 2012).

In most CI, CM, and CR carbonaceous chondrites, a large increase in amino acid concentrations is observed after acid hydrolysis of the water extracts. This is believed to result from a combination of terrestrial protein amino acid contamination if systematic L-excesses of protein amino acids are present and/or precursors of extraterrestrial origin that are

converted to free amino acids through acid hydrolysis. For example, low molecular weight derivatives and acid-labile precursors that could produce free amino acids after hydrolysis have been identified in the CM2 Murchison meteorite, including mono- and dicarboxylic acid amides, hydroxy acid amides, lactams, carboxylactams, N-alkyl amino acids, linear and cyclic dipeptides of glycine, and hydantoins (Cronin 1976; Cooper and Cronin 1995; Shimoyama and Ogasawara 2002). The presence of mostly free glycine in A-12236, as well as the relatively high fractions of other free amino acids including alanine,  $\alpha$ - and  $\beta$ -amino- $n$ -butyric acids,  $\alpha$ -AIB, valine, isovaline, and several other  $C_5$  amino acids (Table 2), is consistent with a more limited duration of low temperature aqueous activity inside the A-12236 meteorite parent body. A more extensive period of parent body aqueous alteration, potentially with wet–dry cycling, may have been required to generate significant quantities of bound peptide-like amino acids, such as the glycine oligomers that were identified in the more aqueously altered CM2 meteorites Y-791198 and Murchison (Shimoyama and Ogasawara 2002).

#### Extraterrestrial Amino Acids and Minimal Terrestrial Contamination of A-12236

Only trace levels ( $0.01$ – $0.09 \text{ nmol}$ ) of L-aspartic acid, L-glutamic acid, L-serine, glycine, L-alanine,  $\epsilon$ -amino- $n$ -caproic acid, and L-valine were measured by UV fluorescence detection in the procedural blank (L-aspartic acid, L-glutamic acid, L-serine, glycine, and L-alanine were identified in the blank by accurate mass), indicating that very little terrestrial amino acid contamination of the A-12236 and EET 96029 meteorites occurred during sample processing and extraction (Figs. 1, 2; Fig. S1). However, the low amino acid concentrations in the procedural blank does not rule out the possibility that some amino acid contamination of the A-12236 meteorite occurred during its residence time in the Antarctic ice, or during collection, handling, and curation of the meteorite after it was discovered in 2012. Based on the low weathering grade A assignment of A-12236, significant alteration and associated organic contamination of this meteorite from the air or ice meltwater exposure in Antarctica are unlikely. However, amino acid measurements of lunar and Martian meteorites collected in Antarctica have shown that some terrestrial amino acid contamination from ice meltwater percolating through the meteorites is possible (McDonald and Bada 1995; Bada et al. 1998). Although Antarctic ice from the Asuka meteorite recovery location was not available for this study, previous analyses of amino acids in a melted  $10 \text{ kg}$

sample of Antarctic blue ice collected in 2006 from the Northern Graves Nunatak region revealed only very trace quantities ( $\sim 0.002$  to  $0.007$  pmol  $\text{g}^{-1}$ ) of D- and L-aspartic acids, L-glutamic acid, L-serine, glycine, and D- and L-alanine (Burton et al. 2012), which is  $\sim 10^3$  to  $10^4$  times lower than the levels of these protein amino acids in A-12236 (Table 2). Therefore, based on the high amino acid concentrations in A-12236 present at nmol  $\text{g}^{-1}$  levels (Table 2), any contributions from terrestrial protein amino acids in the Antarctic ice would have been negligible.

With the exception of glycine, none of the protein amino acids that have been found in Antarctic ice (Burton et al. 2012) were identified in the thermally altered EET 96029 meteorite above the  $0.01$  nmol  $\text{g}^{-1}$  level (Table 2), confirming that amino acid contamination from ice meltwater exposure also did not occur in this Antarctic meteorite. Finally, the presence of elevated abundances of several non-proteinogenic amino acids in A-12236 that are rare or absent in the terrestrial biosphere, including  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), D- and L- $\beta$ -amino-*n*-butyric acid ( $\beta$ -ABA), D- and L-isovaline, and all of the other non-protein C<sub>5</sub> amino acids identified in A-12236 (Table 2), were not even detected in the Antarctic ice above the  $\sim 0.001$  pmol  $\text{g}^{-1}$  level (Burton et al. 2012). Varying amounts of bound terrestrial  $\epsilon$ -amino-*n*-caproic acid or EACA (the amino acid polymer of nylon-6) contamination have been found in some Antarctic meteorites that were collected by the U.S. Antarctic Search for Meteorites (ANSMET) Program and stored in nylon-6 bags (Glavin et al. 2006). Nylon bag contamination may explain the presence of trace amounts of EACA in EET 96029 (Table 2). However, the presence of mostly free EACA ( $\sim 58\%$ , Table 2) in A-12236 indicates that most of the EACA in the meteorite is not derived from nylon-6 contamination. This observation is consistent with the fact that a polyethylene bag was used for the collection of A-12236 in the field without any direct hand contact, and the frozen meteorite was dried in a vacuum desiccator prior to chipping with a hammer and clean metal chisel, and the meteorite was not directly exposed to nylon during processing at NIPR (Naraoka, personal communication).

The high relative abundances of free amino acids in A-12236 (Table 2), including the two common protein amino acids glycine (96% free) and alanine (88% free), also provide compelling evidence against significant biological amino acid contamination, since any protein amino acid contamination of the meteorite would be expected to release amino acids that were predominantly in bound form after acid hydrolysis as was observed in terrestrially contaminated samples of

the Aguas Zarcas CM2 meteorite (Glavin et al. 2020b). We do note that other protein amino acids in the A-12236 water extract including aspartic acid, glutamic acid, and serine do increase in abundance after acid hydrolysis (Table 2). This could be consistent with a biological origin, and possibly an indication of some protein amino acid contamination of the meteorite during or after collection in Antarctica. However, the abundance of alanine (6–10%) and glycine (6–8%) in proteins is typically the same or higher than that of aspartic acid (5–6%), glutamic acid (6–8%), and serine (6–8%) across viruses, archaea, bacteria, and eukarya (Kozłowski 2017). Therefore, a biological contamination origin of the protein amino acids in A-12236 is very difficult to reconcile given the deficiency of bound glycine and alanine relative to other common protein amino acids in this meteorite.

Similar increases of aspartic acid and glutamic acid have also been observed after acid hydrolysis in other carbonaceous chondrites including Murchison and Tagish Lake (Simkus et al. 2019; Glavin et al. 2020b), and carbon isotopic measurements of the acid-hydrolyzed, hot water extracts have shown that the aspartic and glutamic acids in these meteorites are mostly extraterrestrial in origin based on their  $^{13}\text{C}$  enrichments relative to terrestrial organic carbon (Engel and Macko 1997; Glavin et al. 2012, 2020b). For example, carbon isotopic compositions for aspartic acid and glutamic acid in Murchison and Tagish Lake range from  $\delta^{13}\text{C} \sim +6\%$  to  $+32\%$  (Engel et al. 1990; Pizzarello and Cooper 2001; Pizzarello et al. 2004; Glavin et al. 2012, 2020b) and all values fall outside the carbon isotope range of  $\delta^{13}\text{C} = -0.3\%$  to  $-60.9\%$  measured for aspartic acid and glutamic acid in a variety of terrestrial microorganisms (Scott et al. 2006). It is possible that contamination of these meteorites by microorganisms such as fungi could have metabolized  $^{13}\text{C}$ -enriched meteoritic organic matter leading to the production of the observed isotopically enriched protein amino acids with large L-excesses. However, since terrestrial proteins also contain alanine as noted previously, any biological contamination of these meteorites should have also resulted in similarly large L-alanine excesses. Yet, this was not observed in Murchison (Glavin et al. 2020b), Tagish Lake (Glavin et al. 2012; Simkus et al. 2019), or the A-12236 meteorite analyzed in this study which contained racemic alanine (Table 3). For A-12236, similar stable carbon isotopic measurements of aspartic acid, glutamic acid, and serine would help establish the origin of their observed L-excesses (Table 3). To measure the carbon isotope ratio ( $^{13}\text{C}/^{12}\text{C}$ ) of individual amino acids using gas chromatography combustion isotope ratio mass spectrometry (GC-c-IRMS), typically at least  $\sim 1$  nmol of each amino acid is required to

Table 3. Summary of the D/L ratios and corresponding L-enantiomeric excesses (%L<sub>ee</sub> = %L - %D) measured for several amino acids in the non-hydrolyzed (free) and 6 M HCl-hydrolyzed (total) hot water extracts of the CM carbonaceous chondrites Asuka 12236, Paris, and Murchison.<sup>a</sup>

Amino acids	CM carbonaceous chondrites					
	<i>Asuka 12236 (CM3.0/2.9)</i>		<i>Paris (CM2.7)<sup>b</sup></i>		<i>Murchison (CM1.6/2.5)<sup>c</sup></i>	
	<i>free</i> D/L (%L <sub>ee</sub> )	<i>total</i> D/L (%L <sub>ee</sub> )	<i>free</i> D/L (%L <sub>ee</sub> )	<i>total</i> D/L (%L <sub>ee</sub> )	<i>free</i> D/L (%L <sub>ee</sub> )	<i>total</i> D/L (%L <sub>ee</sub> )
Aspartic acid	0.94 ± 0.12 (2.9 ± 6.3)	0.49 ± 0.03 (34 ± 2)	0.74 ± 0.05 (15 ± 3)	0.68 ± 0.03 (20 ± 2)	0.22 ± 0.04 (64 ± 4)	0.20 ± 0.01 (67 ± 1)
Glutamic acid	0.70 ± 0.11 (18 ± 7)	0.37 ± 0.03 (46 ± 3)	0.84 ± 0.08 (8.9 ± 4.4)	0.84 ± 0.09 (8.9 ± 4.7)	0.59 ± 0.04 (26 ± 3)	0.16 ± 0.01 (72 ± 1)
Serine	0.44 ± 0.02 (39 ± 2)	0.22 ± 0.04 (64 ± 4)	n.r.	n.r.	0.08 ± 0.02 (86 ± 2)	0.04 ± 0.01 (93 ± 1)
Alanine	0.96 ± 0.09 (2.0 ± 2.7)	0.93 ± 0.09 (3.4 ± 4.7)	0.67 ± 0.07 (20 ± 4)	0.74 ± 0.05 (15 ± 3)	0.67 ± 0.07 (20 ± 4)	0.73 ± 0.06 (15 ± 3)
Valine	0.89 ± 0.04 (5.6 ± 1.9)	0.82 ± 0.14 (9.7 ± 7.8)	0.98 ± 0.11 (1.1 ± 5.5)	0.93 ± 0.04 (3.0 ± 2.1)	0.90 ± 0.13 (5.3 ± 7.1)	0.20 ± 0.01 (67 ± 1)
β-ABA	1.05 ± 0.04 (-2.3 ± 1.9)	1.02 ± 0.03 (-1.1 ± 1.6)	n.d.	n.d.	1.05 ± 0.06 (-2.3 ± 3.0)	1.1 ± 0.1 (-5.9 ± 4.4)
Norvaline	0.98 ± 0.03 (1.2 ± 1.4)	1.08 ± 0.09 (-3.8 ± 4.4)	n.d.	0.87 ± 0.03 (7.0 ± 1.9)	n.d.	1.0 ± 0.1 (0)
Isovaline	0.95 ± 0.09 (2.5 ± 4.5)	1.05 ± 0.09 (-2.4 ± 4.5)	n.d.	0.99 ± 0.08 (0.2 ± 4.0)	0.78 ± 0.06 (13 ± 3)	0.85 ± 0.07 (8.3 ± 3.6)

n.d. = value not determined due to trace amino acid concentrations or analytical interferences; n.r. = not reported.

<sup>a</sup>The standard errors (δx) for the D/L ratios and L-enantiomeric excesses (%L<sub>ee</sub>) are based on the values and errors from Table 2 propagated through the relevant equations with %L<sub>ee</sub> = ([L-D]/[L + D])\*100. Negative values indicate a D-enantiomeric excess.

<sup>b</sup>GC-MS data for Paris meteorite extract from Martins et al. (2015).

<sup>c</sup>LC-MS data for the 0.08 g extract of Murchison from Glavin et al. (2020b).

permit reproducible and accurate quantification of their <sup>13</sup>C/<sup>12</sup>C ratios and even more material is required for <sup>15</sup>N/<sup>14</sup>N or D/H measurements (Elsila et al. 2009, 2012). Based on this GC-c-IRMS detection limit and the total individual measured concentrations of D- and L-aspartic acids, D- and L-glutamic acids, and D- and L-serine in the A-12236 extract (Table 2), we would require at least ~1 g of meteorite sample to determine the carbon isotope values of these amino acids, which is ~20 times the mass of A-12236 allocated for this study.

### Amino Acid Formation Mechanisms and Effects of Aqueous Alteration on Their Abundances and Relative Distributions

The elevated levels of glycine and other α-amino acids including α-alanine, α-amino-*n*-butyric acid, and α-AIB relative to their β- and γ-isomers (Table 2), as well as the predominance of the C<sub>5</sub> α-amino acids compared to the β-, γ-, and δ-isomers in the A-12236 meteorite as has been observed in other CM2 and CR2 carbonaceous chondrites (Fig. 4), strongly suggest that Strecker-cyanohydrin synthesis was active on the A-12236 parent body during an early aqueous alteration phase. The reaction of HCN, NH<sub>3</sub>, and carbonyl

compounds (aldehydes and ketones) derived from the interstellar medium and/or presolar cloud and incorporated into the parent body will lead to the formation of α-amino, α-hydroxy, and α-imino acids (but not β-, γ-, and δ-amino acids) during aqueous alteration via the Strecker-cyanohydrin reaction pathway (Peltzer and Bada 1978; Peltzer et al. 1984; Lerner and Cooper 2005). Some of the α-amino acids in A-12236 could have also formed by direct HCN polymerization during parent body aqueous alteration (Matthews 1992; Levy et al. 2000). Amino acids could have also formed prior to incorporation into the Asuka meteorite parent body by direct synthesis via gas-phase ion-molecule chemistry in the protosolar nebula (Blagojevich et al. 2003; Herbst and Van Dishoeck 2009) or on ice grain surfaces in the precursor molecular cloud exposed to radiation (Bernstein et al. 2002; Muñoz Caro et al. 2002; Elsila et al. 2007; Nuevo et al. 2008; Meinert et al. 2012b). Regardless of the source of the amino acids or their precursors, the wide diversity of amino acids in A-12236, also including β-, γ-, and δ-amino acids, which cannot be formed by Strecker reactions, indicates that multiple formation mechanisms were active on the A-12236 parent body. It has been proposed that β-amino acids found in

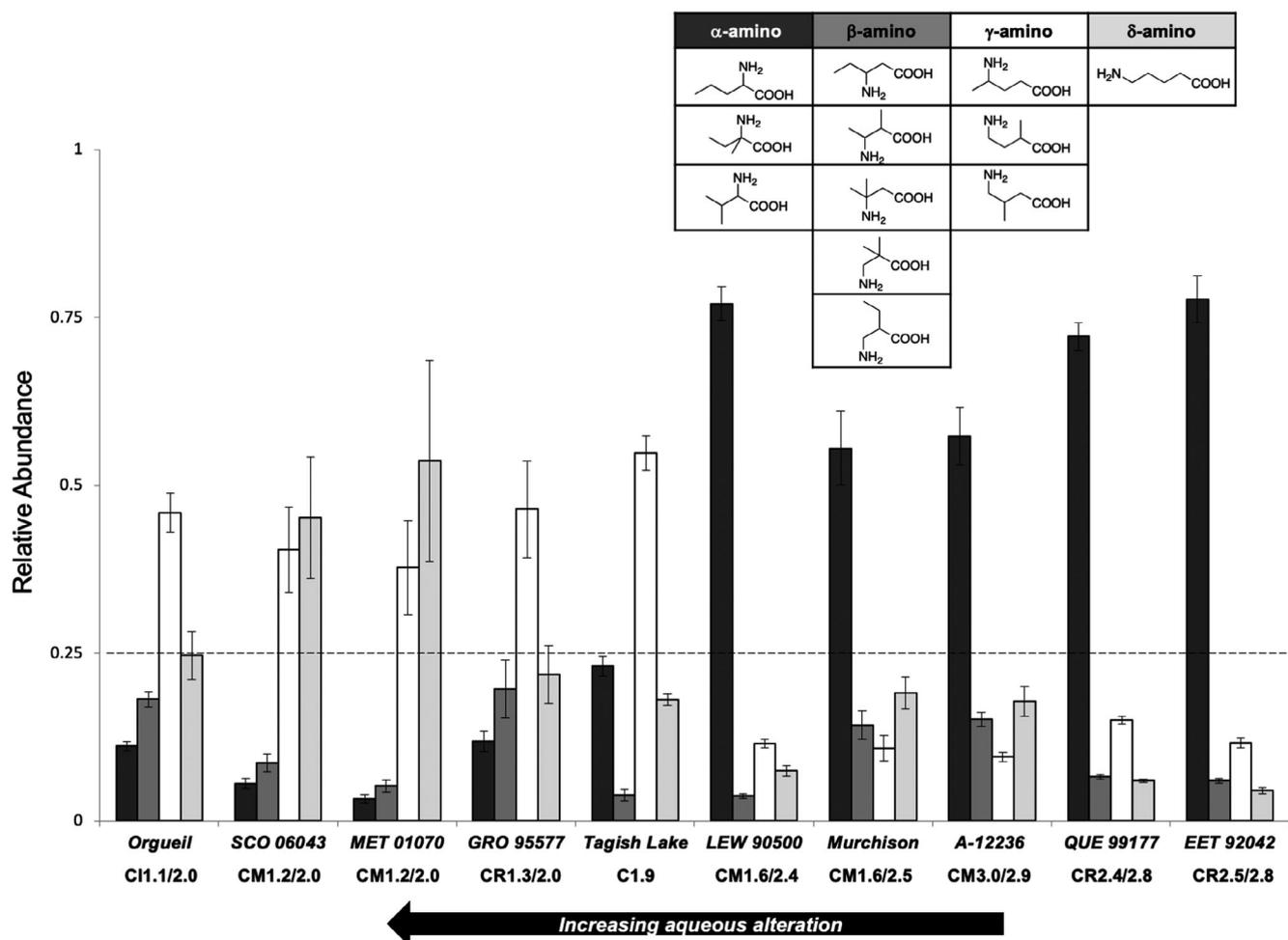


Fig. 4. A comparison of the relative molar abundances of the C<sub>5</sub> amino acids in CI, CM, and CR carbonaceous chondrites as a function of amine position ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -) normalized to the total number of possible structural isomers. The relative abundances for A-12236 were calculated from the data in Table 2 and the uncertainties were determined by standard error propagation of the absolute errors. The dashed line corresponds to the expected relative abundance if the amino acids were formed by a completely random synthetic process as described in Glavin and Dworkin (2009). The data for Orgueil, MET 01070, SCO 06043, GRO 95577, Murchison, LEW 90500, EET 92042, and QUE 99177 are taken from Glavin et al. (2010) and the data for Tagish Lake 5b from Glavin et al. (2012). The arrow indicates increasing aqueous alteration inferred from the meteorite petrologic type assignments as described in Table 1. The data used for this figure can be found in supporting information.

carbonaceous chondrites could have formed under aqueous conditions inside the parent body by Michael addition of ammonia to  $\alpha$ ,  $\beta$ -unsaturated nitriles (Ehrenfreund et al. 2001; Glavin et al. 2010). Some of the  $\gamma$ - and  $\delta$ -amino acids found in the Murchison meteorite may have formed by decarboxylation of  $\alpha$ -amino dicarboxylic acids or the hydrolysis of lactams that have been identified in the meteorite (Cooper and Cronin 1995). Similar origins of the  $\beta$ -,  $\gamma$ -, and  $\delta$ -amino acids that we identified in the A-12236 meteorite are also possible.

It is important to emphasize that the complex distribution of amino acids identified in A-12236 (Figs. 2 and 3), which cannot all be explained solely by gas-phase ion chemistry or UV irradiation of interstellar

ices without subsequent exposure to liquid water and hydrolysis at elevated temperatures, indicates that some aqueous activity must have occurred in the parent body to produce these compounds. Although A-12236 has not yet been found to contain petrologic or isotopic evidence for any significant aqueous alteration or heating (Kimura et al. 2019a, 2019b; Nittler et al. 2020), the presolar silicate abundance reported by Nittler et al. (2020) in the CM3.0/2.9 chondrite A-12236 is much lower than the primitive CR2.4 chondrite QUE 99177 and the CR2.6 chondrite Meteorite Hills (MET) 00426 (Floss and Stadermann 2009), suggesting some alteration of A-12236 occurred. The lower abundances of the C<sub>6</sub> to C<sub>8</sub> primary amino-containing OPA/NAC derivatives in the CM3.0/2.9 A-12236 meteorite (Fig. 3)

are similar to what has been observed previously for other primitive and weakly altered CR2.4/2.5 chondrites QUE 99177 and EET 92042 (Glavin et al. 2010). In contrast to A-12236, the more aqueously altered CM1.6 (2.5 on the Rubin scale) Murchison meteorite displays an even wider diversity and elevated abundances of the larger primary amino-containing OPA/NAC derivatives with up to 10 carbons (Fig. 3), most likely facilitated by a longer period of aqueous alteration on the Murchison parent body leading to additional synthesis of species with amino groups from larger and less abundant carbonyl compounds or possibly from chemical precursors released during hydrothermal alteration of meteoritic IOM (Kebukawa et al. 2017). Much lower amino acid concentrations and even less amino acid complexity was observed in the CM1 SCO 06043 chondrite compared to the CM2 chondrites Murchison and A-12236 (Fig. 3). Although it is possible that the original amino acid precursors in the SCO 06043 meteorite parent body were depleted relative to both Murchison and A-12236, a more likely explanation for these observations is that extended aqueous alteration and elevated temperatures in the SCO 06043 chondrite resulted in increased levels of amino acid degradation by deamination and decarboxylation reactions.

To further understand the effect of parent body aqueous alteration on the formation and decomposition of amino acids in carbonaceous chondrites, we also compared the relative distribution of the C<sub>5</sub> amino acid isomers in A-12236 with other meteorites (see Fig. 4; Fig. S2 in supporting information). Striking similarities in the relative molar abundances of the C<sub>5</sub> amino acid isomers were observed in the A-12236 and Murchison meteorite extracts (Fig. 4). Both meteorites were dominated by the C<sub>5</sub> α-amino acids (valine, isovaline, and norvaline) over the C<sub>5</sub> β-, γ-, and δ-amino acids, indicating that their parent bodies originally had similar distributions of carbonyl compounds or acid-labile precursors including carboxylic acid amides, hydroxy acid amides, lactams, N-alkyl amino acids, and hydantoins, which would have been required for the formation of these C<sub>5</sub> amino acids during aqueous alteration. The C<sub>5</sub> α-amino acids valine, isovaline, and norvaline were also detected in the Paris meteorite at similar concentrations to those measured in A-12236 (Table 2); however, Paris could not be included in the C<sub>5</sub> amino acid relative abundance plots for comparison because the concentrations of the C<sub>5</sub> β-, γ-, and δ-amino acids in Paris were not reported (Martins et al. 2015).

The dashed line in Fig. 4 at a relative abundance of 0.25 indicates the expected ratio if there was an equal probability of forming all of the C<sub>5</sub> amino acid isomers (Glavin and Dworkin 2009); therefore, enhanced and depleted C<sub>5</sub> isomer abundances refer to values that fall

above and below the dashed line, respectively. The enhanced abundances of the C<sub>5</sub> α-amino acids in A-12236 and other weakly or mildly altered CM2 and CR2 chondrites is distinct from the compositions of more aqueously altered CI, CM, and CR type 1 chondrites and the C2 Tagish Lake meteorite, which are dominated by the C<sub>5</sub> γ-amino acids (4-aminopentanoic acid, 4-amino-2-methylbutanoic acid, and 4-amino-3-methylbutanoic acid) and the C<sub>5</sub> δ-amino acid, 5-aminopentanoic acid (Fig. 4). Extensive aqueous alteration of the type 1 carbonaceous chondrites may have resulted in an increase in the rate of hydrolysis of bound amino acid precursors such as lactams, or the thermal decarboxylation of α-aminodicarboxylic acids, yielding elevated abundances of the γ- and δ-amino acids (Glavin et al. 2010). However, comparison of the relative abundances of the C<sub>5</sub> amino acids in the non-hydrolyzed (free) and acid-hydrolyzed (free + bound) water extracts of the aqueously altered CI1 chondrites Orgueil and Ivuna (Burton et al. 2014b) with the less altered CM2 Murchison meteorite (Glavin et al. 2020b) showed no significant differences in the free versus bound C<sub>5</sub> amino acid distributions that might be expected to result from an increase in the rate of hydrolysis of bound amino acid precursors during aqueous alteration. It is also possible that the C<sub>5</sub> γ- and δ-amino acids are much more stable to thermal decomposition than the C<sub>5</sub> α- and β-amino acids, as has been observed previously for some of the C<sub>4</sub> amino acids (Li and Brill 2003). Although the petrologic type of the Tagish Lake 5b meteorite analyzed in this study (C<sub>ung</sub>1.9) indicates that it experienced less aqueous alteration than the Murchison meteorite (a CM1.6 on the same petrologic scale, Table 1), it is possible that additional heating of the Tagish Lake parent body led to the higher relative abundances of the C<sub>5</sub> γ- and δ-amino acids observed compared to Murchison (Fig. 4). We see no obvious trend in the C<sub>5</sub> β-amino acid abundances with degree of alteration in the carbonaceous chondrites studied. In contrast to the relative abundances of the C<sub>5</sub> amino acids plotted by amine position, the relative C<sub>5</sub> amino acid abundances plotted by valeric acid derived structure in the A-12236 meteorite are distinct from the CMs Murchison and Lewis Cliffs (LEW) 90500, with a strong preference for the *iso*-valeric acid structures (valine, 3-amino-3-methylbutanoic acid, and 4-amino-3-methylbutanoic acid). They are also distinct from the CRs QUE 99177 and EET 92042 which have a modest preference for both *sec*- and *iso*-valeric acid structures (Fig. S2). Although we have not identified the mechanism(s) responsible for the variations seen in the C<sub>5</sub> amino acid distributions in these CI, CM, and CR carbonaceous chondrites, the similarities within carbonaceous

chondrite groups that experienced a similar degree of aqueous alteration suggest a solution-based explanation.

Aqueous alteration on the parent bodies of carbonaceous chondrites has also been shown to have a major impact on the absolute amino acid concentrations and the relative abundances of  $\beta$ -alanine compared to glycine and other  $\alpha$ -amino acids in CI, CM, and CR carbonaceous chondrites (Glavin et al. 2006, 2010; Martins et al. 2007a, 2007b, 2015). In Fig. 5, we compare the total amino acid concentrations and the relative molar abundances (relative to glycine = 1) of the amino acids  $\alpha$ -alanine (D + L-enantiomers),  $\beta$ -alanine,  $\alpha$ -AIB, and isovaline (D + L-enantiomers) in a variety of different CI, CM, and CR carbonaceous chondrites in order of degree of aqueous alteration according to the petrologic scales as described in Table 1. The data show a general trend of decreasing total amino acid abundances with increasing aqueous alteration where the highest amino acid abundances are observed in the least altered CR2.4/2.5 chondrites and the lowest total amino acid abundances are observed in the most altered type 1.1 to 1.3 CI, CM, and CR chondrites (Fig. 5). The high total amino acid concentration measured in A-12236 compared to other CM2 chondrites fits this trend well with its designation as a very weakly altered CM3.0/2.9 chondrite (Fig. 5).

Hydrothermal alteration of the CM meteorites is thought to have been the result of impact heating or the melting of ice inside the parent asteroid by radioactive heating, largely from the short-lived radionuclide  $^{26}\text{Al}$  (McSween et al. 2002). Temperatures during parent body alteration ranging from  $\sim 0$  to  $80$  °C have been estimated previously for CM2 meteorites with water/rock ratios of  $\sim 0.3$  to  $0.6$  and aqueous alteration durations over timescales of  $\sim 10^2$  to  $10^6$  years (Zolensky and McSween 1988; Browning et al. 1996; Cohen and Coker 2000; Brearley 2006; Krot et al. 2006; Guo and Eiler 2007; Palguta et al. 2010). Based on the absence of the mineral phase tochilinite in some CM1 chondrites, these meteorites could have been heated to even higher temperatures  $\geq 120$  °C (King et al. 2017; Vacher et al. 2019). During this alteration phase, low temperature chemical oxidation reactions could have resulted in the removal of aliphatic moieties from both soluble and insoluble macromolecular organic matter (Sephton et al. 2004; Cody and Alexander 2005; Martins et al. 2007a), which would have led to lower amino acid concentrations in the more aqueously altered type 1 carbonaceous chondrites. Hydrothermal decomposition of  $\alpha$ -amino acids by  $\alpha$ -decarboxylation and/or  $\alpha$ -deamination to their corresponding primary amines or  $\alpha$ ,  $\beta$ -unsaturated monocarboxylic acid during aqueous alteration could also occur (Simmonds et al. 1972; McCollom 2013; Pietrucci et al. 2018). The notably

higher total amino acid concentrations measured in the CII Orgueil meteorite relative to other type 1 CM and CR chondrites (Fig. 5) may be related to the distinct chemical composition of the CI parent body compared to the CM and CR chondrites that favored the synthesis (rather than decomposition) of  $\beta$ -alanine and glycine in Orgueil during aqueous alteration (Ehrenfreund et al. 2001).

A strong correlation is also observed between the abundance of  $\beta$ -alanine (relative to glycine) and the degree of aqueous alteration in carbonaceous chondrites (Fig. 5), with low  $\beta$ -alanine/glycine ratios of  $\sim 0.06$  to  $0.12$  for the least aqueously altered CR2.4/2.5 chondrites QUE 99177 and EET 92042 ranging up to a ratio as high as  $2.7$  for the most aqueously altered CII.1 Orgueil meteorite (Fig. 5). A lower  $\beta$ -alanine/glycine ratio for the CM2.7 Paris meteorite compared to more altered CM2 chondrites has previously been noted (Martins et al. 2015; Modica et al. 2018). The weakly altered CM3.0/2.9 A-12236 meteorite also has a very low  $\beta$ -alanine/glycine ratio ( $0.13 \pm 0.01$ , calculated from the data in Table 2), which is identical to the  $\beta$ -alanine/glycine ratio of the CM2.7 Paris ( $0.13 \pm 0.02$ , Table 2) and only slightly lower than the  $\beta$ -alanine/glycine ratio of the CM1.6/2.5 Murchison meteorite ( $0.15 \pm 0.01$ , Table 2). The increasing abundance of  $\beta$ -alanine relative to glycine in more aqueously altered meteorites could be related to a greater resistance of  $\beta$ -alanine to thermal decarboxylation compared to glycine (Li and Brill 2003). Even though there is a clear overall trend of increasing  $\beta$ -alanine/glycine ratio with increased aqueous alteration, based on our data, this ratio is not sensitive enough to distinguish between CM and CR meteorites of petrographic types  $\geq 2.5$  on the Rubin scale. It is also apparent from the data that there is not an obvious correlation between the relative abundances of other amino acids ( $\alpha$ -alanine,  $\alpha$ -AIB, and isovaline) with petrographic type of the carbonaceous chondrites studied (Fig. 5). We do note the similarity in the relative amino acid distributions of the CM3.0/2.9 A-12236 and CM2.7 Paris meteorites that are both distinct from other more altered CM carbonaceous chondrites. Future amino acid measurements of the other primitive Asuka CM meteorites (CM2.8 A-12085 and CM3.0 A-12169, see Kimura et al. 2019a) and other weakly altered CM2s will be needed to determine if the amino acid distributions in A-12236 and Paris are signatures of highly primitive CM2 chondrites.

#### **Enantiomeric Ratios and Unusual L-Protein Amino Acid Excesses in A-12236**

In addition to the amino acid abundances and distributions, chirality is another important parameter

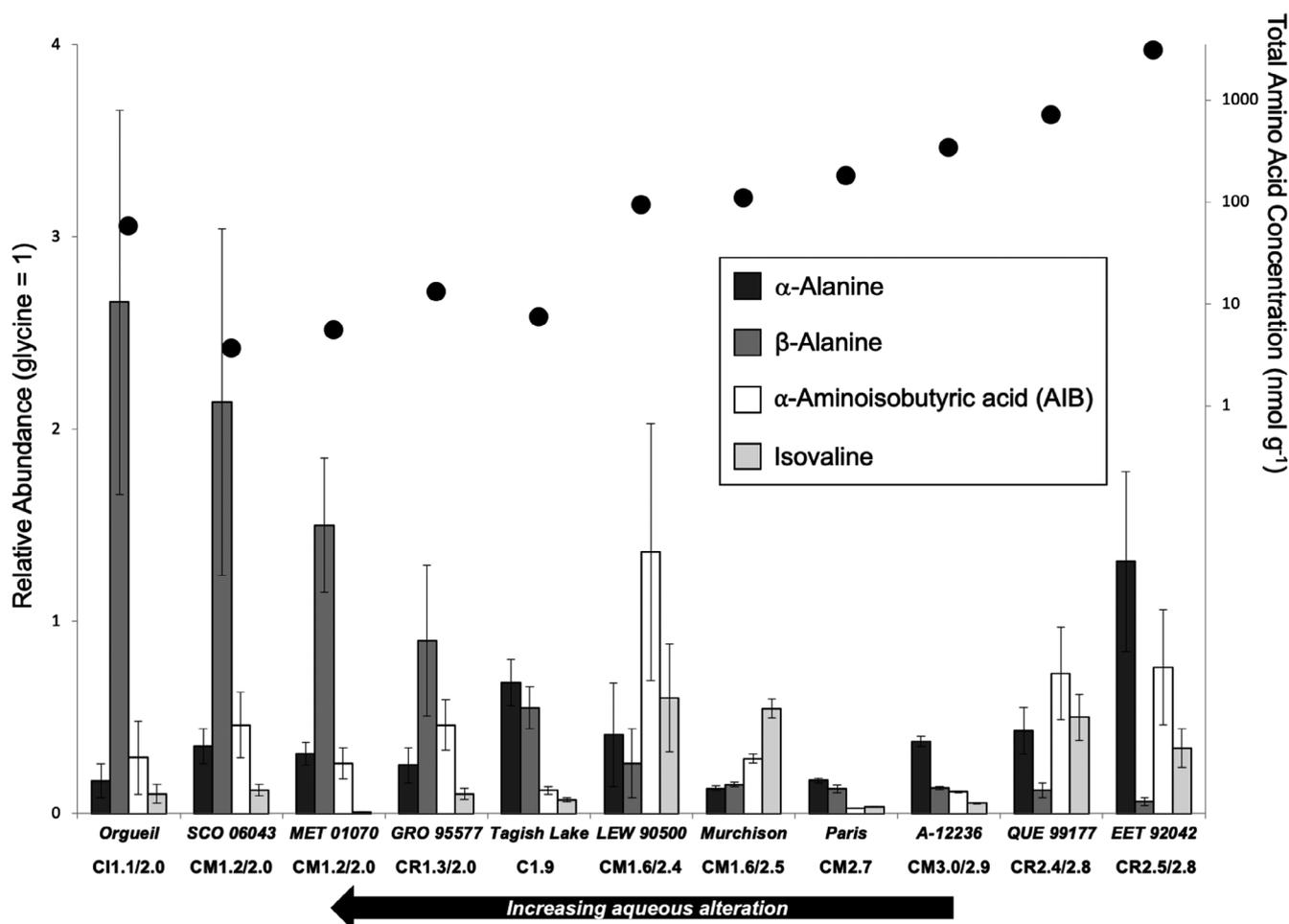


Fig. 5. A comparison of the total amino acid concentrations in  $\text{nmol g}^{-1}$  of aspartic and glutamic acids, serine, glycine, alanine,  $\beta$ -alanine,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -amino-*n*-butyric acids,  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), valine, and isovaline (designated by black circles on log scale) and the relative molar abundances (relative to glycine = 1) of  $\alpha$ -alanine,  $\beta$ -alanine,  $\alpha$ -AIB, and isovaline (shown as bars) in the 6M HCl-hydrolyzed, hot water extracts of select carbonaceous chondrites. The amino acid abundances for Asuka 12236 were taken from the data in Table 2 and the uncertainties in relative abundances were determined by standard error propagation of the absolute errors. The amino acid data for Orgueil, SCO 06043, MET 01070, GRO 95577, LEW 90500, Murchison, EET 92042, and QUE 99177 were taken from Glavin et al. (2010). The amino acid data for the Tagish Lake 5b meteorite were from Glavin et al. (2012), and the data for the Paris meteorite were from Martins et al. (2015). The arrow indicates increasing aqueous alteration inferred from the meteorite petrologic type assignments as described in Table 1. The data used for this figure can be found in supporting information.

to help discriminate between amino acids of biotic and abiotic origins, especially in cases where the amino acid concentrations are low or insufficient sample mass is available to make compound-specific isotope measurements. On Earth, biology almost exclusively uses L-amino acids, whereas the abiotic synthesis of amino acids generally results in equal mixtures of L- and D-amino acids. Therefore, if we assume that the amino acids found in carbonaceous chondrites were all originally racemic ( $D/L \sim 1$ ) prior to their fall to Earth, then their measured  $D/L$  ratios can be used to infer the extent of terrestrial L-amino acid contamination they experienced on Earth. The enantiomeric ratios ( $D/L$ ) for

the protein amino acids including aspartic and glutamic acids, serine, alanine, and valine, and the non-protein amino acids including  $\beta$ -ABA, norvaline, and isovaline and their corresponding L-enantiomeric excesses ( $L_{ee}$ ) calculated from the amino acid data in Table 2 for the A-12236, Murchison, and Paris meteorites are given in Table 3.

The enantiomeric ratios for the non-protein amino acids,  $\beta$ -ABA, norvaline, and isovaline, in the A-12236 non-hydrolyzed (free) and acid-hydrolyzed (total) water extracts were all racemic ( $D/L = 0.95$  to  $1.08$ ) within the  $\pm 0.03$  to  $0.09$  analytical uncertainties of the measurements (Table 3). Similar to A-12236 (CM3.0/

2.9), previous measurements of the Paris meteorite (CM2.7) as well as the primitive Antarctic CR2 chondrites QUE 99177 (CR2.4) and EET 92042 (CR2.5) have also found racemic or near racemic mixtures of these non-protein amino acids, including isovaline with no measurable L-excesses within errors (Glavin et al. 2010; Martins et al. 2015).

In contrast to the most primitive, least aqueously altered CM and CR chondrites, a range of L-isovaline excesses of non-terrestrial origin have been firmly established in the CM1.6 (CM2.5 on Rubin scale) Murchison meteorite ( $L_{ee} \sim 0.2\text{--}18.5\%$ , Table 4). These findings were based on LC-MS, GC-MS, and GC-c-IRMS carbon isotopic measurements made in different laboratories (Pizzarello and Cronin 2000; Pizzarello et al. 2003; Glavin and Dworkin 2009). A variety of other aqueously altered carbonaceous chondrites show L-isovaline excesses, up to values as high as 20.5% in the CH3 chondrite ALH 85085 (Table 4) possibly associated with the heavily hydrated clasts common in CH3 meteorites (Greshake et al. 2002; Burton et al. 2013). Although a general correlation between the extent of aqueous alteration as indicated by petrologic type and the magnitude of the L-isovaline enantiomeric excess has been observed, particularly for the CI, CM, and CR carbonaceous chondrites (Glavin and Dworkin 2009; Glavin et al. 2010), the larger L-isovaline excesses (i.e., those greater than a few percent) have been challenging to explain. This is because the abiotic formation of isovaline and other  $\alpha$ -amino acids (e.g., by the Strecker-cyanohydrin synthesis) in these meteorites should produce racemic mixtures (Wolman et al. 1972).

One hypothesis for chiral amino acid symmetry breaking that has shown promise is the generation of small L-enantiomeric excesses by the preferential synthesis of the L-enantiomer, or preferential destruction of the D-enantiomer on icy grains in the presolar cloud through exposure to circularly polarized radiation generated from nearby massive O- or B-type stars (Flores et al. 1977; Bonner and Rubenstein 1987; Bailey 2001; Takano et al. 2007; Fukue et al. 2010; Meinert et al. 2012a; Modica et al. 2014; Garcia et al. 2019). Laboratory experiments simulating presolar and interstellar environments have shown that slight L- or D-enantiomeric enrichments of 0.2–2.5% of several chiral amino acids, including alanine, valine, norvaline, leucine,  $\alpha$ -amino-*n*-butyric acid, and 2,3-diaminopropanoic acid, can be produced directly from interstellar ice analogs for a given direction of UV circularly polarized light (UV CPL), while no amino acid asymmetry was induced with non-polarized UV light (Modica et al. 2014). Isovaline was not detected in any of these ice irradiation experiments above background levels, but the generation of similarly small

L-isovaline excesses seems plausible based on the well-characterized behavior of isovaline under UV CPL (Meierhenrich et al. 2010; Meinert et al. 2012a). Unfortunately, it is highly unlikely that such small CPL-induced isovaline enantiomeric excesses in primitive CM and CR meteorites could be identified based on current GC-MS and LC-MS measurement uncertainties of  $\pm 2\text{--}5\%$  (Table 4).

Another significant challenge to explain the amino acid observations from meteorites by UV CPL is that, in order to generate the largest ( $\geq 15\%$ ) L-isovaline excesses measured in some aqueously altered chondrites (Table 4),  $\gg 99\%$  of the amino acid would need to be destroyed by the radiation (Flores et al. 1977). UV CPL as the sole mechanism for enantiomeric enrichment, therefore, seems very unlikely given (1) the relatively high concentrations of isovaline that have been found in Murchison and other aqueously altered CM chondrites and (2) chemical evidence that isovaline and other  $\alpha$ -amino acids formed by Strecker synthesis during aqueous alteration inside the CM parent body (Peltzer and Bada 1978).

A variety of other amino acid enantioenrichment mechanisms have been proposed to explain how small initial L-amino acid imbalances could be generated and amplified during aqueous alteration under meteorite parent body conditions. Amplification mechanisms include asymmetric autocatalysis (Soai et al. 1995) and asymmetric amplification of amino acids (e.g., serine) that can have large eutectic enantiomeric excesses of up to 99% due to their equilibrium solid–liquid phase behavior (Blackmond 2004; Klusmann et al. 2006b). Another proposed mechanism is amplification via enantiomeric crystallization and racemization of conglomerate or meta-conglomerate amino acids (Viedma 2001; Noorduin et al. 2008; Viedma et al. 2010) during multiple episodes of aqueous alteration and wet–dry cycling. The mechanism(s) for L-isovaline enrichment in carbonaceous chondrites still remain unclear. However, the observations that isovaline is racemic in the A-12236 meteorite and other weakly altered primitive CM and CR chondrites, and that statistically significant L-isovaline excesses have only been found in the more aqueously altered (petrologic type  $< 2.6$  on the Rubin scale) carbonaceous meteorites, strongly indicate that L-isovaline enrichments occurred inside the parent bodies during aqueous alteration.

In contrast to the racemic, non-protein amino acids including isovaline, norvaline, and  $\beta$ -ABA detected in A-12236 (Table 3), we found that the  $\alpha$ -hydrogen protein amino acids such as aspartic and glutamic acids and serine in the acid-hydrolyzed hot water extract of A-12236 had much lower D/L values ranging from 0.22 to 0.49 with corresponding L-enantiomeric excesses of

Table 4. L-isovaline enantiomeric excesses ( $\%L_{ee} = \%L - \%D$ ) and associated standard errors  $\delta x$  with corresponding number of measurements ( $n$ ) that have been reported in several carbonaceous chondrites. Meteorites are listed in approximate order of highest to lowest L-isovaline excesses.

Meteorite name	Classification <sup>a</sup>	Isovaline $\%L_{ee} \pm \delta x$ (n)	References
ALH 85085	CH3	$20.5 \pm 7.1$ (6)	Burton et al. (2013)
Murchison	CM1.6 (2.5)	$18.5 \pm 2.6$ (20)	Glavin and Dworkin (2009)
		$17.2 \pm 6.7$ (8)	Glavin et al. (2010)
		0.2 to $15.2 \pm 0.2$ -1.3 (5-33)	Pizzarello et al. (2003)
		$13 \pm 30$ (2-5)	Botta et al. (2002)
		$10 \pm 1$ (6); $8.3 \pm 3.6$ (6)	Glavin et al. (2020b)
		$9.7 \pm 1.2$ (3)	Aponte et al. (2014)
		$9.2 \pm 0.6$ (8); <i>corr.</i> 8.4	Cronin and Pizzarello (1997)
		$7.2 \pm 9.3$ (3)	Burton et al. (2014a)
		$6.1 \pm 5.0$ (4)	Friedrich et al. (2018)
		5.6	Callahan et al. (2014)
		$-4.1 \pm 12.9$ (4)	Martins et al. (2007b)
SCO 06043	CM1.2 (2.0)	$16.5 \pm 7.5$ (8)	Glavin et al. (2010)
Orgueil	CII.1 (2.0)	$17.5 \pm 30.7$ (4)	Martins et al. (2007b)
		$15.2 \pm 4.0$ (8)	Glavin and Dworkin (2009)
Aguas Zarcas	CM2	$15 \pm 7$ (6); $11 \pm 6$ (6)	Glavin et al. (2020b)
MIL 07411	CB	$14 \pm 4$ (6)	Burton et al. (2013)
PCA 91467	CH3	$13 \pm 3$ (6)	Burton et al. (2013)
GRO 95577	CR1.3 (2.1)	$11.0 \pm 7.2$ (8)	Glavin et al. (2010)
MIL 05082	CB	$9.7 \pm 3.0$ (6)	Burton et al. (2013)
Mukundpura	CM1 (2.0)	9.7	Pizzarello and Yarnes (2018)
Mighei	CM1.6 (2.3)	$8 \pm 43$ (2-5)	Botta et al. (2002)
Ivuna	CII.1 (2.0)	$7.3 \pm 9.8$ (3)	Burton et al. (2014b)
Murray	CM1.5 (2.4/2.5)	$7.2 \pm 0.7$ (20); <i>corr.</i> 6.0	Pizzarello and Cronin (2000)
Tagish Lake 5b	C <sub>ung</sub> 1.9	$7.0 \pm 1.9$ (8)	Glavin et al. (2012)
Tagish Lake 1	C <sub>ung</sub>	$6.7 \pm 5.9$ (3)	Simkus et al. (2019)
PAT 91546	CH3	$5 \pm 2$ (6)	Burton et al. (2013)
LEW 90500	CM1.6 (2.3/2.4)	$3.3 \pm 1.8$ (23)	Glavin and Dworkin (2009)
GRA 95229	CR2.5 (2.7)	3.0	Pizzarello et al. (2008)
LON 94102	CM1.8 (2.6)	$2.4 \pm 4.1$ (8)	Glavin and Dworkin (2009)
QUE 99177	CR2.4 (2.8)	$0.3 \pm 2.1$ (8)	Glavin and Dworkin (2009)
Paris	CM2.7	$0.2 \pm 4.0$ (9); <i>corr.</i> $-1.4 \pm 2.6$ (9)	Martins et al. (2015)
Tagish Lake 10a	C <sub>ung</sub>	$0.0 \pm 4.1$ (3)	Simkus et al. (2019)
Tagish Lake 11h	C <sub>ung</sub>	$-0.9 \pm 2.6$ (8)	Glavin et al. (2012)
EET 92042	CR2.5 (2.8)	$-1.0 \pm 4.3$ (8)	Glavin and Dworkin (2009)
Asuka 12236	CM3.0 (2.9)	$-2.4$ to $2.5 \pm 4.5$ (6)	This study

<sup>a</sup>Sources and descriptions of some of the meteorite petrologic type assignments are given in Table 1.

$64 \pm 4\%$  for serine,  $46 \pm 3\%$  for glutamic acid, and  $34 \pm 2\%$  for aspartic acid (Table 3). Although smaller, L-excesses of  $\sim 3\%$  to  $39\%$  were also observed for these protein amino acids in the A-12236 non-hydrolyzed hot water extract (Table 3). Given the lack of evidence for significant terrestrial biological contamination of the A-12236 meteorite based on its high percentage of free glycine and other amino acids as discussed previously, and the detection of racemic alanine within errors in both the A-12236 non-hydrolyzed and acid-hydrolyzed water extracts (Table 3), it is possible that at least some of the measured L-aspartic acid, L-glutamic acid, and L-serine excesses in A-12236 are indigenous to the meteorite. Lower L-aspartic acid, L-glutamic acid, and L-

alanine excesses ranging from  $\sim 9\%$  to  $20\%$  (Table 3) were measured in the CM2.7 Paris meteorite (Martins et al. 2015), while no L- excesses for any amino acids were found in the primitive CR2.4/2.5 chondrites QUE 99177 and EET 92042 (Glavin et al. 2010). Martins et al. (2015) do not rule out the possibility that some of the L-protein amino acid excesses in Paris could be indigenous to the meteorite, but the abundances of these amino acids were too low for isotopic measurements needed to establish their origin.

It is highly notable that, just like in the A-12236 meteorite, racemic alanine coupled with similarly large L-aspartic acid and L-glutamic acid excesses ranging from  $\sim 25\%$  to  $60\%$  have also been reported in the

Murchison and Tagish Lake meteorites and an extraterrestrial origin for these amino acids and their L-excesses was firmly established by isotopic measurements that showed significant  $^{13}\text{C}$  and  $^{15}\text{N}$  enrichments relative to terrestrial organic matter (Engel and Nagy 1982; Engel and Macko 1997, 2001; Glavin et al. 2012, 2020a, 2020b). Based on carbon isotope measurements of D- and L-glutamic acid extracted from a 1 g sample of the Murchison meteorite, Glavin et al. (2020b) concluded that up to 40% of the measured L-glutamic acid excess was indigenous to the meteorite. Similar isotopic measurements of these protein amino acids in the A-12236 meteorite will also be required to determine if the L-amino acid excesses are extraterrestrial in origin. For the Murchison and Tagish Lake meteorites, the large L-aspartic acid and L-glutamic acid excesses have been attributed to conglomerate (only enantiomerically pure amino acid crystals can form) crystallization and amplification of small initial L-excesses during parent body aqueous alteration through multiple cycles of dissolution, racemization, and precipitation (Glavin et al. 2012, 2020b). In contrast, amplification of small, initial L-alanine excesses inside the Murchison and Tagish Lake meteorite parent bodies by this same mechanism would not occur, because alanine forms racemic crystals (equal mixture of D- and L-alanine) and would eventually be driven toward a racemic mixture (D/L = 1) with increased parent body aqueous alteration, which is exactly what has been observed for alanine in these aqueously altered meteorites. Although crystallization is currently the best explanation for the large L-excesses of the conglomerate-forming amino acids aspartic and glutamic acids and racemic alanine found in some aqueously altered carbonaceous chondrites, it is not yet clear if a similar level of L-amino acid enrichment by this mechanism could occur in weakly altered meteorites like the CM3.0/2.9 A-12236 and CM2.7 Paris meteorites, which did not experience extensive parent body hydrothermal alteration. It is also not known if amino acid oligomerization during aqueous alteration could facilitate additional amplification of L-amino acid excesses.

### The Significance of Asteroid Sample Return and Predictions for Ryugu and Bennu

JAXA's Hayabusa2 mission and NASA's Origins, Spectral Interpretation, Resource Identification, Security, Regolith Explorer (OSIRIS-REx) mission will return samples collected from the surfaces of the carbonaceous asteroids (162173) Ryugu and (101955) Bennu to Earth in late 2020 and 2023, respectively. These asteroid sample return missions will provide the first opportunities to

investigate the origin of chiral asymmetry of amino acids and other chiral molecules in pristine solar system materials that were collected in context and under conditions where contamination control and knowledge can be carefully tracked (Dworkin et al. 2018). The returned samples from asteroids Ryugu and Bennu will also yield valuable information about the effects of the main alteration processes of primitive organics including parent body aqueous alteration, heating, and exposure to radiation (Brunetto and Lantz 2019). Hayabusa2 will eventually return grains and gas collected from two different sites on Ryugu each totaling ~100 mg in sample mass, while OSIRIS-REx is expected to return at least 60 g of surface material collected from a single sampling site on Bennu.

Ryugu is a rare spectral type C<sub>g</sub>, spinning top shaped, 1 km diameter macroporous rubble pile asteroid with a low albedo ( $4.5 \pm 0.2$  at 550 nm) and a relatively featureless infrared spectrum, with indications of a very weak global hydration feature at 2.72  $\mu\text{m}$  (Kitazato et al. 2019; Sugita et al. 2019; Watanabe et al. 2019). The near-infrared spectra of Ryugu are characteristic of thermally metamorphosed or shocked CI or CM group carbonaceous chondrites and similar to the near-infrared spectrum of the CI1 Ivuna meteorite after heating to 500 °C. While previous amino acid analyses of the aqueously altered CI1 chondrites Orgueil and Ivuna have revealed total amino acid concentrations of ~40 to 70 nmol g<sup>-1</sup> dominated by glycine and  $\beta$ -alanine (Ehrenfreund et al. 2001; Burton et al. 2014b), the thermally altered CI1 chondrites Y-86029 and Y-980115 that have been heated at ~500–600 °C contain only trace quantities (~1–3 nmol g<sup>-1</sup>) of amino acids (Burton et al. 2014b). Similarly, low concentrations of amino acids were also identified in the thermally altered Sutter's Mill CM2 chondrite (Burton et al. 2014a), and from this study, we only identified a few amino acids with only 1.7 nmol g<sup>-1</sup> of glycine in the primitive CM2.7 EET 96029 meteorite that had also been heated to elevated temperatures. If the materials on Ryugu sampled by Hayabusa2 have experienced a similar degree of hydrothermal alteration as these thermally altered CI1 and CM2 chondrites, then the samples could be highly depleted in amino acids. Fortunately, sophisticated laboratory techniques such as nanoliquid chromatography and 2-D liquid chromatography coupled with high resolution mass spectrometry that are capable of measuring trace concentrations of amino acids and their enantiomers extracted from small sample sizes <1 mg (Callahan et al. 2014; Naraoka et al. 2019) will be available to support the analyses of samples returned from Ryugu.

Bennu, a 490 m diameter spectral type B asteroid, is also a dark spinning top-shaped rubble pile with a low

albedo ( $4.4 \pm 0.2$  at 550 nm) and relatively featureless infrared spectrum (DellaGiustina et al. 2019; Lauretta et al. 2019), but with much stronger indications of a global hydration band centered at 2.74  $\mu\text{m}$  and evidence for widespread hydrated minerals on the surface of the asteroid (Hamilton et al. 2019). The infrared spectrum of Bennu is similar to mildly heated and relatively aqueously altered CI and CM carbonaceous chondrites of petrographic subtypes <2.4 based on the Rubin scale (Hamilton et al. 2019). In addition, a complex infrared absorption feature at 3.4  $\mu\text{m}$  on Bennu, which is consistent with the presence of aliphatic organic compounds and carbonate minerals, indicates that this asteroid experienced a significant amount of aqueous activity (Kaplan, personal communication). Although the 2.7  $\mu\text{m}$  hydration feature of Bennu is significantly stronger than Ryugu (Hamilton et al. 2019; Kitazato et al. 2019), consistent with a higher degree of thermal alteration of Ryugu, it is also possible that space weathering has reduced the intensity of the hydration feature in the infrared accessible depth of these asteroids (Lantz et al. 2017). Therefore, the strength of the near-infrared features may not reflect the actual concentrations of hydrated minerals and complex organics in the returned samples from Ryugu and Bennu that will include subsurface materials. Nevertheless, based on the spectral similarities between Bennu and aqueously altered CI and CM chondrites of petrologic types <2.4 and amino acid data from both of these meteorite groups (Glavin et al. 2018), we predict that samples returned from Bennu could contain total amino acid concentrations between  $\sim 10$  and  $100 \text{ nmol g}^{-1}$ , assuming that the samples experienced only mild heating on Bennu. Furthermore, based on the near-infrared spectral evidence for extensive aqueous alteration on Bennu, we also predict that some of the amino acids could contain large L-enantiomeric excesses.

Compared to meteorites recovered from the blue ice fields in Antarctica and other terrestrial finds, as well as rapidly recovered meteorites from observed falls, asteroid samples returned from Bennu and Ryugu will ultimately have a much more limited exposure to terrestrial contamination, and the potential sources of contamination have been archived and are available for study as controls if needed (Dworkin et al. 2018). Such asteroid sample return missions avoid the uncertainties of the extent of biological contamination from sample exposure to unfiltered terrestrial air, soil, liquid water or ice, and during collection by humans, and also take advantage of rigorous spacecraft hardware cleaning procedures and contamination knowledge. Such pristine samples provide researchers the ability to study them without organic contamination from intrusive biology. As such, potential concerns about the effect of an

unknown level of terrestrial amino acid contamination on the measured chiral asymmetry, or changes in the distribution and isotopic compositions of amino acids introduced by biological contamination, are greatly reduced. Therefore, pristine samples returned from the carbonaceous asteroids Ryugu and Bennu will provide the very first opportunity to investigate the origin and extent of amino acid chiral asymmetry produced solely by nonbiological processes.

## CONCLUSIONS

Amino acid analyses of the primitive CM carbonaceous chondrite A-12236 confirmed the presence of a suite of two- to six-carbon primary aliphatic amino acids that are mostly derived from extraterrestrial sources. The elevated abundances of  $\alpha$ -amino acids in the A-12236 meteorite with a relative distribution of five-carbon amino acids that is similar to what has been observed in the CM2 carbonaceous chondrite Murchison suggest that amino acids in the A-12236 meteorite were formed by Strecker synthesis during parent body alteration in the CM meteorite parent body. The total concentration of identified amino acids in A-12236 of  $\sim 360 \text{ nmol g}^{-1}$  is much higher than Murchison and most other CM2 chondrites, and nearly double the concentration of total amino acids that have been measured in another primitive CM2.7 meteorite Paris. In addition, A-12236 has the highest overall percentage of free amino acids (as opposed to bound or acid-produced) of any CI, CM, or CR chondrite analyzed to date. This finding, is unusual, yet consistent with petrologic and isotopic evidence that A-12236 experienced only a limited duration of low temperature aqueous activity in the CM parent body consistent with its petrologic assignment of 3.0/2.9. In sharp contrast to A-12236, we detected only trace total concentrations ( $\sim 1.7 \text{ nmol g}^{-1}$ ) of amino acids in the weakly altered CM2.7 chondrite EET 96029 which may be the result of a significant amount of amino acid decomposition due to heating at  $\sim 400\text{--}600 \text{ }^\circ\text{C}$  in the parent body.

Several non-protein amino acids, including  $\alpha$ -AIB, D,L- $\beta$ -amino-*n*-butyric acid, and D,L-isovaline, and a variety of other non-protein C<sub>5</sub> amino acids were identified in A-12236 at elevated concentrations ranging from  $\sim 1$  to  $18 \text{ nmol g}^{-1}$ . These species are likely to be extraterrestrial in origin as they are rare or nonexistent in terrestrial biology and were not identified as contaminants in the procedural blanks, Antarctic ice, or other control samples. Furthermore, the detection of only free glycine and a racemic mixture of mostly free alanine, two common proteinogenic amino acids that are present in mostly bound form in terrestrial organic matter, provide additional evidence that the A-12236

meteorite was not exposed to significant amounts of biological amino acid contamination. Similar to previous amino acid analyses of the Murchison and Tagish Lake meteorites, we also observed large L-enantiomeric excesses of ~34% to 64% for the protein amino acids, aspartic and glutamic acids and serine, while alanine was racemic. It is possible that some of the L-protein amino acid excesses in A-12236 are non-terrestrial in origin; however, future isotopic measurements will be required to establish the origin of these observed L-excesses.

We surmise that the non-terrestrial L-amino acid enrichments found in some weakly to heavily aqueously altered carbonaceous chondrites can be adequately explained by differences in their crystallization behaviors. Future amino acid analyses of pristine samples returned from carbonaceous asteroids that have not been exposed to terrestrial contamination and additional laboratory experiments to investigate enantioenrichment mechanisms for amino acids under relevant parent body conditions are still needed to support this hypothesis. Currently, the formation of large L-amino acid excesses of conglomerate enantiopure crystals during parent body aqueous alteration remains the most plausible asteroid-relevant amplification mechanism for amino acids. The fact that only L-enantiomeric excesses (and no D-excesses) have been observed in amino acids with a single asymmetric carbon in carbonaceous meteorites so far suggests that the origin of life on Earth or elsewhere in our solar system may have been biased toward L-amino acid homochirality from the very beginning.

The return of pristine materials from the surface of carbonaceous asteroids to Earth for detailed laboratory organic analyses will be essential to advance our understanding of the origin and evolution of amino acid chiral asymmetry in the early solar system given that all meteorites on Earth have been compromised, to some degree, by terrestrial contamination. JAXA's Hayabusa2 mission and NASA's OSIRIS-REx mission will return the first pristine samples collected from the surfaces of the carbonaceous asteroids Ryugu and Bennu. These missions will provide a unique opportunity to evaluate the effects of parent body processing on the distributions and enantiomeric abundances of amino acids and other prebiotic molecules in carbon-rich asteroids.

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## SUPPORTING INFORMATION

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

**Figure S1.** The 2- to 14-min. region of the LC-ToF-MS single ion mass chromatograms corresponding to the OPA/NAC derivatives of aspartic acid (bottom trace:  $m/z = 395.09$ ), glutamic acid (middle trace:  $m/z = 409.11$ ), and serine (top trace:  $m/z = 367.10$ ) in positive electrospray ionization mode.

**Figure S2.** A comparison of the relative molar abundances of the C<sub>5</sub> amino acids in CI, CM, and CR carbonaceous chondrites as a function of valeric acid carbon chain backbone (*n*-, *sec*-, *iso*-, and *tert*-) normalized to the total number of possible structural isomers.

**Data S1.** Excel file containing all of the raw data used to generate the plots shown in Figs. 1–5 and Figs. S1 and S2.