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# Challenges and Opportunities in Using Amino Acids to Decode Carbonaceous Chondrite and Asteroid Parent Body Processes

José C. Aponte,<sup>1</sup> Hannah L. McLain,<sup>1–3</sup> Daniel Saeedi,<sup>4</sup> Amirali Aghazadeh,<sup>4</sup> Jamie E. Elsilá,<sup>1</sup> Daniel P. Glavin,<sup>1</sup> and Jason P. Dworkin<sup>1</sup>

## Abstract

Carbonaceous chondrite (CC) meteorites are fragments of planetesimals that hold clues about the early solar system's organic matter. Amino acids are key to life on Earth; thus their study from extraterrestrial samples may help identify signs of prebiotic chemistry and life on other planets and may reveal how life as we know it began. This study analyzed amino acid concentrations and distributions in 42 CC samples, including returned samples from asteroids Ryugu and Bennu, to investigate the relationship between amino acid composition and parent body processes. We performed a statistical analysis of the amino acid molecular distributions and abundances in the context of meteoritic hydrogen, carbon, nitrogen, and carbonate total contents to explore the links between these organic species and thermal and aqueous processing experienced in the parent bodies. We also evaluated whether meteoritic amino acid ratios can be used as anti-biosignatures, and we re-evaluated the links between L-isovaline enantiomeric excesses and parent body aqueous alteration. While some trends were observed, correlations between amino acid distributions and alteration proxies (H, C, N, carbonates, enantiomeric excess) were generally weak, which indicates the need for larger sample sets. Thermal metamorphism correlated with lower amino acid and elemental [hydrogen (H), carbon (C), and nitrogen (N)] abundances, consistent with diverse parent bodies or localized processing. Ryugu samples exhibited significant amino acid variations despite similar bulk elemental compositions due to parent body heterogeneity. No strong statistical correlations were found between amino acid concentrations and H, C, or N content, which diminishes the reliability of predictions of amino acid abundances based solely on observed elemental abundances. While Ryugu and Bennu may share a common, Ceres-like parent body, observed differences in chemical composition suggest diverse evolutionary pathways. Finally, principal component analysis of amino acid and elemental data revealed distinct groupings that place Ryugu samples in a potentially unique subgroup and Bennu within the C2-ung chondrite group. These findings underscore the need for further study of such materials, especially given our discovery of their distinct nature, and emphasizes the insights gleaned from the ability to analyze returned asteroid samples. Key Words: Amino acids—OSIRIS REx—Hayabusa2—Prebiotic synthesis—Statistical analysis—Meteoritic organics—Biosignatures. Astrobiology 00, 000–000.

## 1. Introduction

Meteorites are fragments of asteroids, extinct comets, and planetary bodies such as the Moon and Mars. These extraterrestrial rocks contain a wealth of information

about the nature of the dust, gas, and organic matter present when and where they formed in the solar nebula, protoplanetary disk, or parent body. Many meteorites are composed of minerals that formed in the cold outer regions of the solar nebula, as well as water-soluble organic compounds (e.g.,

<sup>1</sup>Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA.

<sup>2</sup>Department of Chemistry, The Catholic University of America, Washington, DC, USA.

<sup>3</sup>Center for Space Science and Technology, University of Maryland Baltimore County, Baltimore, Maryland, USA.

<sup>4</sup>School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA.

amino acids) that predate planetary formation (Ehrenfreund and Cami, 2010; Glavin et al., 2018). Furthermore, the meteoritic organic matter reveals potential mechanisms and ingredients that contributed to the emergence of biological systems. It also aids in the search for life beyond our planet by identifying pivotal organic compounds that could signal prebiotic chemistry and help differentiate these from biological signatures on other planetary bodies (Johnson et al., 2018; Cleaves et al., 2023).

Carbonaceous chondrites (CCs) are classified into distinct groups (including CI, CM, CR, C2-ung, etc.), each with a unique set of petrological, mineralogical, and bulk chemical compositions. Variations in hydrogen (H), carbon (C), and nitrogen (N) contents among these groups offer insights into the different processes and environments they have experienced, including aqueous processing (Busemann et al., 2006; Alexander et al., 2007). A number is also assigned to CCs based on how they were changed by processes that operated in their parent bodies. Type 1 chondrites were the most affected by water at low temperatures. Type 2 chondrites experienced intermediate levels of aqueous alteration. Type 3 chondrites were the least affected by water and thermal metamorphism, while types 3.1–3.9 experienced an increasingly intense thermal metamorphism (Van Schmus and Hayes, 1974; Weisberg et al., 2006). Types 4–6 are assigned to chondrites that experienced sufficient thermal metamorphism to have equilibrated their minerals and recrystallize, hence erased, primary petrologic features to varying extents (Huss et al., 2006). Aqueous alteration of meteorite organic compounds occurred when liquid water interacted with minerals and organic molecules, which caused significant chemical synthesis and structural transformations. These interactions took place in meteorite parent bodies where water may have existed in various forms, including liquid in transient or stable environments (Zolensky and McSween, 1988). Mighei-type (CM) and Renazzo-type (CR) chondrites underwent wide ranges in the extents of aqueous alteration that they experienced (i.e., both groups include types 1–3). The extent of alteration is reflected in their water/OH contents (expressed as the bulk hydrogen weight percent; H wt.%) stored in phyllosilicate minerals. Broadly, the abundances of amino acids, particularly alpha amino acids, decrease with increasing extents of aqueous alteration (Martins et al., 2007; Glavin et al., 2010; Elsila et al., 2016).

The analysis of extraterrestrial samples, for example, CCs, achondrites, and other meteorites, has typically been done with two main sample caveats in mind, which include an unknown level of terrestrial contamination and an unknown link to specific parent bodies in the asteroid belt. However, recently JAXA's Hayabusa2 and NASA's Origins, Spectral Interpretation, Resource Identification, Security-Regolith Explorer (OSIRIS-REx) sample return missions to near Earth asteroids Ryugu and Bennu, respectively, have enabled for the first time the study of extraterrestrial materials that have been protected from the terrestrial biosphere (Tachibana et al., 2022; Lauretta et al., 2021, 2022). An important question regarding these asteroid samples, however, is their potential genetic relationship with meteorite samples collected on Earth, which are available for study. CCs are classified based on petrologic properties and by their elemental ratios, bulk composition, and oxygen isotopic measurements

(Weisberg et al., 2006; Rubin et al., 2007; Alexander et al., 2013); however, these analyses can fall short on explaining the organic composition and the effects of aqueous processing that occurred in the parent body.

Aliphatic amino acids have been extensively studied in CCs (Pizzarello and Cronin, 1998; Botta et al., 2002; Elsila et al., 2016) due to their critical role in Earth's biosphere. Their presence in these meteorites suggests that such life-building molecules could be widespread in the solar system. This supports the idea that the basic ingredients for life might be common and thus increases the possibility of life elsewhere. Additionally, studying these amino acids helps refine chemical evolution models, which improves our understanding of how simple organic molecules evolve into complex biomolecules. Varying levels of parent body aqueous processing are associated with lower concentrations of meteoritic amino acids (Ehrenfreund et al., 2001; Glavin et al., 2010). Specifically, the  $\beta$ -alanine/glycine ( $\beta$ -Ala/Gly) molar ratios in CCs serve as indicators of the mechanism of amino acid formation (e.g., Strecker, formose-like, Michael addition reactions) and/or destruction, which empirically correlates to the extent of aqueous alteration with higher ratios correlating with higher alteration levels and lower amino acid abundances (Glavin and Dworkin, 2009; Glavin et al., 2010).

The  $\alpha$ -dialkyl amino acid isovaline is scarce in terrestrial biology. Nevertheless, meteoritic isovaline has shown up to  $\sim 20\%$  L-enantiomeric excess (L-*ee*) in some CCs that isotopic studies have shown to be indigenous (Pizzarello et al., 2003; Glavin and Dworkin, 2009; Burton and Berger, 2018). This, added to its stability and resistance to racemization, provides valuable insights into amino acid formation and preservation in chondrites, as well as into the origins of homochirality in Earth's living organisms (Bonner et al., 1979). Glavin and Dworkin (2009) suggested a positive relationship between meteoritic aqueous alteration and the magnitude of L-isovaline *ee* in CI, CM, and CR type CCs. However, there have been no systematic studies of correlations between amino acid concentrations, H, C, and N bulk contents, aqueous processing variables (e.g., amino acid ratios and carbonate abundances), and enantiomeric excesses.

In this study, we analyzed the abundances and molecular distributions of 34 aliphatic amino acids (AA [C]), including the L-isovaline *ee* (Iva L-*ee*), in 16 CCs with evidence of limited terrestrial contamination and with varying levels of aqueous alteration and low thermal alteration from the C2, C2-ung, CM1/2, CM2, and CR2 types. We used previously published bulk weight percentages of hydrogen (H wt.%), carbon (C wt.%), and nitrogen (N wt.%), and concentrations of carbonates ( $\text{CO}_3^{2-}$ ) to assess statistical correlations between meteoritic amino acid abundances, aqueous alteration, and enantiomeric excess. We excluded CV3, CO3, CH3, and CB from this work because their evolution was dominated by thermal metamorphism. The extent of contamination in the analyzed samples was assessed by analyses of the molecular distribution and enantiomeric compositions of proteinogenic amino acids. Finally, we used these statistical analyses to evaluate the extent of alteration of samples from asteroids Ryugu and Bennu relative to the meteorites found on Earth.

## 2. Materials and Methods

We evaluated the C2 to C6 aliphatic primary amino acid abundances and molecular diversities (including enantiomeric distributions) in 16 CCs (Supplementary Table S1). All glass and ceramics were cleaned by heating at 500°C overnight to combust organics. All samples were processed in parallel with similarly heated serpentinite and procedural blanks. Meteorite chips were separately crushed into powders using a ceramic mortar and pestle. The samples were then transferred to glass ampoules and flame-sealed for extraction at 100°C for 24 h in 1 mL of Milli-Q ultrapure water (Millipore Integral 10, 18.2 M $\Omega$ -cm, <3 ppb TOC). The water supernatants were then removed, dried under reduced pressure, and desalted using a cation-exchange resin (AG50W-X8, 100–200 mesh, hydrogen form, BIO-RAD). The isolated amino acids were derivatized before identification, quantification, and enantiomeric separation using *o*-phthaldialdehyde/*N*-acetyl-L-cysteine. Amino acids were chromatographically resolved using a Waters BEH C18 column (2.1  $\times$  50 mm, 1.7  $\mu$ m bead) and a Waters BEH phenyl column (2.1  $\times$  150 mm, 1.7  $\mu$ m bead) in series. Both columns were maintained at 30°C. The analyses were performed using a Waters Xevo G2-XS liquid chromatograph with UV fluorescence and quadrupole time-of-flight mass spectrometry detection (LC-FD/Q-ToF-MS) operating in positive ion mode and following previously published methods (Glavin et al., 2006, 2010, 2025).

### 2.1. Classification and statistical analysis

In our classification study using the Random Forest classifier from *scikit-learn* [2], we predicted meteorite types based on chemical properties (H wt.%, C wt.%, N wt.%, and AA [C]). We refined the dataset by removing samples with missing values and meteorite types with single occurrences, then standardized features using *StandardScaler*. Our validation approach employed a twofold *StratifiedKfold* cross-validation, with nested Leave-One-Out cross-validation to optimize the number of estimators based on the highest weighted F1-score. We evaluated model performance using weighted F1-score, Precision, and Recall metrics. To ensure robust assessment, we repeated this process across 20 random seeds, averaging the metrics across all seeds and folds.

## 3. Results

### 3.1. Amino acid analyses

Examination of the exact mass chromatogram of the hot-water extracts of the carbonaceous meteorites shows the amino alkanolic acid isomers that eluted in the 0–35 min region (Supplementary Data, Supplementary Figure S1). The amounts of meteorite sample extracted (50–200 mg), their site and year of collection, and petrologic types are shown in Supplementary Table S1. All identified amino acid peaks were confirmed by comparison with the UV fluorescence and exact mass retention times of pure standards using previously published methods (e.g., Glavin et al., 2006, 2012, 2025). We were able to obtain separation of all possible C<sub>5</sub> amino acids including D- and L-isovaline enantiomers (Supplementary Fig. S2, peaks 26 and 28). We did not investigate the abundance of amino acids after acid hydrolyses. The total

concentration of unhydrolyzed amino acids ranged from 20 to 850 nmol/g of meteorite in CM2, 130–970 nmol/g of meteorite in C2, 4–3600 nmol/g of meteorite in CM-anomalous, and 1–277,100 nmol/g of meteorite in CR2 (Tables 1 and 2). All samples exhibited racemic or near-racemic mixtures of isovaline (within experimental error) except for LEW 85311 (L-isovaline *ee* = 3.5  $\pm$  2.9; Supplementary Fig. S2).

We plotted the AA [C], bulk H, C, and N wt.% for a Bennu aggregate sample (OREX-803001-0), two Ryugu aggregate samples (A0106 and C0107), and 33 meteorites from the CI1, C2, C2-ung, CM1/2, CM1, CM2, CM3, CM-an, CR1, and CR2 subgroups in Figure 1. The bulk carbon content (C wt.%) was higher in the majority of samples relative to the H and N wt.% values. Samples SCO 060043 (CM1), GRO 95577 (CR1), and GRO 17063 (CR2) were exceptions in which the H wt.% was higher than the C wt.%. The N wt.% was lower than the H wt.% and C wt.% in all samples. The amount of H in H<sub>2</sub>O and OH (bulk H wt.%) in Bennu sample OREX-803001-0 ranked 22nd among the 36 studied samples, while that in Ryugu samples A0106 and C0107 ranked 9th and 16th, respectively. However, OREX-803001-0 exhibited the highest C wt.% and the second highest N wt.% among all studied samples, yet its amino acids concentration ranked 24.

### 3.2. Statistical analyses

We analyzed Pearson's *r* correlations for all pairs of the variables: H wt.%, C wt.%, N wt.%, AA [C],  $\beta$ -Ala/Gly,  $\alpha$ -AIB/Gly,  $\beta$ -Ala/ $\alpha$ -AIB,  $\beta$ -Ala/D-Ala, carbonate [CO<sub>3</sub><sup>2-</sup>], and Iva L-*ee* (Fig. 2 and Supplementary Table S3). To calculate the Pearson's *r* correlation between any two variables, we excluded samples with missing values for either variable and then computed the correlation. Statistical significance is defined as *p* < 0.05, while *p*  $\geq$  0.05 was considered not significant. Correlation strength is classified as strong (*r* = 0.7–1.0), moderate (*r* = 0.4–0.7), weak (*r* = 0.1–0.4), or negligible (*r* = 0.0–0.1). In addition to Pearson's *r*, we also used the Maximal Information Coefficient (MIC; Reshef et al., 2011; Pedregosa et al., 2011) to detect potential nonlinear relationships. We interpreted MIC values close to 0 as suggesting little to no association, whereas values that approach 1 indicated a strong association, whether linear or nonlinear (Supplementary Table S4).

H wt.% showed weak positive correlations with both C wt.% (*r* = 0.32, *p* < 0.05) and N wt.% (*r* = 0.34, *p* < 0.05). A strong positive correlation was found between C wt.% and N wt.% (*r* = 0.81, *p* < 10<sup>−8</sup>). Weak and statistically insignificant correlations were observed between H wt.% and amino acid concentration (AA [C]) (*r* = −0.16, *p* > 0.31), H wt.% and  $\alpha$ -AIB/Gly (*r* = 0.29, *p* > 0.08), or H wt.%. No linear correlation was observed between H wt.% and  $\beta$ -Ala/D-Ala (*r* = 0.06, *p* > 0.71).

Pearson's *r* correlation coefficients were calculated to assess the relationships between amino acid ratios. Positive, moderate, and statistically significant correlations were observed between  $\beta$ -Ala/Gly and  $\beta$ -Ala/ $\alpha$ -AIB (*r* = 0.43, *p* < 0.01) and between  $\beta$ -Ala/Gly and  $\beta$ -Ala/D-Ala (*r* = 0.65, *p* < 10<sup>−5</sup>). In contrast, a weak and statistically insignificant correlation was observed between  $\beta$ -Ala/D-Ala and  $\beta$ -Ala/ $\alpha$ -AIB (*r* = 0.24, *p* > 0.16), as well as between  $\beta$ -Ala/ $\alpha$ -AIB and  $\alpha$ -AIB/Gly (*r* = −0.18, *p* > 0.29). No linear correlation

TABLE 1. BLANK-CORRECTED ABUNDANCES (NMOL/G OF METEORITE) OF TWO- TO SIX-CARBON AMINO ACIDS IN THE NON-HYDROLYZED (FREE) HOT-WATER EXTRACTS OF METEORITES POWDERS MEASURED BY LC-FD/Q-ToF-MS<sup>a</sup>

| Amino acid                                     | NWA 13456  |  | Essebi      |  | Kolang           |  | GRA 98005  |  | Mighei     |  | Murray    |  | Nogoya     |  | LAP 02333  |  |
|------------------------------------------------|------------|--|-------------|--|------------------|--|------------|--|------------|--|-----------|--|------------|--|------------|--|
|                                                | C2         |  | C2-ung      |  | CM1/2            |  | CM2        |  | CM2        |  | CM2       |  | CM2        |  | CM2        |  |
| D-Aspartic acid                                | 5.8 ± 0.1  |  | 1.0 ± 0.01  |  | 0.10 ± 0.01      |  | 0.3 ± 0.01 |  | 0.4 ± 0.04 |  | 0.7 ± 0.2 |  | 0.7 ± 0.1  |  | 4.7 ± 0.1  |  |
| L-Aspartic acid                                | 27 ± 0.3   |  | 2.6 ± 0.03  |  | 0.12 ± 0.01      |  | 0.4 ± 0.01 |  | 0.6 ± 0.03 |  | 0.9 ± 0.2 |  | 2.1 ± 0.1  |  | 4.7 ± 0.1  |  |
| L-Glutamic acid                                | 11 ± 0.1   |  | 0.2 ± 0.02  |  | 0.29 ± 0.09      |  | 0.1 ± 0.1  |  | 1.1 ± 0.02 |  | 1.7 ± 0.2 |  | 1.2 ± 0.1  |  | 3.4 ± 0.1  |  |
| D-Glutamic acid                                | 2.3 ± 0.1  |  | 0.1 ± 0.01  |  | 0.28 ± 0.01      |  | <0.1       |  | 0.6 ± 0.01 |  | 1.0 ± 0.2 |  | 0.4 ± 0.0  |  | 1.7 ± 0.1  |  |
| D-Serine                                       | 35.7 ± 1   |  | 0.1 ± 0.02  |  | 0.04 ± 0.01      |  | <0.1       |  | 0.1 ± 0.01 |  | 0.3 ± 0.1 |  | 0.4 ± 0.0  |  | 2.2 ± 0.02 |  |
| L-Serine                                       | 179 ± 3    |  | 0.6 ± 0.1   |  | 0.06 ± 0.01      |  | <0.1       |  | 0.1 ± 0.04 |  | <0.1      |  | 0.8 ± 0.2  |  | 2.4 ± 0.01 |  |
| Glycine                                        | 494 ± 27   |  | 38 ± 3      |  | 3.0 ± 0.1        |  | 6.8 ± 0.4  |  | 31 ± 3     |  | 67 ± 18   |  | 43 ± 7     |  | 357 ± 7    |  |
| $\beta$ -Alanine                               | 102 ± 2    |  | 60 ± 3      |  | 1.1 ± 0.1        |  | 3.6 ± 0.1  |  | 20 ± 0     |  | 13 ± 4    |  | 23 ± 3     |  | 58 ± 0.4   |  |
| D-Alanine                                      | 23 ± 0.2   |  | 1.7 ± 0.1   |  | 0.79 ± 0.05      |  | 0.8 ± 0.02 |  | 2.2 ± 0.1  |  | 13 ± 4    |  | 1.3 ± 0.2  |  | 38 ± 0.5   |  |
| L-Alanine                                      | 51 ± 0.7   |  | 1.2 ± 0.1   |  | 0.78 ± 0.05      |  | 0.7 ± 0.03 |  | 2.5 ± 0.1  |  | 16 ± 4    |  | 4.6 ± 0.9  |  | 60 ± 0.7   |  |
| $\gamma$ -ABA + D,L- $\beta$ -AIB <sup>b</sup> | 5.7 ± 0.7  |  | 15 ± 7      |  | 1.0 ± 0.1        |  | 1.7 ± 0.1  |  | 6.1 ± 0.1  |  | 10 ± 3    |  | 11 ± 2     |  | 37 ± 5     |  |
| D- $\beta$ -ABA                                | 2.3 ± 0.2  |  | 1.6 ± 0.3   |  | 0.59 ± 0.03      |  | 1.1 ± 0.1  |  | 4.9 ± 0.1  |  | 7.2 ± 1.7 |  | 2.8 ± 0.6  |  | 25 ± 0.2   |  |
| L- $\beta$ -ABA                                | 4.1 ± 0.5  |  | 2.5 ± 0.5   |  | 0.50 ± 0.03      |  | 1.3 ± 0.1  |  | 5.3 ± 0.0  |  | 6.3 ± 1.9 |  | 3.2 ± 0.6  |  | 36 ± 0.2   |  |
| $\alpha$ -AIB                                  | 4.4 ± 0.7  |  | 5.1 ± 1.3   |  | 1.2 ± 0.1        |  | 0.9 ± 0.1  |  | 33 ± 0.3   |  | 74 ± 16   |  | 7.5 ± 1.7  |  | 83 ± 1     |  |
| D,L- $\alpha$ -ABA                             | 1.0 ± 0.1  |  | 0.4 ± 0.1   |  | 0.53 ± 0.02      |  | 0.2 ± 0.10 |  | 1.0 ± 0.0  |  | 14 ± 2    |  | 0.6 ± 0.1  |  | 25 ± 0.3   |  |
| $\epsilon$ -ACA                                | 0.7 ± 0.1  |  | 3.8 ± 0.5   |  | 5.6 ± 0.2        |  | 0.9 ± 0.1  |  | 1.6 ± 0.1  |  | <0.1      |  | <0.1       |  | 10 ± 0.2   |  |
| Total C2-C5 amino acids                        | 949 ± 37   |  | 135 ± 16    |  | 10 ± 1           |  | 19 ± 1     |  | 111 ± 4    |  | 226 ± 56  |  | 103 ± 17   |  | 747 ± 16   |  |
| Total C2-C5 (w/o $\epsilon$ -ACA)              | 948 ± 36   |  | 131 ± 15    |  | 5 ± 0.4          |  | 18 ± 1     |  | 109 ± 4    |  | 226 ± 56  |  | 103 ± 17   |  | 737 ± 16   |  |
|                                                |            |  |             |  |                  |  |            |  |            |  |           |  |            |  |            |  |
| Amino acid                                     | LEW 85311  |  | WIS 91600   |  | EET 92042        |  | PCA 91082  |  | QUE 99177  |  | GRA 06100 |  | GRO 03116  |  | GRO 17063  |  |
|                                                | CM-an      |  | CM-an       |  | CR2              |  | CR2        |  | CR2        |  | CR2       |  | CR2        |  | CR2        |  |
| D-Aspartic acid                                | 5.3 ± 0.1  |  | <0.1        |  | 1,028 ± 157      |  | 15 ± 0.1   |  | 0.68       |  | <0.1      |  | 0.1 ± 0.01 |  | <0.1       |  |
| L-Aspartic acid                                | 7.1 ± 0.1  |  | 0.2 ± 0.0   |  | 1,016 ± 147      |  | 15 ± 0.1   |  | 0.69       |  | <0.1      |  | 0.2 ± 0.01 |  | <0.1       |  |
| L-Glutamic acid                                | 8.4 ± 0.2  |  | <0.1        |  | 10,088 ± 1743    |  | 110 ± 0.6  |  | 1.61       |  | 0.2 ± 0.2 |  | 0.1 ± 0.02 |  | <0.1       |  |
| D-Glutamic acid                                | 4.9 ± 0.2  |  | <0.1        |  | 10,180 ± 1743    |  | 68 ± 0.5   |  | 1.65       |  | <0.1      |  | <0.1       |  | <0.1       |  |
| D-Serine                                       | 5.9 ± 0.1  |  | <0.1        |  | 2584 ± 1420      |  | 36 ± 0.1   |  | 0.55       |  | <0.1      |  | 0.1 ± 0.01 |  | <0.1       |  |
| L-Serine                                       | 8.4 ± 0.2  |  | 0.6 ± 0.04  |  | 2266 ± 1237      |  | 42 ± 0.1   |  | 0.52       |  | 0.4 ± 0.0 |  | 0.1 ± 0.03 |  | 1.4 ± 0.04 |  |
| Glycine                                        | 803 ± 118  |  | 0.8 ± 0.2   |  | 82,823 ± 22,501  |  | 3747 ± 5   |  | 99.92      |  | 0.1 ± 0.9 |  | 1.4 ± 0.4  |  | <0.1       |  |
| $\beta$ -Alanine                               | 76 ± 2     |  | 0.5 ± 0.02  |  | 4162 ± 1,183     |  | 96 ± 0.8   |  | 8.24       |  | <0.1      |  | 4.3 ± 0.1  |  | 0.5 ± 0.03 |  |
| D-Alanine                                      | 143 ± 5    |  | <0.1        |  | 40,107 ± 9,275   |  | 568 ± 0.3  |  | 4.15       |  | <0.1      |  | <0.1       |  | <0.1       |  |
| $\gamma$ -ABA + D,L- $\beta$ -AIB <sup>b</sup> | 224 ± 6    |  | 0.8 ± 0.1   |  | 36,461 ± 7,806   |  | 610 ± 0.7  |  | 10.07      |  | <0.1      |  | 0.7 ± 0.04 |  | <0.1       |  |
| D- $\beta$ -ABA                                | 90 ± 12    |  | 1.2 ± 0.0   |  | 2620 ± 982       |  | 65 ± 1     |  | 0.68       |  | <0.1      |  | 1.8 ± 0.1  |  | 0.4 ± 0.1  |  |
| L- $\beta$ -ABA                                | 47 ± 1     |  | <0.1        |  | 2855 ± 580       |  | 46 ± 0.5   |  | 1.11       |  | <0.1      |  | <0.1       |  | <0.1       |  |
| $\alpha$ -AIB                                  | 61 ± 2     |  | 0.1 ± 0.03  |  | 3160 ± 852       |  | 50 ± 0.4   |  | 2.25       |  | <0.1      |  | <0.1       |  | <0.1       |  |
| D,L- $\alpha$ -ABA                             | 290 ± 5    |  | 0.1 ± 0.01  |  | 56,825 ± 15,592  |  | 452 ± 15   |  | 41.90      |  | <0.1      |  | <0.1       |  | <0.1       |  |
| $\epsilon$ -ACA                                | 172 ± 3    |  | 0.02 ± 0.01 |  | 20,859 ± 5,653   |  | 296 ± 2    |  | 4.15       |  | <0.1      |  | <0.1       |  | <0.1       |  |
| Total C2-C5 amino acids                        | 78 ± 2     |  | 5.9 ± 0.3   |  | 51,371 ± 13,566  |  | 107 ± 1    |  | 0.75       |  | 19 ± 1    |  | 112 ± 4    |  | 0.8 ± 0.2  |  |
| Total C2-C5 (w/o $\epsilon$ -ACA)              | 2025 ± 157 |  | 10 ± 1      |  | 328,405 ± 84,667 |  | 6324 ± 29  |  | 179        |  | 20 ± 2    |  | 120 ± 4    |  | 3 ± 0.3    |  |
|                                                | 1947 ± 154 |  | 4 ± 0       |  | 277,034 ± 71,101 |  | 6216 ± 27  |  | 178        |  | 1 ± 1     |  | 9 ± 1      |  | 2 ± 0.1    |  |

Sample petrologic type given under sample name.

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

<sup>b</sup>The amino acids  $\gamma$ -ABA and  $\beta$ -AIB coelute and the D- and L- $\beta$ -AIB enantiomers could not be separated under the chromatographic conditions.

LC-FD/Q-ToF-MS, liquid chromatograph with UV fluorescence and quadrupole time-of-flight mass spectrometry detection; OPA/NAC, o-phthalaldehyde/N-acetyl-L-cysteine.



TABLE 2. BLANK-CORRECTED ABUNDANCES (NMOL/G OF METEORITE) OF FIVE-CARBON AMINO ACIDS IN THE NON-HYDROLYZED (FREE) HOT-WATER EXTRACTS OF METEORITES POWDERS MEASURED BY LC-FD/Q-ToF-MS<sup>a</sup>

| Amino acid                                   | NWA 13456  |  | Eschbi    |  | Kolang           |  | GRA 98005   |  | Mighei      |  | Murray     |  | Nogoya     |  | LAP 02333  |  |
|----------------------------------------------|------------|--|-----------|--|------------------|--|-------------|--|-------------|--|------------|--|------------|--|------------|--|
|                                              | C2         |  | C2-Ung    |  | CM1/2            |  | CM2         |  | CM2         |  | CM2        |  | CM2        |  | CM2        |  |
| D-Norvaline (D-2-apa)                        | <0.1       |  | <0.1      |  | <0.1             |  | <0.1        |  | <0.1        |  | 2.5 ± 0.6  |  | <0.1       |  | 1.0 ± 0.04 |  |
| L-Norvaline (L-2-apa)                        | <0.1       |  | <0.1      |  | <0.1             |  | <0.1        |  | <0.1        |  | 2.1 ± 0.6  |  | <0.1       |  | 0.6 ± 0.5  |  |
| D-Isovaline (D-2-a-2-mba)                    | 0.7 ± 0.2  |  | <0.1      |  | 1.16 ± 0.03      |  | 0.04 ± 0.01 |  | 2.0 ± 0.02  |  | 38 ± 1     |  | 0.4 ± 0.01 |  | 3.9 ± 0.2  |  |
| L-Isovaline (L-2-a-2-mba)                    | 0.7 ± 0.2  |  | <0.1      |  | 1.29 ± 0.02      |  | 0.1 ± 0.01  |  | 1.7 ± 0.05  |  | 38 ± 1     |  | 0.4 ± 0.01 |  | 3.7 ± 0.1  |  |
| D-Valine (D-2-α-3-mba)                       | 0.4 ± 0.3  |  | <0.1      |  | 0.7 ± 0.1        |  | <0.1        |  | 0.1 ± 0.02  |  | 9.1 ± 0.3  |  | 0.1 ± 0.01 |  | 4.4 ± 0.2  |  |
| L-Valine (L-2-α-3-mba)                       | 1.3 ± 0.5  |  | <0.1      |  | 1.33 ± 0.01      |  | 0.2 ± 0.03  |  | 0.4 ± 0.02  |  | 10 ± 0.4   |  | 0.8 ± 0.03 |  | 4.1 ± 0.1  |  |
| D,L-3-apa <sup>b</sup>                       | 1.6 ± 0.6  |  | 0.1 ± 0.1 |  | 1.90 ± 0.03      |  | 0.1 ± 0.04  |  | 0.8 ± 0.04  |  | 4.7 ± 0.2  |  | 0.8 ± 0.04 |  | 5.9 ± 0.3  |  |
| D,L- and <i>allo</i> -3-α-2-mba <sup>b</sup> | 5.6 ± 1.3  |  | 1.8 ± 1.5 |  | 1.74 ± 0.03      |  | <0.1        |  | 2.7 ± 0.03  |  | 25 ± 1     |  | 1.9 ± 0.1  |  | 77.8 ± 2.6 |  |
| 3-α-3-mba <sup>c</sup>                       | <0.1       |  | <0.1      |  | <0.1             |  | <0.1        |  | <0.1        |  | 1.5 ± 0.01 |  | <0.1       |  | <0.1       |  |
| 3-α-2,2-dmpa                                 | 1.4 ± 0.3  |  | <0.1      |  | 1.09 ± 0.03      |  | 0.1 ± 0.01  |  | 0.5 ± 0.02  |  | 4.0 ± 0.3  |  | 0.4 ± 0.04 |  | 4.7 ± 0.2  |  |
| D,L-3-α-2-epa <sup>d,e</sup>                 | 1.2 ± 0.3  |  | <0.1      |  | <0.1             |  | <0.1        |  | 0.4 ± 0.02  |  | 2.2 ± 0.1  |  | 0.6 ± 0.1  |  | 4.2 ± 0.2  |  |
| D,L-4-apa <sup>b</sup>                       | 1.5 ± 0.6  |  | <0.1      |  | 2.9 ± 0.1        |  | <0.1        |  | 0.5 ± 0.3   |  | 0.3 ± 0.1  |  | 0.3 ± 0.1  |  | 3.0 ± 1.4  |  |
| D,L-4-α-2-mba <sup>d</sup>                   | 3.9 ± 0.7  |  | <0.1      |  | 2.6 ± 0.1        |  | <0.1        |  | <0.1        |  | 2.0 ± 0.1  |  | 0.4 ± 0.05 |  | 2.6 ± 0.1  |  |
| D,L-4-α-3-mba <sup>d</sup>                   | 0.1 ± 0.02 |  | <0.1      |  | 0.45 ± 0.02      |  | <0.1        |  | 0.02 ± 0.01 |  | 0.2 ± 0.01 |  | <0.1       |  | <0.1       |  |
| 5-apa                                        | 5.2 ± 1.6  |  | <0.1      |  | 3.0 ± 0.3        |  | 0.2 ± 0.01  |  | 0.4 ± 0.01  |  | 5.0 ± 0.1  |  | 0.9 ± 0.02 |  | 4.4 ± 0.1  |  |
| Total C6 amino acids                         | 24 ± 7     |  | 2 ± 2     |  | 18 ± 1           |  | 1 ± 0       |  | 9 ± 1       |  | 146 ± 5    |  | 7 ± 1      |  | 120 ± 6    |  |
| Total amino acids                            | 972 ± 43   |  | 133 ± 17  |  | 23 ± 2           |  | 19 ± 1      |  | 118 ± 4     |  | 372 ± 60   |  | 110 ± 17   |  | 857 ± 22   |  |
|                                              |            |  |           |  |                  |  |             |  |             |  |            |  |            |  |            |  |
| Amino acid                                   | LEW 85311  |  | WIS 91600 |  | EET 92042        |  | PCA 91082   |  | QUE 99177   |  | GRA 06100  |  | GRO 03116  |  | GRO 17063  |  |
|                                              | CM-an      |  | CM-an     |  | CR2              |  | CR2         |  | CR2         |  | CR2        |  | CR2        |  | CR2        |  |
| D-Norvaline (D-2-apa)                        | 17 ± 2     |  | <0.1      |  | <0.1             |  | 16 ± 2      |  | 8.2 ± 0.5   |  | <0.1       |  | <0.1       |  | <0.1       |  |
| L-Norvaline (L-2-apa)                        | 18 ± 2     |  | <0.1      |  | <0.1             |  | 14 ± 2      |  | 8.3 ± 0.6   |  | <0.1       |  | <0.1       |  | <0.1       |  |
| D-Isovaline (D-2-a-2-mba)                    | 121 ± 16   |  | <0.1      |  | 2.4 ± 0.3        |  | 140 ± 1     |  | 47 ± 2      |  | <0.1       |  | <0.1       |  | <0.1       |  |
| L-Isovaline (L-2-a-2-mba)                    | 148 ± 21   |  | <0.1      |  | 3.7 ± 0.6        |  | 140 ± 2     |  | 48 ± 1      |  | <0.1       |  | 0.1 ± 0.01 |  | <0.1       |  |
| D-Valine (D-2-α-3-mba)                       | 272 ± 39   |  | <0.1      |  | <0.1             |  | 102 ± 2     |  | 29 ± 2      |  | <0.1       |  | <0.1       |  | <0.1       |  |
| L-Valine (L-2-α-3-mba)                       | 329 ± 43   |  | <0.1      |  | 3.9 ± 0.7        |  | 105 ± 3     |  | 33 ± 1      |  | <0.1       |  | 0.4 ± 0.01 |  | <0.1       |  |
| D,L-3-apa <sup>b</sup>                       | 48 ± 3     |  | <0.1      |  | 9.0 ± 0.6        |  | 10 ± 0.2    |  | 5.1 ± 0.1   |  | <0.1       |  | <0.1       |  | <0.1       |  |
| D,L- and <i>allo</i> -3-α-2-mba <sup>b</sup> | 575 ± 75   |  | <0.1      |  | 7.0 ± 0.4        |  | 82 ± 4      |  | 15 ± 1      |  | <0.1       |  | <0.1       |  | <0.1       |  |
| 3-α-3-mba <sup>c</sup>                       | <0.1       |  | <0.1      |  | <0.1             |  | <0.1        |  | <0.1        |  | <0.1       |  | <0.1       |  | <0.1       |  |
| 3-α-2,2-dmpa                                 | 41 ± 5     |  | <0.1      |  | 7.9 ± 0.4        |  | 2.1 ± 0.02  |  | 2.7 ± 0.2   |  | <0.1       |  | <0.1       |  | <0.1       |  |
| D,L-3-α-2-epa <sup>d,e</sup>                 | 12 ± 1     |  | <0.1      |  | 12 ± 2           |  | 3.0 ± 0.1   |  | 6.6 ± 0.5   |  | <0.1       |  | <0.1       |  | <0.1       |  |
| D,L-4-apa <sup>b</sup>                       | 47 ± 31    |  | <0.1      |  | 16 ± 1           |  | 11 ± 6      |  | 11 ± 8      |  | <0.1       |  | <0.1       |  | <0.1       |  |
| D,L-4-α-2-mba <sup>d</sup>                   | 14 ± 2.0   |  | <0.1      |  | 6.1 ± 0.2        |  | <0.1        |  | 13 ± 1      |  | <0.1       |  | <0.1       |  | <0.1       |  |
| D,L-4-α-3-mba <sup>d</sup>                   | 2.4 ± 0.3  |  | <0.1      |  | 29 ± 5           |  | 0.2 ± 0.01  |  | 13 ± 1      |  | <0.1       |  | <0.1       |  | <0.1       |  |
| 5-apa                                        | 31 ± 4     |  | <0.1      |  | 2.3 ± 0.3        |  | 4.6 ± 0.2   |  | 4.9 ± 0.1   |  | <0.1       |  | 0.3 ± 0.03 |  | <0.1       |  |
| Total C6 amino acids                         | 1677 ± 246 |  | <0.1      |  | 99 ± 12          |  | 631 ± 23    |  | 236 ± 10    |  | <0.1       |  | 1 ± 0      |  | <0.1       |  |
| Total amino acids                            | 3624 ± 400 |  | 4 ± 1     |  | 277,133 ± 71,113 |  | 6848 ± 50   |  | 414 ± 10    |  | 1 ± 1      |  | 10 ± 1     |  | 2 ± 1      |  |

Sample petrologic type given under sample name.

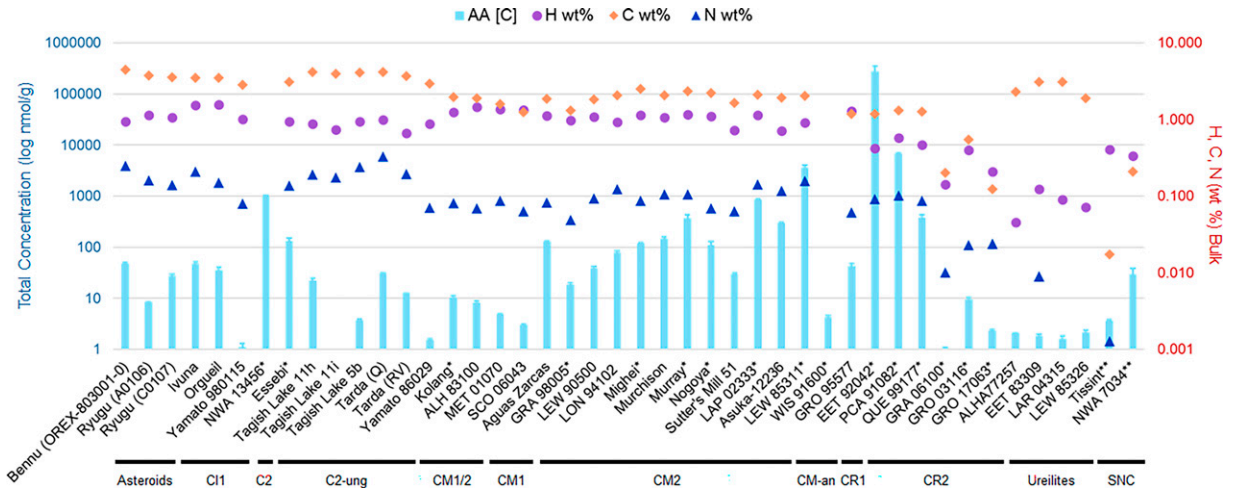
<sup>a</sup>Extracts were analyzed by OPA/NAC derivatization (15 min) and LC-FD/Q-ToF-MS. For the LC-FD/Q-ToF-MS data, the mono-isotopic masses ( $m/z$  379.13 ± 0.02) of each protonated OPA/NAC amino acid derivative (M + H<sup>+</sup>) were used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The uncertainties ( $\delta x$ ) are based on the standard deviation of the average value of 3–6 separate measurements ( $n$ ) with a standard error,  $\delta x = \sigma_x (n - 1)^{1/2}$ .

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

<sup>c</sup>3-α-3-mba co-elutes with one of the enantiomers of D,L-4-apa; therefore, upper limits for 3-α-3-mba were estimated by taking the difference in peak areas of the two D,L-4-apa enantiomers.

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

<sup>e</sup>Poor chromatographic resolution of D,L-3-α-2-epa prevented its accurate quantification; therefore, only upper limits are reported.



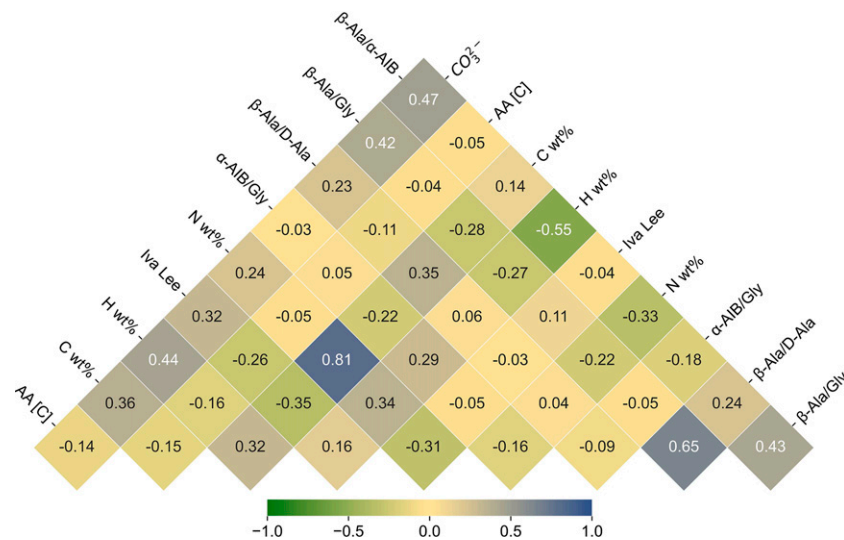
**FIG. 1.** Relative total amino acid concentrations (AA[C]), H, C, and N wt.% (Wright et al., 1988; Leshin et al., 1996; Grady et al., 1998; Burton et al., 2012, 2014a,b; Summons et al., 2014; Friedrich et al., 2016, 2018; Glavin et al., 2006, 2010, 2012, 2018, 2020, 2021, 2024, 2025; Glavin and Dworkin, 2009; Parker et al., 2023; Qasim et al., 2023; Alexander et al., 2007, 2012, 2013; Steele et al., 2012; Chennaoui-Aoudjehane et al., 2012; Agee et al., 2013; Williams et al., 2013). Data of newly published samples studied here are shown using (\*). Excepting asteroid samples, the meteorites are ordered from least to most aqueously altered (right to left) as inferred from their petrologic type assignments based on the abundance of H in OH/H<sub>2</sub>O (Alexander et al., 2007, 2012, 2013). (\*\*) These samples are heavily contaminated by biology (Summons et al., 2014; Schmitt-Kopplin et al., 2023). Data used to generate this figure are shown in Supplementary Table S2.

was detected between  $\beta$ -Ala/Gly and  $\alpha$ -AIB/Gly ( $r = -0.05$ ,  $p > 0.78$ ) or between  $\beta$ -Ala/D-Ala and  $\alpha$ -AIB/Gly ( $r = -0.09$ ,  $p > 0.61$ ).

Next, we determined Pearson's  $r$  correlations between meteoritic carbonate concentration ( $\text{CO}_3^{2-}$ ) and several variables: AA [C], hydrogen content (H wt.%), and amino acid ratios. A weak negative correlation was observed between  $\text{CO}_3^{2-}$  and AA [C] ( $r = -0.14$ ,  $p > 0.56$ ). Moderate positive correlations were found between  $\text{CO}_3^{2-}$  and H wt.% ( $r = 0.44$ ,

$p > 0.06$ )  $\text{CO}_3^{2-}$  and  $\beta$ -Ala/ $\alpha$ -AIB ( $r = 0.47$ ,  $p > 0.06$ ), and  $\text{CO}_3^{2-}$  and  $\beta$ -Ala/Gly ( $r = 0.42$ ,  $p > 0.08$ ). None of these correlations reached statistical significance.

Finally, we assessed Pearson's  $r$  correlations between isovaline *L-ee* (Iva *L-ee*) in 16 meteorites (Supplementary Table S4) and the variables shown in Figure 2. Weak positive correlations were identified between Iva *L-ee* and H wt.% ( $r = 0.16$ ,  $p > 0.53$ ), Iva *L-ee* and  $\beta$ -Ala/Gly ( $r = 0.11$ ,  $p > 0.65$ ), and Iva *L-ee* and  $\text{CO}_3^{2-}$  ( $r = 0.32$ ,  $p > 0.30$ ).



**FIG. 2.** Pearson's  $r$  correlation matrix of chemical and amino acid parameters in meteorite samples. The matrix displays correlations between H, C, N weight percentages (wt.%), amino acid concentrations (AA [C]), amino acid ratios ( $\beta$ -Ala/Gly,  $\beta$ -Ala/ $\alpha$ -AIB, and  $\beta$ -Ala/D-Ala), carbonate concentrations ( $\text{CO}_3^{2-}$ ), and *L*-isovaline enantiomeric excess (Iva *L-ee*). For each variable pair, samples with missing values for those specific variables were excluded before calculating the Pearson correlation coefficient ( $r$ ). The  $r$  values, shown within the squares, range from  $-1$  to  $1$ , indicating the strength and direction of linear relationships:  $1$  signifies a perfect positive correlation,  $-1$  a perfect negative correlation, and  $0$  no significant linear relationship. The threshold of significance ( $p$ -value) used was  $0.05$  (Supplementary Table S4). Color intensity corresponds to correlation strength. Data used to generate this figure are shown in Supplementary Table S3.

A weak negative correlation was found between Iva L-*ee* and C wt.% ( $r = -0.35$ ,  $p > 0.15$ ). No linear correlations were observed between Iva L-*ee* and  $\beta$ -Ala/D-Ala, or Iva L-*ee* and  $\alpha$ -AIB/Gly. However, none of these correlations reached statistical significance.

We employed the dataset comprising 44 samples (Supplementary Data) to analyze and categorize CCs based on the content of AA [C], H wt.%, C wt.%, and N wt.%. After removing meteorite types represented by only a single occurrence, our classification using Random Forests achieved an average F1-score of  $0.62 \pm 0.01$ , Recall  $0.67 \pm 0.01$ , and Precision  $0.63 \pm 0.01$  (refer to Section 2 for accuracy testing details). Additionally, we performed a principal component analysis (PCA) on these four variables to compare unknown asteroid Ryugu and Bennu aggregate samples among a set of meteorites available on Earth (Fig. 3).

## 4. Discussion

### 4.1. Analysis of meteoritic aliphatic amino acids

It has been reported that the concentration of meteoritic amino acids varies depending on the analytical methods used for extraction and analyses (Simkus et al., 2019). Any correlation that involves amino acid abundances from different studies inherently includes undefined quantitative errors. Differences in extraction efficiencies among applied protocols and resulting data variability must be considered. Therefore, the astrobiology community could benefit from implementing future ring tests, as commonly used in environmental laboratories, to ensure consistent and reliable results for correlative analyses.

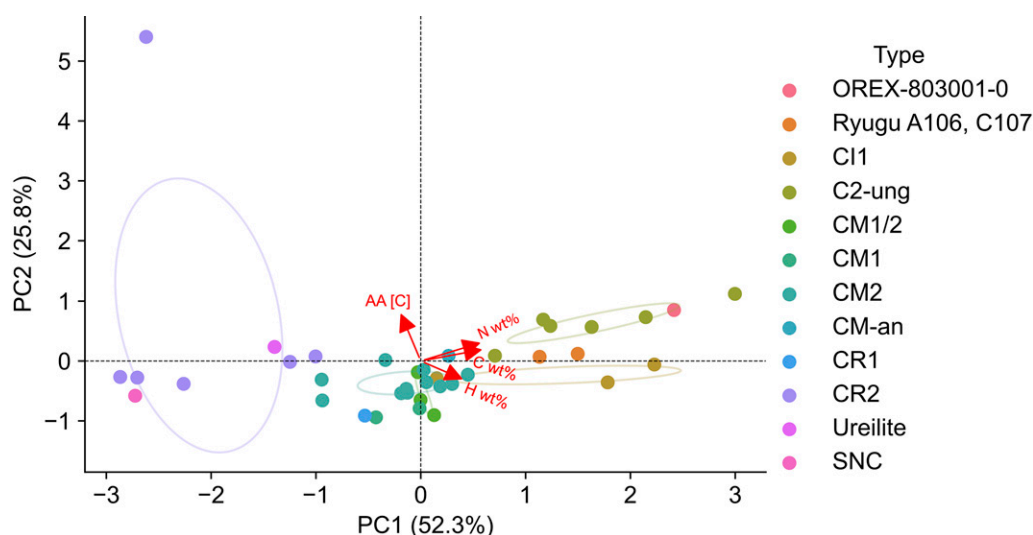
In this work, we focused on the analysis of amino acids performed using the same analytical protocols and tools (see Section 2). Typically, the abundance of amino acids increases after the water extract that contains the amino acid fraction is subjected to acid hydrolysis (e.g., Glavin et al., 2010; Burton et al., 2013). In this work, we focused on comparing the unhydrolyzed amino acid abundances only and

did not compare our results with previous analyses of hydrolyzed amino acids (Tables 1 and 2). We identified and quantified two- to six-carbon (C2–C6) aliphatic amino acids (glycine, alanine, aminobutyric acids, valine, and their isomers and enantiomers and leucine and some of its isomers and enantiomers). We also analyzed the  $\alpha$ -H protein-amino acids including aspartic, glutamic acids, threonine, and serine. The total amino acid concentrations ranged from  $\sim 1$  to 277,000 nmol/g of meteorite (Fig. 1). Terrestrial contamination is a main concern during the quantification of meteoritic proteinogenic amino acids. We performed blank subtractions to the values reported here; however, the total amino acid abundances found may include a low contribution of L-proteinogenic amino acids.

There are over 600 CCs currently classified as CM2 alone. In this work, we analyzed 16 meteorite samples and combined this data with that of 26 other previously analyzed meteorites from different petrologic types. The 42 samples we investigated here account for less than 4% of the total number of CCs available for study, without considering sample heterogeneity, which would significantly increase the number of specimens. Our current understanding of how thermal and aqueous processes shape the molecular distributions of meteoritic amino acids is based on statistics from a relatively small sample size. Thus, even when negative correlations are observed experimentally between amino acid concentrations and H wt.%, the correlations that tested links between amino acid concentrations, amino acid ratios, carbonate abundances, and L-isovaline *ee* had low statistical significance or are without statistical significance.

### 4.2. Higher temperatures, low amino acid contents

Although the synthesis of water-soluble organic compounds could happen effectively at temperatures of several hundred degrees Celsius through Fischer-Tropsch-type and Haber-Bosch reactions (Friedel and Sharkey, 1963; Anders et al., 1973), thermal metamorphism in the parent body



**FIG. 3.** Principal component analysis (PCA) of H, C, N wt.% and AA [C] in 42 extraterrestrial samples. Samples with missing values for these four variables were excluded from the analysis. Arrow directions indicate the relationship between the original variables and the principal components, while their lengths represent each variable's contribution to the principal components.

appears to be a key factor in determining amino acid concentrations in carbonaceous meteorites. High-temperature events, such as impacts on the parent bodies of these meteorites, are linked to lower amino acid concentrations, as seen in the CM chondrites Yamato 86029, Sutter's Mill, and WIS 91609 (Huss et al., 2006; Zheng et al., 2024). Additionally, thermal metamorphism in the CR2 chondrites GRA 06100, GRO 03116, and GRO 17063 may contribute not only to reduced amino acid concentrations but also to lower C, H, and N weight percentages (wt.%) in these samples. These findings raise questions about the nature of the meteorite parent bodies. Given the significant differences in amino acid concentrations, it is worth considering whether all of these meteorite samples are indeed fragments of the same parent body that underwent localized but distinct processing or if they originate from multiple parent bodies that experienced separate and independent alteration histories. The total amino acid abundance in two samples from asteroid Ryugu shows distinct values ( $8.3 \pm 0.1$  and  $27.3 \pm 1.9$  nmol/g in samples A0106 and C0107, respectively; Naraoka et al., 2023; Parker et al. 2023; Potisziel et al., 2025), despite their bulk C, H, and N wt.% (mass weighted average values) being similar (Fig. 1). These findings suggest that meteorite samples can originate from the same parent body and still exhibit significant heterogeneity in amino acid contents. Future analysis of different lithologies in the samples from asteroid Bennu could provide additional insights into the amino acid heterogeneity in meteorites.

#### 4.3. Amino acid concentrations as a function of bulk H, C, and N wt.%

Bennu aggregate sample OREX-803001-0 has the highest carbon content (C wt.%) and the second-highest nitrogen content (N wt.%) of the astromaterials discussed here, yet its AA [C] ranks 16th among all the 42 samples studied. Similarly, Ryugu samples A0106 and C0107 rank 6th and 8th in C wt.%, with notable N wt.% (9th and 13th, respectively), yet their AA [C] only ranks 23th and 29th. The bulk H contents in OREX-803001-0, A0106, and C0107 are not among the highest when compared to those of CCs (Fig. 1); added to this are the ureilites LAR 04315 and EET 83309, which have bulk C wt.% values higher than those of some CCs, yet the ureilites' AA [C] is among the lowest in this dataset. These observations raise two important questions: Why do samples such as Bennu (OREX-803001-0), Ryugu (A0106 and C0107), and the ureilites, have low amino acid concentrations despite their high carbon and nitrogen contents? And why do some CR2 meteorites with lower carbon content than the Bennu and Ryugu samples exhibit the highest amino acid concentrations in this study?

Hydrothermal alteration of the parent body could provide some answers to these questions. It is possible for hydrothermal alteration to have a negligible impact on the extent of alteration of the IOM (i.e., bulk C and N abundances) yet to significantly alter the more labile amino acids and other soluble organic matter. In such a scenario, high bulk organic C and N contents would then mostly reflect the amount of IOM (and other sources of carbon, such as graphite and amorphous carbon) in the samples, and the IOM content would not correlate positively with the content of soluble organics such as amino acids. Given the lower water content of CR2

chondrites, it seems likely that the aqueous hydrothermal alteration in Bennu and Ryugu's parent bodies was more extensive than in other CR2 parent bodies. In this type of situation, the sensitivity of amino acids to aqueous processing makes it challenging to hypothesize a scenario in which the amino acids found in Bennu and Ryugu samples were formed in those asteroids. It is more likely that their amino acids are remnants of the chemical processes that occurred in their parent bodies or as a result of their interstellar heritage (i.e., they were incorporated into the parent body on icy interstellar grains during solar system formation; Garcia et al., 2024; Materese et al., 2024).

Parent body aqueous alteration processes are often cited to explain variations in AA [C]; as expected, our Pearson's *r* correlation and PCA analyses (Figs. 2 and 3) show negative correlations between AA [C] and H wt.%. However, the relationship between bulk meteoritic carbon and nitrogen content (C and N wt.%) and AA [C] has received less attention. Our statistical analysis revealed a strong positive linear correlation between C and N wt.%, which indicates that carbon and nitrogen abundances are linked. Conversely, C and N wt.% are negatively correlated with AA [C], which suggests that, similar to H wt.%, amino acid concentrations may decrease as C and N wt.% increase or that, at best, the AA [C] would remain unchanged with a variation of C and N wt.%.

This inverse correlation between AA [C] and H, C, and N wt.% does not clarify whether AA [C] depends on these variables. The MIC score, a reliable indicator of variable independence, showed that none of the variable pairs met the criteria for independence (i.e., close to zero; Supplementary Table S4). Even knowing that the AA [C] could decrease or remain unchanged (but not be higher in any case), we cannot definitively conclude whether the AA [C] is independent of H, C, and N wt.%. Therefore, it is not clear at this time whether higher H, C, and N contents would necessarily yield larger concentrations of amino acids or other organics needed for the origins of life in extraterrestrial samples. These findings are crucial for understanding the amino acid molecular inventory in future samples returned from Mars by NASA's and ESA's Mars Sample Return campaign, and from Phobos by JAXA's Martian Moons eXploration, or from other solar system bodies that may be future targets for robotic sample return based on their high carbon and nitrogen contents (e.g., Ceres).

#### 4.4. When and where did aqueous alteration happen?

It has been suggested that the carbonates in CCs formed from a mixture of CO/CO<sub>2</sub> and H<sub>2</sub>O ices at temperatures between 50 and 100 K, beyond the snow line at a distance of less than 4 to 15 AU from the Sun (Alexander et al., 2015). After the accretion of the parent body at that distance, one of the primary sources of heating was the radioactive decay of short-lived radionuclides (e.g., <sup>26</sup>Al; Huss et al., 2006). This heating melted the ice and triggered much of the aqueous alteration observed in these meteorite samples, including the synthesis and destruction of meteoritic amino acids and their chemical precursors.

The effects of hydrothermal aqueous alteration are also evident from the presence of abundant phyllosilicates and the fact that these samples are breccias, with each fragment having a different alteration history, indicating that the formation



of these minerals occurred before the rock reaccrreted (Zolensky and McSween, 1988; Krot et al., 2006). Furthermore, Mn-Cr dating of carbonates suggests that the formation of these aqueously produced minerals began early in the life of the parent body and may have continued for at least nine million years (Tanaka et al., 2024). To sustain internal temperatures high enough to maintain liquid water for this duration, the parent body likely had a radius of at least 50 km (Fujiya et al., 2013).

We now understand that Bennu and Ryugu are second or later generation ( $n$ th generation) rubble-pile asteroids (Walsh, 2018; Watanabe et al., 2019; Jourdan et al., 2023). While localized, late-stage heating events, such as impacts, cannot be entirely ruled out, the small size of Bennu and Ryugu likely limits their capacity to generate significant impact heating, as any impact would more likely dissipate material from the asteroid rather than heat it (DellaGiustina et al., 2019; Walsh et al., 2022). Therefore, it is almost certain that the formation and decomposition of amino acids occurred within the first tens of millions of years after the formation of Bennu and Ryugu's parent bodies.

Asteroid families such as New Polana and Eulalia have been proposed as the original parent bodies for Bennu and Ryugu; moreover, it has been suggested that both asteroids derived from the same parent body (Takir et al., 2024; Walsh et al., 2013, 2022, 2024). Given the presence of ammonium salts and amorphous carbon in Ceres (De Sanctis et al., 2015; De Sanctis et al., 2017; Prettyman et al., 2016; Marchi et al., 2019) and in comet 67P/Churyumov-Gerasimenko (Altwegg et al. 2016; Rubin et al., 2020), added to evidence for CO<sub>2</sub> trapped in Ryugu grains (which would suggest that Ryugu's parent body formed behind the snow line; Nakamura et al., 2023), it is reasonable to argue that New Polana and Eulalia could have been a Ceres-like or a large asteroid-like icy body that experienced extensive liquid water alteration but, unlike Ceres, has not undergone complete differentiation (Glavin et al., 2025; McCoy et al., 2025). However, there are important physicochemical differences, such as pH, and amino acid, sulfides, and evaporites abundances between Bennu and Ryugu samples (Parker et al., 2023; Glavin et al., 2025); therefore, having similar or identical origins implies that these differences may evidence a largely heterogeneous common parent body, or their different experiences in the inner solar system.

#### 4.5. Amino acid ratios as an anti-biosignature

We used the hydrogen weight percentage (H wt.%) as an indicator of hydration content in each meteorite sample (Alexander et al., 2012, 2013). Typically, a positive correlation between water content or the degree of aqueous alteration and the amino acid ratios of  $\beta$ -Ala/Gly,  $\beta$ -Ala/D-Ala,  $\alpha$ -AIB/Gly, and  $\beta$ -Ala/ $\alpha$ -AIB has been reported (e.g., Ehrenfreund et al., 2001; Botta et al., 2002; Glavin et al., 2010; Modica et al., 2018; Potiszil et al., 2025). However, our Pearson's  $r$  correlation analyses (Fig. 2) show negative correlations between H wt.% and  $\beta$ -Ala/Gly and  $\beta$ -Ala/ $\alpha$ -AIB, and a positive correlation between H wt.% and  $\alpha$ -AIB/Gly and  $\beta$ -Ala/D-Ala. Therefore, while  $\beta$ -Ala/D-Ala and  $\alpha$ -AIB/Gly ratios can continue to be used as indicators of aqueous parent body processing,  $\beta$ -Ala/Gly and  $\beta$ -Ala/ $\alpha$ -AIB ratios should be used with caution.

Several experimental setups have been tested to evaluate the larger  $\beta$ -Ala/Gly values observed in some aqueously altered meteorites, such as Orgueil (e.g., Vinogradoff et al., 2020; Garcia et al., 2024; Materese et al., 2024). The Strecker, Formose, and Maillard reactions have been pointed out as the main routes for the synthesis and destruction for the amino acid molecular distribution we see in CCs. Yet less effort has been put into validating the initial concentrations of key synthetic substrates such as ammonia, cyanide, carbon monoxide and dioxide, formaldehyde, and so on, as well as other simple physicochemical conditions such as the pH, temperature, and the mineralogical composition of the reactive environment. Given the complexity of secondary processing, further research is needed to better understand the interplay of various organic molecules.

What are the implications of finding higher concentrations of  $\beta$ -Ala and  $\alpha$ -AIB compared with typically more abundant amino acids such as Gly and  $\alpha$ -Ala? Given that under hydrothermal conditions the decarboxylation rates for  $\alpha$ -amino acids are faster than those of  $\beta$ -amino acids (Li and Brill, 2003), the most straightforward explanation is that elevated  $\beta$ -Ala levels could indicate more extensive aqueous processing in an extraterrestrial sample. It could also suggest that the starting materials for  $\beta$ -Ala synthesis (e.g.,  $\alpha$ - $\beta$ -unsaturated carboxylic acids or amines) or the synthetic pathways leading to its formation were more abundant or predominant in that sample. Regardless, if  $\beta$ -Ala and  $\alpha$ -AIB levels exceed those of simpler and more common  $\alpha$ -amino acids found in terrestrial biology, this might indicate a signature opposite to that of life as we know it. The ratios of  $\beta$ -Ala/D-Ala and  $\alpha$ -AIB/Gly, along with other potential organic biosignatures (e.g., amino acid enantiomeric excess, carbonates isotopic values), could be used as either indicators of the absence of life or as evidence of a form of life that is different from what we currently understand (Chandru et al., 2024). Therefore, the molecular distribution of amino acids, and specifically the  $\beta$ -Ala and  $\alpha$ -AIB compositions, constitutes an example of how the analysis of organic compounds may be used in future planetary missions.

#### 4.6. Meteoritic L-isovaline enantiomeric excess

The origin of Earth's homochirality in life remains an unsolved mystery, with some CCs being the only natural abiotic samples where measurable enantiomeric excess of amino acids has been observed. Due to its rarity in terrestrial biology and resistance to racemization, the  $\alpha,\alpha$ -dialkyl amino acid isovaline has been the most extensively studied for extraterrestrial enantiomeric excess. Further, the L-*ee* of Iva is inversely correlated with biological terrestrial contamination as inferred by the L-*ee* of alanine (Supplementary Fig. S3). To date, L-isovaline enantiomeric excess has been detected in 18 meteorites from different petrologic classes (Burton and Berger, 2018; Glavin et al., 2018), with L-*ee* ranging from 0% up to 18.5% in the Murchison meteorite (Pizzarello et al., 2003; Glavin and Dworkin 2009). A direct relationship between higher meteoritic amino acid abundances and larger L-isovaline enantiomeric excess has not been established; however, a linear positive relationship between L-isovaline excess and the extent of meteorite aqueous processing (or lower AA [C]) has been suggested (Glavin and

Dworkin 2009). Our results indicate positive relationships between L-isovaline *ee* and aqueous processing expressed either by H wt.%, carbonate concentrations, or  $\beta$ -Ala/Gly ratios. Amino acid concentrations, particularly those of isovaline enantiomers, have been analyzed in only a small fraction of available CCs (Elsila et al., 2016; Glavin et al., 2018; Simkus et al., 2019). Future studies that measure amino acids and other soluble organics in samples with varying levels of aqueous and thermal processing are essential to validate potential relationships between synthetic pathways that lead to a break in symmetry and the amplification of enantiomeric excess and parent body alterations (Bocková et al., 2023).

#### 4.7. Using the amino acid molecular distributions to classify samples of asteroids Ryugu and Bennu

The high friability of Ryugu and Bennu materials implies that these samples would be destroyed upon entering Earth's atmosphere or impacting the ground, and that we can have them in an intact form only because of the sample return missions Hayabusa2 and OSIRIS-REx, respectively. Thus, because of their friable nature, these asteroid samples may be unique and different from all other meteorite samples that survived crossing Earth's atmosphere and landing. We analyzed the concentration and molecular distributions of free amino acids in CCs and used previously published H, C, and N wt.% data (Naraoka et al., 2023; Yokoyama et al., 2023; Parker et al., 2023; Lauretta et al., 2024; Glavin et al., 2025; McCoy et al., 2025), and the AA [C] to determine the closest subgroup of CCs that samples from asteroids Bennu and Ryugu would belong to using PCA (Fig. 3). Our statistical analyses effectively grouped CCs from eight different types. Those results showed clear distinctions between the C2-ung, CI1, CM2, and CR2 groups. Additionally, the arrows confirmed the inverse relationship between AA [C] and H wt.%, and the positive correlation between N and C wt.% previously found using Pearson's *r* correlations.

Among the 42 samples analyzed, asteroid Ryugu samples A0106 and C0107 were found outside but in close proximity to the CI1 and C2-ung types, which suggests that, although closely related, A0106 and C0107 do not belong to those CC types, and that rather they may constitute their own carbonaceous subgroup. Further, the PCA analysis placed asteroid Bennu sample OREX-803001-0 in the same group as C2-ung CCs. These results agree with those results by Glavin et al. (2025), which suggest a potential genetic link between asteroid Bennu and C2-ung meteorites such as Tarda, Tagish Lake, and Essebi. Future analyses of more Ryugu and Bennu samples are needed to fully understand the links between meteorite samples found on Earth and those collected by sample return missions.

## 5. Conclusions and Implications

This study evaluated amino acid concentrations and molecular distributions in 16 CCs, combined with data from 26 additional samples. The 42 samples represent less than 4% of all available specimens. Although some trends were observed between amino acid distributions and factors typically used to explain parent body aqueous alteration processes, that is, H, C, N, carbonate content, and enantiomeric excesses, most attempts to establish meaningful links

showed low or no statistical significance. This highlights the need for larger and more diverse sample sets.

Thermal metamorphism is associated with lower amino acid concentrations and reduced H, C, and N contents. This suggests that CCs may originate from multiple parent bodies with distinct alteration histories or from a single body with localized processing variations. The significant differences in amino acid abundances observed in Ryugu samples, despite similar bulk elemental content, highlight the heterogeneity of the parent body. Future analyses of Bennu samples may provide further insights into the complex chemical diversity of meteorites.

Our findings revealed no definitive evidence of strong positive or negative correlations between amino acid concentrations and H, C, or N contents. Therefore, planning future sample return missions with the expectation of discovering abundant amino acids or other life-relevant organic compounds solely based on high carbon or nitrogen levels, as observed on Mars or Ceres, should be approached with caution.

Asteroid families such as New Polana and Eulalia have been proposed as potential parent bodies for Bennu and Ryugu, with some studies suggesting a shared origin. The presence of ammonium salts and amorphous carbon in Ceres and comet 67P, along with CO<sub>2</sub> trapped in Ryugu grains, supports the hypothesis that their parent body may have been a Ceres-like icy body that underwent extensive aqueous alteration without complete differentiation. However, significant differences in pH, amino acids, sulfides, and evaporites between Bennu and Ryugu samples suggest these variations may result from a highly heterogeneous parent body or their distinct evolutionary pathways within the inner solar system.

As previously reported, the detection of higher concentrations of  $\beta$ -Ala and  $\alpha$ -AIB in comparison to Gly and  $\alpha$ -Ala suggests a more extensive chondritic aqueous processing. Here, we hypothesize that the elevated levels of  $\beta$ -Ala and  $\alpha$ -AIB relative to amino acids commonly found in terrestrial life may imply either the existence of a form of life distinct from our current understanding or the absence of life altogether. Therefore, the analysis of  $\beta$ -Ala/D-Ala and  $\alpha$ -AIB/Gly ratios in conjunction with other potential organic markers could offer valuable insights for future planetary missions and help identify potentially novel biochemical signatures.

Analysis of free amino acid concentrations and molecular distributions, combined with existing elemental data, successfully classified CCs into distinct groups. Principal component analysis revealed Ryugu samples A0106 and C0107 as potentially representing a unique CC subgroup, distinct from but related to CI1 and C2-ung types. Bennu sample OREX-803001-0 clustered with C2-ung chondrites, supporting previous findings of a genetic link between Bennu and C2-ung meteorites. These results remark the unique nature of returned asteroid samples and urge the need for further analyses to fully characterize their relationship to existing meteorite classifications.

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#### Supplementary Material

Supplementary Data

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Address correspondence to:

José C. Aponte  
Astrochemistry Laboratory, Code 691  
NASA Goddard Space Flight Center  
Greenbelt  
MD 20771  
USA

E-mail: jose.c.aponte@nasa.gov

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#### Abbreviation Used

ANSMET = Antarctic Search for Meteorites  
CC = Carbonaceous chondrite  
CRESST II = Center for Research and Exploration in Space Science and Technology II  
FLaRe = Fundamental Laboratory Research