# EVIDENCE FOR EXTRATERRESTRIAL L-AMINO ACID EXCESSES IN THE CM2 AGUAS ZARCAS AND MURCHISON METEORITES: PREDICTIONS FOR RYUGU AND BENNU.

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**Introduction:** Meteorites provide a record of the chemical processes that occurred in the early solar system before life began on Earth. The delivery of organic compounds by carbonaceous chondrites to the early Earth and other planetary bodies could have been an important source of prebiotic material required for the emergence of life [1]. The amino acid contents of a variety of carbonaceous chondrites, in particular the CMs, have been studied extensively because these prebiotic molecules are essential components of life as the monomers of proteins and enzymes. To date, 96 different amino acids have been named in the Murchison CM2 meteorite including 12 of the 20 most common protein amino acids found in biology [2]; however, the vast majority of amino acids identified in Murchison are rare or absent in the terrestrial biosphere. In addition, the non-protein α-dialkyl amino acid isovaline in Murchison has significant L-enantiomeric excesses of extraterrestrial origin up to ~18% [3], suggesting that the origin of life on Earth could have been biased towards L-amino acids from the very beginning.

On April 23, 2019, a meteorite fall was reported in Aguas Zarcas (hereafter AZ), San Carlos county, Alajuela province, Costa Rica. Hundreds of individual fragments were recovered from the strewn field totaling 27 kg in mass, of which ~11 kg was recovered before it rained in the area [4]. Based on its mineralogy, elemental abundances, and O-isotope composition, AZ has been classified as a CM2 carbonaceous chondrite and some of the pre-rain fragments were noted to give off a "Murchison-like" odor [4]. The recent fall and rapid recovery of the AZ meteorite provides a rare opportunity to investigate a carbon-rich meteorite using state-of-the-art analytical techniques that will also be used to study the samples returned from asteroids Ryugu and Bennu by Hayabusa2 and OSIRIS-REx in late 2020 and 2023, respectively.

Here, we report the first amino acid analyses of the AZ meteorite [5]. The total abundances, enantiomeric ratios and stable C-isotope compositions of amino acids extracted from two different pre-rain fragments of the AZ meteorite, a soil sample collected from the AZ fall site, and the Murchison meteorite were determined using a combination of ultrahigh performance liquid chromatography with UV fluorescence and quadrupole time-of-flight mass spectrometry (LC-FD/Q-ToF-MS) detection and gas chromatography-mass spectrometry coupled with isotope ratio-mass spectrometry (GC-MS/IRMS).

**Materials and Methods:** Two individual (~0.5 g) pre-rain fragments of AZ obtained by the University of Arizona from Mike Farmer (UA 2741) and Robert Ward (UA 2746) were separately crushed to powder and homogenized by mixing using a ceramic mortar and pestle inside a positive pressure HEPA filtered laminar flow hood at NASA's Goddard Space Flight Center. Tiny plant fragments were observed in the powdered sample of UA 2746, but not in UA 2741. As controls, a soil sample collected from the AZ strewn field by Greg Hupe, and a sample of Murchison (Chicago Field Museum) that had been kept sealed inside a glass desiccator were processed in parallel.

The samples were individually extracted in water at 100°C, acid-hydrolyzed under HCl vapor, desalted, and 1% derivatized by *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) and analyzed by LC-FD/Q-ToF-MS to determine the total amino acid abundances and enantiomeric ratios. The remaining ~99% of the extracts were derivatized with isopropanol and trifluoroacetic anhydride to measure the stable carbon isotope values ($\delta^{13}C$) of the individual amino acids using GC-MS/IRMS. Separate extracts from the same meteorite powders were analyzed for amines, aldehydes, ketones, carboxylic acids, and cyanide by LC- and GC-MS [6].

**Results:** A variety of two- to six-carbon amino acids were identified in the UA 2741 meteorite with abundances ranging from ~0.2 to 28 nmol/g (Table 1). Two rare, non-protein amino acids α-aminoisobutyric acid (AIB) and isovaline were present at elevated abundances in UA 2741 relative to the UA soil sample 2745 where they were only present at trace levels, providing evidence that AIB and isovaline are extraterrestrial in origin. The total abundances of AIB and isovaline in UA 2741 were similar (~6 nmol/g, Table 1); unsurprisingly, the UA 2746 meteorite with plant fragments and the soil had higher relative abundances of alanine and several other common protein amino acids including glycine, aspartic and glutamic acids, serine, threonine, and valine indicating that UA 2746 has more amino acid contamination. Moreover, the enantiomeric ratios of alanine in UA 2741 and UA 2746 (D/L ~ 0.5, Table 1) were much lower than in

Murchison (D/L ~ 1), also indicating some terrestrial L-alanine contamination of the AZ meteorites.

**Table 1.** Summary of the total amino acid abundances, D/L ratios and L-enantiomeric excesses ($L_{ee}$) measured in the CM2 Murchison and AZ (UA 2741) meteorites. Uncertainties based on the standard error of the average value of three to six measurements.

| | **Murchison** | | **AZ (UA 2741)** | |
|---|---|---|---|---|
| | Total (nmol/g) | D/L (% $L_{ee}$) | Total (nmol/g) | D/L (% $L_{ee}$) |
| **Acidic amino acids** | | | | |
| D-aspartic acid | 0.95 ± 0.04 | 0.56 ± 0.04 | 0.16 ± 0.06 | 0.32 ± 0.17 |
| L-aspartic acid | 1.7 ± 0.1 | (28 ± 3) | 0.5 ± 0.2 | (52 ± 15) |
| D-glutamic acid | 2.7 ± 0.1 | 0.36 ± 0.02 | 0.59 ± 0.01 | 0.16 ± 0.01 |
| L-glutamic acid | 7.6 ± 0.4 | (48 ± 2) | 3.7 ± 0.1 | (73 ± 1)† |
| **Hydroxy amino acids** | | | | |
| D-serine | 0.4 ± 0.1 | 0.7 ± 0.2 | 0.3 ± 0.2 | 0.20 ± 0.18 |
| L-serine | 0.6 ± 0.1 | (20 ± 12) | 1.5 ± 0.9 | (67 ± 18) |
| D-threonine | 0.17 ± 0.01 | 0.53 ± 0.06 | 0.2 ± 0.2 | 0.007 ± 0.001 |
| L-threonine | 0.32 | (31 ± 4) | 28 ± 1 | (99 ± 1) |
| **C2 amino acid** | | | | |
| glycine | 32 ± 3 | - | 20 ± 3 | - |
| **C3 amino acids** | | | | |
| β-alanine | 16 ± 1 | - | 0.9 ± 0.1 | - |
| D-alanine | 8.3 ± 0.8 | 1.0 ± 0.1 | 1.6 ± 0.1 | 0.46 ± 0.06 |
| L-alanine | 8.2 ± 0.7 | (0) | 3.5 ± 0.4 | (37 ± 4)† |
| **C4 amino acids** | | | | |
| D,L-α-ABA | 2.4 ± 0.3 | nd | 1.4 ± 0.4 | nd |
| D,L-β-ABA | 2.5 ± 0.4 | nd | 0.38 ± 0.04 | nd |
| γ-ABA | 2.0 ± 0.2 | - | 1.4 ± 0.1 | - |
| α-AIB | 10.4 ± 0.8 | - | 5.6 ± 0.8 | - |
| **C5 amino acids** | | | | |
| D-valine | 0.62 ± 0.01 | 0.67 ± 0.03 | 0.35 ± 0.03 | 0.29 ± 0.03 |
| L-valine | 0.93 ± 0.04 | (20 ± 2) | 1.2 ± 0.1 | (55 ± 3) |
| D-isovaline | 9.5 ± 0.1 | 0.83 ± 0.01 | 2.8 ± 0.2 | 0.8 ± 0.1 |
| L-isovaline | 11.5 ± 0.1 | (10 ± 1) | 3.5 ± 0.4 | (11 ± 6) |
| *Other C5 amino acids | 15 ± 1 | - | 7 ± 2 | - |
| **C6 amino acid** | | | | |
| ε-amino-*n*-caproic acid | 2.2 ± 0.2 | - | 0.7 ± 0.4 | - |
| **Sum AA (nmol/g)** | **~136** | - | **~85** | - |

*Many other C5 amino acid isomers identified [5]. nd = not determined; ABA = amino-*n*-butyric acid; AIB = aminoisobutyric acid; $\%L_{ee} = [(L - D)/(L+D)]*100$. †Significant L-amino acid contamination likely based on carbon isotope ($\delta^{13}C$) values (Table 2).

Although the total amino acid abundance of AZ UA 2741 (~85 nmol/g, Table 1) is less than the Murchison meteorite (~136 nmol/g), the free amino acid abundances in AZ are slightly higher than in Murchison (Fig. 1). The distribution and high relative abundances of α-amino acids found in AZ and Murchison are quite similar (Table 1), consistent with a Strecker-cyanohydrin synthesis on these meteorite parent bodies. Moreover, the striking similarities in abundances and isomeric distributions of other free soluble organic compound classes in these meteorites also indicate similar chemical formation processes and/or parent body conditions for AZ and Murchison [6].

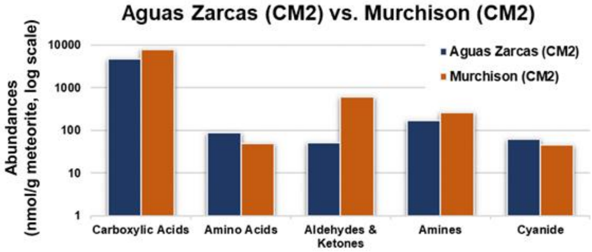

**Figure 1.** Comparison of the free soluble organic compound abundances in the Aguas Zarcas and Murchison meteorites [5,6].

Despite some terrestrial contamination, $\delta^{13}C$ values that fall outside of the typical terrestrial range (Table 2) prove that many of the amino acids in the AZ meteorites and Murchison are extraterrestrial in origin; however, for many of the protein amino acids in the meteorites, the L-enantiomer is less enriched in $^{13}C$ than the D-enantiomer suggesting a terrestrial L-amino acid contribution (Table 2). Interestingly, the $\delta^{13}C$ values of D- and L-isovaline in UA 2741 are both similar within errors and enriched in $^{13}C$, indicating that the measured L-isovaline excess of 11 ± 6% is non-terrestrial in origin. $\delta^{13}C$ measurements also confirm that the ~10% L-isovaline excess and most of the measured L-glutamic acid excess of ~48% in Murchison (Table 1) are also non-terrestrial in origin.

**Table 2.** Summary of the $\delta^{13}C$ values (avg. of 3 measurements in ‰, VPDB) of amino acids in the AZ meteorites and soil and Murchison.

| **Amino Acids** | **Aguas Zarcas** | | | **Murchison** |
|---|---|---|---|---|
| | **UA 2741** | **UA 2746** | **Soil UA 2745** | |
| D-Glu | +20 ± 8 | -7 ± 13 | -14 ± 9 | +31 ± 3 |
| L-Glu | -10 ± 4 | -12 ± 4 | -15 ± 5 | +15 ± 3 |
| Gly | +15 ± 6 | +6 ± 9 | +5 ± 4 | +24 ± 4 |
| D-Ala | +40 ± 3 | -7 ± 3 | -18 ± 4 | +49 ± 5 |
| L-Ala | +16 ± 2 | -2 ± 5 | -11 ± 3 | +38 ± 5 |
| β-Ala | +9 ± 4 | -17 ± 3 | -22 ± 2 | +10 ± 1 |
| α-AIB | +17 ± 5 | +30 ± 12 | nd | +33 ± 6 |
| D-Isovaline | +25 ± 3 | +32* | nd | +18 ± 6 |
| L-Isovaline | +32 ± 5 | +34* | nd | +26 ± 7 |

nd = not determined due to trace abundances and/or chromatographic interferences. *Values shown without an error were derived from a single measurement.

**Conclusions:** The discovery of extraterrestrial amino acids including L-isovaline excesses in AZ and Murchison provides evidence of an early solar system bias towards L-amino acids prior to the origin of life. Future analyses of samples returned from asteroids Ryugu and Bennu that have experienced much less exposure to the terrestrial environment will provide the first opportunity to measure the extent of chiral asymmetry produced solely by non-biological processes. In this presentation we will also make predictions about the amino acid composition of samples returned from these asteroids based on their spectroscopic similarities to altered CI and CM carbonaceous chondrites [7,8].

**References:** [1] Chyba, C. and Sagan, C. (1992) *Nature, 355,* 125-132. [2] Glavin, D. P. et al. (2020) *Chem. Rev., 120,* 4660-4689. [3] Glavin, D. P. and Dworkin, J. P. (2009) *PNAS, 106,* 5487-5492. [4] Meteoritical Bulletin 108, *MAPS, 55,* 1146-1150. [5] Glavin, D. P. et al. (2020) *MAPS,* doi: 10.1111 /maps.13451. [6] Aponte, J. C. et al. (2020) *MAPS, 55,* 1509-1524. [7] Hamilton, V. et al. (2019) *Nat. Astron., 3,* 332-340. [8] Kitazato, K. et al. (2019) *Science 364,* 272-275.