EXTRATERRESTRIAL AMINO ACIDS IN THE CM2 AGUAS ZARCAS AND MURCHISON CARBONACEOUS CHONDRITES. D. P. Glavin[1], J. E. Elsila[1], H. L. McLain[1,2], J. C. Aponte[1,2], E. T. Parker[1], J. P. Dworkin[1], D. H. Hill[3], H. C. Connolly Jr.[3,4], D. S. Lauretta[3], [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, E-mail: daniel.p.glavin@nasa.gov, [2]Catholic University of America, Washington DC 20064, [3]Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721, [4]Rowan University, Glassboro, NJ 08028.

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. Several non-protein α-dialkyl amino acids in Murchison contain significant L-enantiomeric excesses of prebiotic origin up to ~18% [3,4], suggesting that the origin of life on Earth could have been biased towards L-amino acid homochirality from the very beginning. Large excesses of L-alanine (~33%) have also been reported in Murchison [5], however confirmation of an extraterrestrial origin of L-protein amino acid excesses can be more difficult due to terrestrial contamination.

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 [6]. 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 [6]. The recent fall and rapid recovery of AZ 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. 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 time of flight mass spectrometry (LC-FD/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) 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/ToF-MS to determine the total amino acid abundances and enantiomeric ratios [4]. 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 as described elsewhere [7].

Amino Acid Results: A variety of two- to six-carbon amino acids were identified in the AZ meteorite UA 2741 with abundances ranging from ~0.1 to 20 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 AZ soil sample UA 2745 where they were only present at trace levels (Fig. 1), providing evidence that AIB and isovaline are extraterrestrial in origin. The total abundances of AIB and isovaline in UA 2741 and UA 2746 were similar (~5 to 6 nmol/g, Table 1); unsurprisingly, UA 2746 and the soil had higher relative abundances of alanine (Fig. 1) and several other common protein amino acids including glycine, aspartic and glutamic acids, serine and valine indicating that UA 2746 has more terrestrial amino acid contamination. Moreover, the enantiomeric ratios of alanine in UA 2741 and UA 2746 (D/L ~ 0.5) were much lower than in Murchison (D/L ~ 0.85), also indicating some terrestrial L-alanine contamination of the AZ meteorites.

Table 1. Summary of the total amino acid abundances (nmol per gram) and D/L ratios measured in the CM2 Murchison and AZ (UA 2741) meteorites.

	Murchison		**AZ (UA 2741)**	
	Total	D/L	Total	D/L
Acidic amino acids				
D-aspartic acid	0.85 ± 0.13	0.71 ± 0.15	0.12 ± 0.04	0.30 ± 0.13
L-aspartic acid	1.18 ± 0.16		0.40 ± 0.12	
D-glutamic acid	1.56 ± 0.14	0.37 ± 0.04	0.50 ± 0.05	0.13 ± 0.01
L-glutamic acid	4.24 ± 0.29		3.91 ± 0.22	
Hydroxy amino acid				
D-serine	0.21 ± 0.07	0.43 ± 0.17	0.34 ± 0.07	0.22 ± 0.07
L-serine	0.49 ± 0.08		1.52 ± 0.34	
C2 amino acid				
glycine	59.0 ± 9.8	-	20.3 ± 2.8	-
C3 amino acids				
β-alanine	15.7 ± 1.8	-	0.93 ± 0.09	-
D-alanine	4.62 ± 0.48	0.85 ± 0.15	1.58 ± 0.12	0.54 ± 0.14
L-alanine	5.46 ± 0.66		2.94 ± 0.76	
C4 amino acids				
D,L-α-amino-*n*-butyric acid	3.07 ± 0.43	nd	1.36 ± 0.18	nd
D,L-β-amino-*n*-butyric acid	8.10 ± 1.73	nd	1.09 ± 0.41	nd
γ-amino-*n*-butyric acid	6.24 ± 0.81	-	1.43 ± 0.13	-
α-aminoisobutyric acid	22.3 ± 4.6	-	5.61 ± 0.90	-
C5 amino acids				
D-valine	0.57 ± 0.10	0.42 ± 0.07	0.27 ± 0.03	0.25 ± 0.04
L-valine	1.36 ± 0.07		1.06 ± 0.10	
D-isovaline	12.0 ± 1.4	0.92 ± 0.15	2.82 ± 0.19	0.82 ± 0.10
L-isovaline	13.0 ± 1.3		3.45 ± 0.35	
C6 amino acid				
ε-amino-*n*-caproic acid	2.61 ± 1.40	-	0.73 ± 0.25	-
Sum AA (nmol/g)*	**~162**	-	**~50**	-

*Only includes most abundant amino acids in Murchison; many other amino acids have been reported [2]. nd = not determined.

Even including the small terrestrial amino acid contributions to AZ, the total amino acid abundance of UA 2741 (~50 nmol/g, Table 1) is roughly one third that of the Murchison meteorite (~162 nmol/g). The relative distribution of α-amino acids found in UA 2741 and Murchison is quite similar, however it is notable that both AZ meteorites are depleted in β-amino acids (β-alanine and D,L-β-ABA) relative to Murchison. The lower β-alanine abundances in AZ (Table 1, Fig. 1) may indicate that this meteorite experienced less parent body aqueous alteration compared to Murchison based on previous trends observed for CI, CM, and CR carbonaceous chondrites [8].

Carbon isotope values ($\delta^{13}C$) of amino acids that fall outside of the typical terrestrial range (Table 2) prove that many of the amino acids in AZ and Murchison are extraterrestrial in origin, although for some protein amino acids in the meteorites, the L-enantiomer is less enriched in ^{13}C than the D-enantiomer suggesting a terrestrial contribution to the L-enantiomer. The $\delta^{13}C$ values of the protein amino acids in UA 2746 are also less enriched than UA 2741 and similar to the soil, which is consistent with higher levels of terrestrial amino acid contamination in UA 2746. Interestingly, the $\delta^{13}C$ values of D- and L-isovaline in UA 2741 are similar within errors and highly enriched in ^{13}C, indicating the measured L-isovaline excess of ~10% is non-terrestrial in origin.

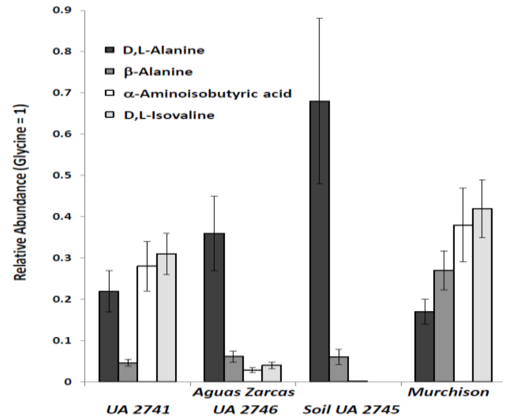

Figure 1. Comparison of the molar abundances relative to glycine of D,L-alanine, β-alanine, α-aminoisobutyric acid (AIB), and D,L-isovaline in the AZ meteorites (UA 2741 and UA 2746), a soil sample from the AZ strewn field (UA 2745), and Murchison.

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

Amino Acids	**Aguas Zarcas**			**Murchison**
	UA 2741	**UA 2746**	**Soil UA 2745**	
D-aspartic acid	nd	-15 ± 21	-18 ± 7	nd
L-aspartic acid	nd	-9 ± 27	-5 ± 7	nd
D-glutamic acid	+20 ± 8	-7 ± 13	-14 ± 9	+31 ± 3
L-glutamic acid	-10 ± 4	-12 ± 4	-15 ± 5	+15 ± 3
glycine	+15 ± 6	+6 ± 9	+5 ± 4	+24 ± 4
D-alanine	+40 ± 3	-7 ± 3	-18 ± 4	+49 ± 5
L-alanine	+16 ± 2	-2 ± 5	-11 ± 3	+38 ± 5
β-alanine	+9 ± 4	-17 ± 3	-22 ± 2	+10 ± 1
AIB	+17 ± 5	+30 ± 12	nd	+33 ± 6
D-isovaline	+25 ± 3	+32*	nd	+16*
L-isovaline	+32 ± 5	+34*	nd	+27*

*No error since the value was derived from a single measurement. nd = not determined due to trace levels and/or analytical issues.

Conclusions: The discovery of extraterrestrial amino acids including L-isovaline excesses in AZ provides evidence of an early solar system formation 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.

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