EXTRATERRESTRIAL AMINO ACIDS IN THE C2 UNGROUPED CARBONACEOUS CHONDRITE TARDA: A UNIQUE DISTRIBUTION.

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Introduction: Meteorites provide a record of the chemical processes that occurred in the early solar system. The delivery of organic matter by carbonaceous chondrites to the early Earth could have been an important source of amino acids and other prebiotic organic molecules required for the emergence of life [1]. To date, 96 amino acids have been named in meteorites, most of which are rare or absent in the biosphere [2]. The variability in amino acid concentrations and isomer distributions measured in carbonaceous chondrites can be explained by differences in parent body chemistry and alteration conditions [3]. In addition, aqueous alteration was likely important in the amplification of some left-handed amino acids over their right-handed forms (L-excesses up to ~60%) in the Tagish Lake meteorite [3], suggesting that the origin of life on Earth and possibly elsewhere in the solar system was biased towards L-amino acids.

On August 25, 2020, a fireball was witnessed in southern Morocco and the first pieces of the meteorite fall were recovered the following day near the town of Tarda [4]. Thousands of individual fragments were recovered from the strewn field totaling ~4 kg [4]. Based on petrographic observations, bulk mineralogy, and chemical and O-isotopic analyses, Tarda has been classified as a C2 ungrouped carbonaceous chondrite with similarities to Tagish Lake (though more primitive), as well as CI, CY, and CR chondrites [4,5]. The fall and rapid recovery of the Tarda stones provide an important opportunity to investigate a C-rich meteorite using the state-of-the-art techniques that will also be used to study the samples returned from asteroids Ryugu and Bennu by the Hayabusa2 and OSIRIS-REx missions, respectively.

Here, we report the first amino acid analyses of the Tarda meteorite. The total concentrations, enantiomeric ratios and relative distributions of amino acids were determined using ultrahigh performance liquid chromatography with UV fluorescence and time-of-flight mass spectrometry (LC-FD/ToF-MS) at NASA GSFC. This analytical technique was employed on extracts from two different pre-rain Tarda meteorite fragments and a sample of sand collected from the Tarda fall site for the purpose of assessing potential terrestrial contamination. Bulk H, C, and N elemental and isotopic analyses were also conducted at the Carnegie Institution for Science (CIS) to assist with petrologic type classification using elemental analysis isotope ratio mass spectrometry (EA-IRMS).

Materials and Methods: Individual fragments from two different Tarda meteorite stones (Tarda #1: ~1 g and Tarda #2: 270 mg) obtained from meteorite dealers Roberto Vargas (#1), Bruno Fectay/Carine Bidaut (#2) were wrapped in aluminum foil and sealed in plastic bags prior to shipping to GSFC. At GSFC, the Tarda meteorite samples were separately crushed to powder using a ceramic mortar and pestle inside a positive pressure HEPA filtered laminar flow hood at GSFC. A 5.4 g sample of desert sand from the Tarda meteorite strewn field, stored in a sealed plastic container, was processed in parallel. The collection and curation histories of these samples were not thoroughly documented; however, all samples were collected before it rained in the area. A small aliquot of each powdered sample (~15-20 mg) was used for EA-IRMS measurements at CIS.

Portions of the Tarda meteorite powders (Tarda #1: 723 mg; Tarda #2: 193 mg) and sand (748 mg) were extracted in ultrapure water at 100°C for 24 h, acid-hydrolyzed under 6M HCl vapor at 150°C for 3 h, desalted using cation-exchange chromatography, concentrated by evaporation under vacuum, derivatized by *o*-phthaldialdehyde/*N*-acetyl-L-cysteine and then analyzed by LC-FD/ToF-MS to determine the total amino acid concentrations and enantiomeric ratios [3]. 75% of the remaining water extracts as well as the solid residues were stored at –20°C for future analyses.

Results: A variety of two- to six-carbon amino acids were identified in the Tarda samples with concentrations ranging from ~0.02 to 26 nmol/g (Table 1). The two Tarda stones had similar relative amino acid distributions dominated by glycine, glutamic acid, alanine, β-alanine, and γ-amino-*n*-butyric acid. The combined observations of these amino acids also being in the sand, and the low enantiomeric ratio of glutamic acid in the Tarda stones (D/L ~ 0.11 to 0.13), which are similar to the sand (D/L ~ 0.18), indicates there was terrestrial protein amino acid contamination of Tarda after its fall. However, the elevated abundance of D-

alanine in the Tarda meteorites (D/L ~ 0.58) compared to the sand (D/L ~ 0.14) indicates that at least some of the alanine is extraterrestrial. Compound-specific stable isotopic measurements are needed to firmly establish the origin of the measured L-enantiomeric excesses of alanine and the other protein amino acids in Tarda.

Several non-protein amino acids, including α-aminoisobutyric acid (α-AIB), β-amino-*n*-butyric acid (β-ABA), and isovaline were identified in both Tarda samples, but not in the sand above the 0.01 nmol/g detection limit (Table 1). β-ABA and isovaline were also present as racemic mixtures (D = L), providing evidence of their non-biological origins (Table 1). The relative abundances of AIB and isovaline in Tarda are similar to that found in the least altered Tagish Lake (C2) 5b lithology [3,6], although the total amino acid concentrations in Tarda are ~4-5 times higher than in 5b, which could suggest that Tarda is less altered than this Tagish Lake lithology (Fig. 1). The bulk H abundances in the Tarda #1 and #2 stones were 0.68 and 0.98 wt.%, which correspond to petrologic types of C2.2 and C1.8, respectively. This range of petrologic types is similar to those of Tagish Lake [7].

Table 1. Summary of the total amino acid concentrations (nmol/g) in the acid hydrolyzed, hot water extracts of the Tarda meteorites and a sand sample from the meteorite strewn field. Uncertainties are based on the standard error of the average value of 3 to 6 measurements.

	Tarda #1	Tarda#2	Tarda Sand
Dicarboxylic amino acids			
D-aspartic acid	0.42 ± 0.01	0.39 ± 0.01	0.93 ± 0.03
L-aspartic acid	0.95 ± 0.03	0.79 ± 0.02	2.34 ± 0.06
D-glutamic acid	0.79 ± 0.04	0.39 ± 0.02	1.88 ± 0.04
L-glutamic acid	7.0 ± 0.1	3.01 ± 0.07	10.5 ± 0.1
Hydroxy amino acids			
D-serine	0.21 ± 0.01	0.30 ± 0.01	0.61 ± 0.02
L-serine	0.78 ± 0.03	1.25 ± 0.04	1.48 ± 0.04
C2 amino acid			
glycine	11.2 ± 0.5	26.1 ± 0.5	9.2 ± 0.2
C3 amino acids			
β-alanine	3.8 ± 0.1	6.7 ± 0.2	0.25 ± 0.01
D-alanine	0.93 ± 0.04	1.21 ± 0.04	0.35 ± 0.01
L-alanine	1.62 ± 0.06	2.09 ± 0.06	2.58 ± 0.06
C4 amino acids			
D, L-α-ABA	0.91 ± 0.01	0.25 ± 0.01	0.03 ± 0.01
D-β-ABA	0.58 ± 0.02	0.69 ± 0.02	< 0.01
L-β-ABA	0.60 ± 0.02	0.67 ± 0.01	< 0.01
γ-ABA	2.9 ± 0.1	2.67 ± 0.09	0.22 ± 0.01
α-AIB	0.54 ± 0.03	0.67 ± 0.03	< 0.01
C5 amino acids			
D-valine	0.05 ± 0.01	0.02 ± 0.01	0.14 ± 0.01
L-valine	0.81 ± 0.01	0.11 ± 0.01	5.6 ± 0.2
D-isovaline	0.08 ± 0.01	0.05 ± 0.01	< 0.01
L-isovaline	0.08 ± 0.01	0.05 ± 0.01	< 0.01
*Other C5 amino acids	3.1 ± 0.1	1.7 ± 0.2	0.06 ± 0.01†
C6 amino acid			
ε-amino-*n*-caproic acid	< 0.03	< 0.04	< 0.01
Sum AA (nmol/g)	**~37**	**~49**	**~36**

*Sum of all other C5 amino acid isomers identified. †Only δ-aminovaleric acid.

Other amino acid indicators of aqueous activity in carbonaceous chondrite parent bodies include the total amino acid concentration, which decreases with increasing aqueous alteration, and the relative abundance of β-alanine to glycine, which typically increases as a result of extended aqueous alteration (Fig. 1). This

may be related to the enhanced stability of β-amino acids to thermal degradation compared to α-amino acids [8]. These amino acid trends with hydrothermal alteration are illustrated in Fig. 1. Although the relative amino acid abundances in Tarda #1 (Tarda #2 data identical to Tarda #1) appear to be distinct from CI, CM, and CR chondrites, the relative abundance of β-alanine and the total amino acid concentration in Tarda #1 are consistent with its C2.2 petrologic type (Fig. 1).

Figure 1. Total amino acid concentrations and relative amino acid abundances in the C2 ungrouped Tagish Lake and Tarda meteorites and several CI, CM, and CR chondrites. The arrow represents increasing aqueous alteration as inferred from the meteorite petrologic type assignments based on the amount of bulk H in OH and H_2O [9].
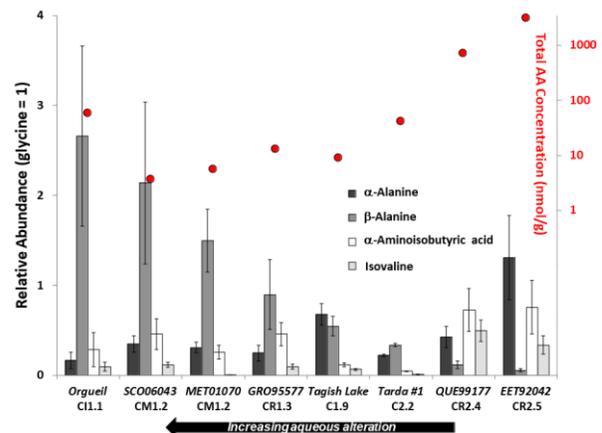
Conclusions: The relative amino acid abundances in Tarda are similar to, but not identical with Tagish Lake, and are distinct from CI, CM, and CR chondrites. Several non-protein amino acids in Tarda (e.g., AIB, β-ABA, and isovaline) are extraterrestrial. Some protein amino acids may also be extraterrestrial, but contamination of Tarda makes this very difficult to assess. Analyses of samples returned from asteroids Ryugu and Bennu that experienced much less exposure to the terrestrial environment will provide the first opportunity to measure the extent of chiral asymmetry in protein amino acids produced solely by non-biological processes. The results from these sample-return missions will provide valuable opportunities to compare the findings in the current work to pristine asteroid samples to evaluate potential parent bodies of Tarda.

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