AMINO ACIDS FROM MARS? CLUES FROM THE MARTIAN SHERGOTTITE ROBERTS MASSIF (RBT) 04262

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Introduction: Martian meteorites afford the only opportunity to directly study samples from Mars using state-of-the-art laboratory techniques on Earth. Previous studies have searched for organic compounds in martian meteorites in an attempt to find evidence of past or present life on Mars [1, 2]. Amino acids are a particularly attractive target because they are essential for life as we know it and highly sensitive methods have been developed for their extraction and analysis from meteorites [3]. Amino acid analyses of the Martian meteorites EET 79001, Nakhla, ALH 84001 and MIL 03346 using traditional high performance liquid chromatography with UV fluorescence detection revealed that these meteorites contained only trace levels of amino acids that were likely to be the result of terrestrial contamination [4-7].

We recently performed amino acid analyses of Martian shergottite Roberts Massif (RBT) 04262 by using highly sensitive and selective Ultra-High Performance Liquid Chromatography with UV-fluorescence detection and time-of-flight mass spectrometry (UHPLC-FD/ToF-MS) instrumentation. For comparison, a sample of Antarctic ice from Graves Nunataks, and several thermally altered Antarctic meteorites were also extracted and examined using the same techniques [9]. Carbon isotopic ratios of two amino acids were also measured in RBT 04262 using gas chromatography combustion isotope ratio mass spectrometry. To our knowledge, there have been no compound specific isotope measurements previously reported for amino acids or any other organic compound in martian meteorites. Amino acid and carbon isotope results from RBT 04262 are reported here [8].

Samples and Analytical Techniques: The Antarctic shergottite RBT 04262 was provided by the Antarctic meteorite curator at the NASA Johnson Space Center. A single fragment of RBT 04262 (split 59, parent 0, mass 820 mg) was crushed into a fine powder with an annealed (500 ºC overnight) porcelain mortar and pestle in a positive pressure (1-µm filtered air) laminar flow hood and then transferred to a clean vial. A separate allocation of RBT 04262 (split 65, parent 63, mass 4.1 g) was also crushed and used for amino acid carbon isotope measurements. Crushed serpentine (a hydrated magnesium silicate) that had been heated at 500 °C for several hours was used as a procedural blank. Amino acids and their enantiomeric abundances were investigated using UHPLC-FD/ToF-MS. A total of 191 mg of RBT 04262 was sealed in a clean glass test tube with 1 ml of double-distilled water and incubated at 100 ºC for 24 h; serpentine and water control samples were treated in an identical fashion. The test tubes were then cracked open and centrifuged to separate out the particulate from the water supernatant. One half of the water extract was transferred to a new test tube, dried under vacuum and desalted by using cation exchange resin (AG50W-X8, 100-200 mesh, Bio-Rad) prior to UHPLC analysis to determine the abundance of free amino acids associated with the bulk sample (unhydrolyzed water soluble fraction). The remaining water supernatant was transferred to a separate test tube, dried under vacuum, hydrolyzed under 6 M HCl vapor at 150 ºC for 3 h and then desalted. Both the hydrolyzed and unhydrolyzed fractions were analyzed by *o*-pthaldialdehyde / *N*-acetyl-L-cysteine (OPA/NAC) derivatization and UHPLC separation to determine bound amino acids in the bulk sample (hydrdolyzed water-soluble fraction).

Table 1. Comparison of selected amino acid abundances (in ppb) for Martian meteorites.

	Nakhla [2]	MIL 03346 [5]	RBT 04262
D-aspartic acid	23 ± 7	6	<1
L-aspartic acid	63 ± 12	52	<1
D-glutamic acid	44 ± 9	33[a]	<1
L-glutamic acid	278 ± 7		<1
D-serine	21 ± 13	4	<2
L-serine	81 ± 35	4	<2
D-alanine	18 ± 12	3	<6
L-alanine	55 ± 11	25	4 ± 1
glycine	327 ± 1	43	22 ± 3
β-alanine	100 ± 15	17	64 ± 17
γ-amino-*n*-butyric acid	99 ± 11	22	133 ± 12

[a]The D- and L-enantiomers were not resolved.

Results and Discussion: UHPLC analyses of RBT 04262 revealed that it contains trace levels of amino acids (Table 1). In contrast with Nakhla and MIL 03346, RBT 04262 is nearly devoid of several common proteinogenic amino acids including aspartic and glutamic acids, serine, and alanine (Table 1), indicating

a lack of terrestrial protein amino acid contamination. For Nakhla, the amino acids are consistent with a bacterial origin derived from the landing site environment [5]. In contrast, RBT 04262 contains primarily glycine and the straight chain, amino-terminal amino acids (*n*-ω-amino acids) β-alanine and γ-amino-*n*-butyric acid. Another *n*-ω-amino acid, ε-amino-*n*-caproic acid was also detected in RBT 04262, but this amino acid is present predominantly in bound form, indicating its primary source is likely the Nylon-6 bags used during collection in Antarctica [1].

We also observed *n*-ω-amino acid relative abundances similar to those in RBT 04262 in several thermally metamorphosed ureilites and CO and CV carbonaceous chondrites (Fig. 1); the amino acids in those meteorites were argued to be extraterrestrial in origin. [6]. We were able to measure the carbon isotopic ratios of β-alanine (-24 ± 6 ‰) and ε-amino-*n*-caproic acid (-27 ± 5 ‰) from an extraction of the larger mass of RBT 04262. These values are also similar to the carbon isotopic ratios measured for γ-amino-*n*-butyric acid and ε-amino-*n*-caproic acid in the CV3 chondrite LAP 02206 [9]. In the case of ε-amino-*n*-caproic acid, the likely source is the Nylon-6 bags used for meteorite collection, an assertion supported by the $\delta^{13}C$ value of -27‰. The presence of β-alanine and γ-amino-*n*-butyric acid are not as easily explained as terrestrial contamination because these compounds do not come from the bags, they are not found in significant levels in several samples of Antarctic ice, and their high abundances relative to glycine are not consistent with the relative abundances found in biology. The absence of appreciable levels of proteinogenic amino acids in RBT 04262 other than glycine argues against biological contamination, and suggests that the observed amino acids may be of extraterrestrial origin, although when and how the observed amino acids were formed remains unclear. The $\delta^{13}C$ value of -24‰ measured for β-alanine is in the terrestrial range but also consistent with values obtained for reduced organics in Martian meteorites (-19.8 ± 4.3 ‰; [2]) and may be a signature of high-temperature amino acid synthesis. Further work is needed to test whether the observed isotopic ratios are consistent with values obtained for amino acids produced from thermal amino acid synthesis in the laboratory.

Conclusion: The amino acid inventory of the Martian meteorite RBT 04262 was determined. In contrast with previously analyzed Martian meteorites, RBT 04262 appears to have experienced little to no contamination from terrestrial biology. This meteorite contains predominantly *n*-ω-amino acids, giving it an amino acid distribution similar to what we observed in thermally metamorphosed meteorites. If these amino acids are extraterrestrial, they could have formed from high-temperature amino acid synthesis either below the Martian surface or during the impact that led to the ejection of the RBT 04262 parent body, or been delivered to the Martian surface from the impactor itself. An extraterrestrial origin for these amino acids would be strengthened if the SAM wet chemistry experiment aboard the Curiosity rover [10] is able to detect a similar distribution of *n*-ω-amino acids on Mars.

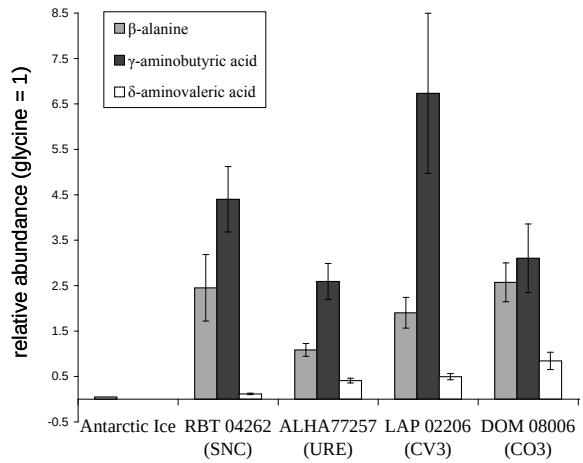

Figure 1: A comparison of the relative molar abundances (glycine = 1.0) of β-ala, γ-ABA, and δ-AVA in the 6 M HCl-hydrolyzed, hot-water extracts of RBT 04262, thermally altered carbonaceous meteorites and Antarctic ice. The uncertainties were calculated by standard error propagation of the absolute errors. Figure adapted from [8].

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