Extraterrestrial Non-Protein Amino Acids Identified in Carbon-Rich Particles Returned from Asteroid Itokawa

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In this work, amino acid analyses of the acid hydrolyzed hot water extracts of gold foils containing five Category 3 (*i.e.,* carbon-rich) [1-4] particles returned by the JAXA Hayabusa mission were performed by liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS). In advance of LC-FD/ToF-MS analysis, and after hot water extraction and acid hydrolysis, samples underwent pre-column derivatization using *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC), which is a fluorescent tagging agent that facilitates chromatographic separation of chiral primary amines. Initial analyses of these particles by JAXA using field emission scanning electron microscopy with energy dispersion X-ray spectrometry suggested the particles possessed significant amounts of carbon. Prior to amino acid analysis, infrared and Raman microspectroscopy analyses revealed highly primitive organic carbon was present in some grains [5]. Some terrestrial contamination, primarily as L-protein amino acids, was observed in all sample extracts. However, several terrestrially uncommon non-protein amino acids were also identified. Some particle extracts were characterized by racemic (D ≈ L) mixtures of the non-protein amino acids β-amino-*n*-butyric acid (β-ABA) and β-aminoisobutyric acid (β-AIB) at low abundances ranging from 0.09 to 0.31 nmol g^{-1}. A larger abundance of β-alanine (9.2 nmol g^{-1}, ≈4.5 times greater than background levels), also a non-protein amino acid, were measured in a combined extraction of three particles. This β-alanine abundance in these Hayabusa particles was ≈6 times higher than that (1.49 nmol g^{-1}) measured in an extract of a grain of the CM2 Murchison meteorite, which was processed in parallel. The comparatively high abundance of β-alanine in these three Hayabusa grains is surprising because Itokawa possesses similar features to that of amino acid poor LL ordinary chondrites, suggesting that perhaps the amino acid content observed in this study may be a result of exogenous delivery, as has been reported in the analyses of other Hayabusa particles [1,6]. Elevated abundances of β-alanine and racemic β-AIB and β-ABA in Hayabusa particles suggest these non-protein amino acids are not of terrestrial origin. These Itokawa results represent the first presentation of amino acids not of terrestrial origin in the extracts of material collected by an asteroid sample-return mission. Furthermore, these results demonstrate the analytical capabilities of the protocols used in this work as viable options with which to explore the soluble organic chemistry of asteroids Ryugu and Bennu returned by the Hayabusa2 and OSIRIS-REx missions, respectively.

References

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