Extraterrestrial Amino Acids and Amines Identified in Asteroid Ryugu Samples Returned by the Hayabusa2 Mission

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Analyses of amino acids and aliphatic amines were performed on the hot water extracts of two asteroid Ryugu samples returned by the JAXA Hayabusa2 mission. The two samples were A0106, which was comprised of surface material, and C0107, which was comprised of both surface and possible subsurface material. Prior to amino acid analysis, portions of each sample extract underwent acid vapor hydrolysis, while other portions remained unhydrolyzed to allow for a respective comparison between bound and free amino acids. Subsequently, these extracts were derivatized with *o*-phthaldialdehyde/N-acetyl-L-cysteine, a chiral, fluorescent tag that enhances analytical specificity and sensitivity for primary amines, and then analyzed using ultrahigh performance liquid chromatography with fluorescence detection and high-resolution mass spectrometry. Prior to the analysis of aliphatic amines, separate portions of each sample extract were derivatized with AccQ•Tag, a florescent tag that is insensitive to salts and targets primary amines and select secondary amines, and then analyzed by ultraperformance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry. The analyses performed here focused on the abundances and relative distributions of amino acids and aliphatic amines, as well as determining the enantiomeric compositions of detected chiral amino acids. For contamination control and background subtraction purposes, procedural and analytical blanks were processed and analyzed in parallel with the Ryugu samples.

In total, 13 amino acids were detected and quantitated here. Five additional amino acids were tentatively identified, but not quantitated. Abundances of individual amino acids of the C_2 – C_6 variety were measured to vary between 0.02 and 15.8 nmol g^{-1}. Among those amino acids identified, several were non-protein amino acids that are uncommon in biology. These included β-aminoisobuytric acid (β-AIB) and β-amino-*n*-butyric acid (β-ABA), which were measured to be racemic or very nearly racemic, suggesting that these species were likely to be indigenous to the sample and extraterrestrial in nature. While trace quantities of select protein amino acids were found to be enriched in the L-enantiomer, elevated abundances of racemic, free alanine were observed, indicating that the Ryugu sample studied here were exposed to minimal terrestrial contamination.

The analyses of aliphatic amines revealed four species of the C_1 – C_3 variety, which were identified and measured above background levels. These aliphatic amines were methylamine, ethylamine, isopropylamine, and propylamine, in order of descending abundances. These aliphatic amine species were individually measured at abundances ranging from 0.05 – 34.14 nmol g^{-1} in the unhydrolyzed hot water extracts of Ryugu samples A0106 and C0107.

It has been reported that Ryugu samples are chemically similar to CI-type chondrites [1,2]. However, the abundances and relative distributions of amino acids and aliphatic amines in Ryugu are strikingly different from those of CI1.1/2.0 Orgueil. More specifically, CI1.1/2.0 Orgueil contains upwards of 5.6x the total abundance of amino acids as Ryugu, and more than 5x the total abundance of aliphatic amines as Ryugu. These observed abundance differences could be caused by discrepancies in alteration conditions experienced by the parent bodies of Orgueil and Ryugu, or variabilities in original parent body chemical conditions. Additionally, it is plausible the lower overall abundances of amino acids and amines in the near-surface samples collected by Ryugu may be due to the loss of these compounds, or their volatile precursors, via such factors as space weathering and solar heating in a hard vacuum environment. These possible loss mechanisms are worthy of further exploration. Regarding amino acid distributions observed in Ryugu, α-amino acids, which could have been generated by the Strecker cyanohydrin synthesis, were identified, along with β-, γ-, and δ-amino acids. Examples of the latter included C_3 – C_5 straight-chain *n*-ω-amino acids. The observed amino acid distribution indicates that more than one formation mechanism occurred on the Ryugu parent body and was responsible for the amino acids reported here. Lastly, the analytical techniques used here were sufficiently sensitive to detect and quantify the target analytes under the limited sample mass conditions of the current work, which offers strong evidence that these methods will likely perform similarly well when applied to the analyses of amino acids and aliphatic amines in asteroid Bennu samples returned by the NASA OSIRIS-REx mission in September 2023.

References

[1] Yada, T. et al. (2022) *Nature Astronomy*, 6, 214-220. [2] Yokoyama, T. et al. (2022) *Science*, eabn7850.

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