

Detection of Purine and Pyrimidine Nucleobases in the Ryugu Sample

Toshiki Koga¹, Yasuhiro Oba², Yoshinori Takano¹, Hiroshi Naraoka³

¹*Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC)*

²*Institute of Low Temperature Science (ILTS), Hokkaido University*

³*Department of Earth and Planetary Sciences, Kyushu University*

Nucleobases, nitrogen (N)-containing heterocyclic compounds, are essential components of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), which preserve and transfer genetic information crucial for all life on Earth. These nucleobases and their derivatives, found in extraterrestrial materials, have garnered significant interest due to their implications for the chemical evolution of primordial molecules within the Solar System and their potential link to the emergence of genetic functions on early Earth. Our analytical methods, which involve high-performance liquid chromatography paired with electrospray-ionization high-resolution mass spectrometry (HPLC/ESI-HRMS), have identified all five canonical nucleobases (uracil, cytosine, thymine, adenine, and guanine) in the CM2 Murchison carbonaceous meteorite [1].

In the initial analyses of Hayabusa2 samples allocated to the SOM (Soluble Organic Molecules) team [2], aggregate samples of Ryugu grains (A0106 and C0107) were analyzed using HPLC/ESI-HRMS. The pyrimidine nucleobase uracil was identified in hot water extracts from the Ryugu A0106 and C0107 samples, with concentrations ranging from 11 to 32 ng/g [3]. Despite the successful detection of uracil, purine nucleobases were not found in the Ryugu samples under the experimental conditions used in the initial analysis. However, subsequent improvements in extraction, purification, and analysis methods for extraterrestrial nucleobases enabled us to detect nucleobases at an order of magnitude higher abundance than previously detected [4]. Therefore, using these improved methodologies, we requested new Ryugu samples through JAXA's 3rd Announcement of Opportunity (AO3) and received aggregate samples A0480 (11.9 mg) and C0370 (8.3 mg) to clarify the presence of nucleobases other than uracil in the type-C asteroid Ryugu.

All extraction procedures for the Ryugu aggregate samples were performed with thermally treated glassware on an International Organization for Standardization (ISO) 5 (Class 100) clean bench inside an ISO 6 (Class 1000) clean room at Kyushu University. The Ryugu A0480 and C0370 samples underwent (1) water extraction at ambient temperature with sonication (H₂O extracts), followed by (2) 6 M HCl extraction at 110 °C for 20 hours (HCl extracts). The H₂O and HCl extracts were purified using cation exchange chromatography and analyzed by HPLC/ESI-HRMS.

We identified all five canonical nucleobases (uracil, cytosine, thymine, adenine, and guanine), other N-heterocycles (e.g., xanthine, hypoxanthine, and nicotinic acid), and N-containing molecules (e.g., amino acids and urea) in the H₂O and HCl extracts from the Ryugu A0480 and C0370 samples [5]. The chromatographic peaks of nucleobases obtained from the Ryugu samples were significantly higher than those of a procedural blank, indicating that these nucleobases are indigenous to the Ryugu samples. The total concentration of nucleobases in the C0370 sample (~170 ng/g) was more than three times greater than that of the A0480 sample (~50 ng/g), but approximately 50% of that in the B-type asteroid Bennu sample (~340 ng/g; Glavin et al., accepted) and approximately 10% of that in the Murchison meteorite (~1,650 ng/g; [4]). In the Ryugu samples, guanine was identified as the most abundant nucleobase, with its concentration being higher in the HCl extract (67 ng/g) than in the H₂O extract (17 ng/g) for the C0370 sample. The conclusive identification of guanine in the HCl extract of the C0370 sample was achieved through MS/MS experiments. The simultaneous detection of both pyrimidine and purine nucleobases in the Ryugu samples has profound cosmochemical and prebiotic implications, suggesting that these essential components of DNA and RNA were widespread in the Solar System and could have been delivered to early Earth.

References

[1] Oba et al. (2022) *Nat. Commun.*, 13: 2008. [2] Naraoka et al. (2023) *Science*, 379: eabn9033. [3] Oba et al. (2023) *Nat. Commun.*, 14: 3107. [4] Koga et al. (2024) *GCA*, 365: 253–265. [5] Koga et al. in preparation.

Acknowledgments

The Ryugu samples in this study were allocated through the 3rd Announcement of Opportunity (AO3) by JAXA/ISAS. The authors thank JAXA/ISAS for the support of our analyses. We acknowledge the entire Hayabusa2 team for making Ryugu sample analysis possible.