Determination of Amino Acid Enantiomers in Antarctic Meteorites by 3D-HPLC

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A wide variety of organic compounds including amino acids have been found in extraterrestrial bodies such as carbonaceous chondrites and comets. Amino acids have enantiomers, and D/L ratios or enantiomeric excesses of amino acids have been used for their indigenousness in extraterrestrial bodies and/or possible seeds of homochirality in terrestrial life (Glavin et al., 2020; Takahashi and Kobayashi, 2019). Thus, it is important to determine amino acid enantiomers in extraterrestrial bodies. In these days, not only meteorites but also cosmic dusts, samples from comets, and asteroids are targeted to examine the possible contribution of extraterrestrial organic compounds to the generation of life. Thus, the present methods to determine enantiomers of amino acids in meteorites could be applied to such novel astrobiological samples.

Carbonaceous chondrites used in the present study were 4 Antarctic meteorites (Y980511.46, Y793321.102, A-881458.62, Y-982086.106) and Murchison meteorite: 10-25 mg of each meteorite was subjected to analysis. Each sample was powdered and amino acids in it were extracted with 100 mL of 6 M HCl at 100°C for 20 h. The supernatant was recovered, evaporated to dryness, and then the residue was dissolved in 50 mL of double distilled water. Amino acids in the solution were converted to nitrobenzofrazan (NBD)-derivatives, and then were determined by 3D-HPLC (Furusho et al., 2020; Ishii et al., 2023).

Various amino acids were detected in all of the five meteorite samples, and glycine was always predominant. Glycine concentration in the 3 Antarctic meteorites was less than 10% of that in Murchison. Other proteinic amino acids detected were alanine, serine, aspartic acid, and valine. Both L-isomers and D-isomers were detected, but the former was a little more than the latter. The procedural blank showed the presence of L-isomers of these proteinic amino acids and glycine, which was the reason why an excess of the L-isomers was observed. Such non-proteinic amino acids as 2-aminobutyric acid, isovaline, and norvaline were detected as racemic mixtures, which showed the meteorites contained indigenous amino acids.

The present technique was applied to the analysis of amino acids in the sample of asteroid Ryugu returned by Hayabusa2 (Naraoka et al., 2023). Racemic mixtures of various amino acids in it showed the presence of indigenous amino acids in the asteroid, and a strong connection between carbonaceous asteroids and carbonaceous chondrites. It was suggested that amino acids in asteroids could be synthesized by aqueous alteration in the interior of asteroids (Kebukawa et al., 2022). Such amino acids could have been delivered to early Earth not only meteorites but also cosmic dusts. Chyba and Sagan (1992) suggested that much more organic carbons were delivered by cosmic dusts than by meteorites. It was not known, however, what concentration of amino acids was present in cosmic dusts. In the Tanpopo Mission, dusts flying in low Earth orbit were captured by using ultralow density silica aerogel equipped on the Exposed Facility of the Japanese Experimental Module of the International Space Station (Yamagishi et al., 2021). Amino acids in the aerogel fragments containing dusts were now under analysis by using the present method.

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References

Chyba, C., Sagan, C., Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life, Nature, 355, 125-132, 1992.
Furusho, A., Akita, T., Mita, M., Naraoka, H., Hamase, K., Three-dimensional high-performance liquid chromatographic analysis of chiral amino acids in carbonaceous chondrites. J. Chromatogr. A, 1625, 461255, 2020.
Glavin, D. P., Burton, A. S., Elsila, J. E., Aponte, J. C., Dworkin, J. P., The search for chiral asymmetry as a potential biosignature in our solar system, Chem. Rev., 120, 4660-4689, 2020.
Ishii, C., Morinaga, R., Takahashi, M, Mita, M., Akita, T., Hamase, K., Development of a three-dimensional HPLC system for acidic amino acid enantiomers and determination of their amounts in mice lacking D-aspartic acid oxidase activity, J. Pharm. Biomed. Anal. Open, 1, 100004, 2023.

Kebukawa, Y., Asano, S., Tani, A., Yoda, I., Kobayshi, K., Gamma-ray-induced amino acid formation in aqueous small bodies in the early solar system, ACS Cent. Sci, 8, 1864-1871, 2022.
Naraoka, H., Takano, Y., Dworkin, J. P., Oba, Y., Hamase, K. et al., Soluble organic molecules in samples of the carbonaceous asteroid (162173) Ryugu, Nature, 379, 6634, 2023.
Takahashi, J., Kobayashi, K., Origin of Terrestrial Bioorganic Homochirality and Symmetry Breaking in the Universe, Symmetry, 11, 919, 2019.
Yamagishi, A., Yokobori, S., Kobayashi, K., Mita, H., Yabuta, H. et al., Scientific Targets of Tanpopo: Astrobiology Exposure and Micrometeoroid Capture Experiments at the Exposure Facility of the International Space Station, Astrobiology, 21, 1451-1460, 2021.