Hydroxy amino acids identified in the Murchison meteorite and their plausible formation pathways

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Introduction

The occurrence of meteoritic amino acids has been extensively examined using carbonaceous chondrites, particularly the Murchison meteorite since its fall in 1969, because the amino acids are one of the essential building blocks of the terrestrial life. Even though the terrestrial life adapt 20 amino acids, all of which are α-amino acids bearing carboxyl and amino group at the same carbon, the meteoritic amino acids have various structures including β, γ and δ structures with dicarboxyl and diamino functional groups. Up to date, 86 amino acids are reported between C_2 and C_8 from Murchison [1]. The concentration and structural diversity of amino acids increase after hydrolysis of the water extract of meteorites, suggesting that the meteoritic amino acids are present mainly as their precursors. In addition, the amino acid distribution (e.g. α-aminoisobutyric acid and β-alanine [2]) and L-enantiomeric excess (Lee) of isovaline [3] could be correlated with the degree of aqueous alteration. Although these results suggest that the aqueous alteration had have influenced on amino acid synthesis on the meteorite parent body, the detailed formation mechanisms remain unclear. The Strecker reaction has been considered as an important mechanism to synthesize α-amino acids. However, β- and γ-amino acids cannot be produced by the Strecker reaction. In this study, we revisited amino acid analysis of the Murchison meteorite to persue their formation mechanisms and performed the amino acid synthesis experiments simulating the condition of meteorite parent body.

Materials and Method

Interior fragments of the Murchison meteorite were powdered and extracted with hot water at 100 °C for 20 h in a N_2-purged glass ampoule. The supernatant and the extract residue were subjected to acid hydrolysis with 3M and 6M HCl, respectively. After desalting using an ion exchange column to purify amino acids, both fractions were reacted with isopropanol(iPrOH)/HCl and trifluoroacetic anhydrite (TFAA). The resultant TFA-amino acid-OiPr derivatives were analyzed by gas chromatography/mass spectrometry with a Chirasil-L-Val capillary column. The amino acids were identified and quantified based on their retention times and mass spectra of standard amino acids.

The simulation experiments of amino acid synthesis were performed as follows. The aqueous solution (300 μL) containing ammonia/formaldehyde/acetaldehyde and/or glycolaldehyde (100/10/1/1 by mol) with NH_3/H_2O (1/100) was heated at 60 °C for 6 days in a N_2-purged glass ampoule with or without olivine powder (San Carlos, 27.0 mg). The reaction products were analyzed by the same procedure as described above.

Results and Disccusion

Totally more than 20 amino acids between C_2 and C_5 were identified in the extract of Murchison, in which glycine was the most abundant (up to approximately 3.1 ppm in the supernatant and the extract residue fraction). Other characteristic amino acids such as β-alanine, isovaline and α-aminoisobutyric acid were also found (1.8, 1.6, 1.0 ppm, respectively), which were reported as indigenous amino acids in CM chondrites by previous studies.

In addition to these amino acids, new six C_4 hydroxy amino acids (γ–amino-α-hydroxybutyric acid, β-amino-α-(hydroxymethyl)propionic acid, β-homoserine, γ–amino-β-hydroxybutyric acid, α-methylserine, isothreonine and allo-isothreonine) have been newly identified from the Murchison extract. The concentration ranged from ~20 to ~140 ppb relative to bulk meteorite. A new dicarboxy amino acid, β-(aminomethyl)succinic acid, was also detected as a relatively large peak (~90 ppb). The discovery of new six C_4 amino acids is striking after rigorous search of amino acids since half century ago. These amino acids were discriminated clearly from the hydrolyzed sample of the residue fraction due to disappearance of other chromatographic peaks. Therefore, it seems that the hydroxy amino acids are more intimately associated with clay minerals than other compounds.

The simulation experiments gave various amino acids including the hydroxy amino acids with the most abundant of glycine as identified in the Murchison extract. In particular, β-(aminomethyl)succinic acid was produced using formaldehyde, acetaldehyde and ammonia in the presence of olivine, but not detected in the absence of olivine. The hydroxy amino acids were also identified using glycolaldehyde in addition to formaldehyde, acetaldehyde and ammonia. These results indicate that formose reaction with ammonia is an important pathway to produce meteoritic amino acids. The role of anhydrous minerals including olivine could be significant as a catalyst during aqueous alteration on the meteorite parent body. Further study is needed to identify the amino acid precursors for the detailed reaction mechanism(s).

References

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