Amino acid synthesis from aldehydes and ammonia in the presence of olivine

*Toshiki Koga[1], Hiroshi Naraoka[1]

1.Department of Earth and Planetary Sciences Kyushu University

[Introduction]

Carbonaceous chondrites, which have primitive chemical compositions in the Solar System, contain a diverse suite of extraterrestrial amino acids. Since the discovery of the building blocks of terrestrial life in the extraterrestrial materials, the amino acids have been most investigated among meteoritic organic compounds. In particular, the degree of aqueous alteration on meteorites appears to have correlation to the amino acid distribution (e.g. α-aminoisobutyric acid and β-alanine) and L-enantiomeric excess (Lee) of isovaline. Although these results suggest that aqueous alteration have influence on amino acid synthesis on the meteorite parent body, the detailed formation mechanisms remains unclear. In this work, we performed the amino acid synthesis experiments simulating the condition of meteorite parent body to investigate their distribution and enantiomeric composition to infer the formation mechanism of meteoritic amino acids.

[Materials and Methods]

Aqueous solution (300 μL) containing ammonia/formaldehyde/acetaldehyde or ketone (100/10/1 by mol) was heated at 60 °C for 6-28 days in a N_2-purged glass ampoule with or without olivine powder (San Carlos, 27.0 mg). The reaction product was extracted with hot water, and the supernatant was divided into two fractions. Then one was subjected to acid hydrolysis with 6M HCl, the other was not hydrolyzed. After purification using ion exchange column, both fractions were derivatized with iPrOH/HCl and trifluoroacetic anhydrite. The resultant amino acid derivatives were analyzed by gas chromatography/mass spectrometry. The amino acids were identified and quantified based on their retention times and mass spectra of standards.

[Results and Discussion]

Totally 16 amino acids up to C_5 were identified, in which glycine was the most abundant (up to approximately 3500 ppm relative to carbon amount of reactants). Other amino acids are composed mainly of serine, isoserine, alanine, β-alanine, β-(aminomethyl)succinic acid, β-aminobutyric acid, homoserine, aspartic acid and glutamic acid (up to approximately 600, 250, 240, 240, 160, 110, 60, 60 and 50 ppm, respectively). In the absence of olivine, relatively small amounts of glycine, serine, isoserine, alanine, β-alanine and β-aminobutyric acid were detected (up to approximately 840, 30, 110, 80, 90, and 90 ppm, respectively) from the hydrolyzed fraction. In contrast, in the presence of olivine, the concentration of most of the amino acids (up to approximately 3500, 600, 250, 240, 240 and 110 ppm, respectively) increased significantly in the hydrolyzed fraction. The amino acid concentration increased significantly after hydrolysis, which is similar to the occurrence of meteoritic amino acids.

The amino acid distribution (e.g. absence of α-aminoisobutyric acid and isovaline) implies a different formation pathway from the Strecker-type reaction, which has been proposed for meteoritic amino acid synthesis. We propose other formation mechanisms: iminium cation produced from aldehydes and ammonia is subjected to nucleophilic addition by formyl anion followed by chemical oxidation, giving α-amino acids detected in this experiment. In addition, larger amino acids ($> C_3$) are synthesized through aldol condensation, explaining the occurrence of α-, β-amino acids detected.

Further experimental studies are needed to reveal the detailed formation mechanism of amino acids from aldehydes and ammonia with olivine.

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