

Possible amino acid formation pathways in submarine hydrothermal systems

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In prior to the generation of terrestrial life, bioorganic compounds such as amino acids are essential. Possible sites for the formation of amino acids are (i) interstellar space, (ii) primitive atmosphere and (iii) submarine hydrothermal systems. If the primitive Earth atmosphere was neutral (i.e., chiefly composed of carbon dioxide and nitrogen), formation of amino acids was quite limited, but carboxylic acids could be formed by spark discharges and other energy sources. If the carboxylic acids, especially keto acids, formed in the atmosphere were introduced to submarine hydrothermal systems, we can expect the formation of amino acids from carboxylic acids and ammonia dissolved there. In the present work, we examined possible formation of keto acids from simulated primitive atmosphere, and possible formation of amino acids from keto acids and ammonia by using a flow reactor simulating submarine hydrothermal systems.

Spark discharge experiments: A mixture of carbon dioxide (300 Torr) and nitrogen (300 Torr) was introduced to a 400-mL Pyrex flask over 5 mL of water, and spark discharges were applied to the gas mixture for 12 hours. After discharges, the resulting products were recovered from the flask, and amino acids were analyzed after acid-hydrolysis of the product.

Flow reactor experiments: We constructed a specially designed flow reactor (supercritical water flow reactor [1]), which allowed aqueous samples heated up to 673 K for minutes without pre-heating and then quenched to 273 K. The pressure was maintained at 25 MPa during the heating. A mixed solution of 10 mM of pyruvic acid and 10 mM of ammonia was injected to the flow reactor, and heated at 473-673 K for 2 min. The resulting products recovered were acid-hydrolyzed, desalted with a Monospin SCX cation-exchange resin, and applied to an amino acid analyzer (Shimadzu LC-10A).

In the spark discharge products, we could not detect amino acids, but some carboxylic acids were detected by capillary electrophoresis. Thus it is difficult to obtain amino acids by spark discharges in neutral atmosphere. We are trying to detect keto acids in the discharge products.

Amino acids (glycine and serine) were detected after a mixture of pyruvic acid and ammonia was heated at 523 K in the flow reactor. It suggested that carboxylic acids and ammonia formed from neutral atmosphere could react to give amino acids in submarine hydrothermal systems.

[1] Islam, Md. N. et al., Bull. Chem. Soc. Jpn., 76, 1171-1179 (2003).

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