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Formation of Amino Acids in Simulated Submarine Hydrothermal Systems Using a Supercritical Water Flow Reactor

Md. Nazrul Islam[1], Masahiro Murata[2], Kensei Kobayashi[2]

[1] Faculty of Engeering, Yokohama National Univ., [2] Dept. Chem. Biotech., Yokohama Natl. Univ.

The discovery of submarine hydrothermal systems in the late 1970's stimulated geophysical, geochemical, microbiological, ecological and ore deposit research on submarine hydrothermal systems. Since these systems present reducing, energy-rich and metal ion-rich conditions in the present terrestrial environment, they are considered to be ideal sites for present day abiogenic synthesis of organic compounds and have been suggested as a possible environment for chemical evolution and the origin of life. Several theoretical and experimental works have been performed for the simulation of submarine hydrothermal systems (SHSs). In most of the experiments, however, reactants (aqueous solution) were heated in closed heating systems such as in autoclaves. Most of theoretical studies also have been done simulating closed systems. Whereas, actual SHSs can be regarded as flow reaction systems, where sea water penetrating into the earth crust can be reached nearer to magma-zone (1100C) and be heated by magma over supercritical point of water. In the natural systems at least 300C temperature needed to mix-up the crust with sea water and at least this temperature is essential to get actual reaction in the natural systems. Thus we constructed a supercritical water flow reactor (SCWFR) to examine possible reactions in SHSs.

We examined the possible formation of amino acids hydrothermally when a solution of HCHO (0.1M), KCN (0.1M) and NH4HCO3 (0.05M) was pumped in to the SCWFR and heated at 50-400C under 25 MPa. Where, the sample was heated for 2, 5 or 10 minutes for the reaction. The samples were acid hydrolyzed and then analyzed by amino acid analysis system (Shimadzu LC-6A) associated with Shim-pack ISC-07/S1504 (sodium type, 4.0 mm i. d. x 150 mm). Glycine, alanine, sarcosine, beta-alanine, gamma-aminobutyricacid, delta-aminovaleric acid and epsilion-aminocaproic acid were detected from the products. The latter four non-porteinous omega-amino acids were detected only higher temperature ranging from 300 to 400C.

The other type of experiments, where, we examined some reactions of serine and imidazole simulating SHSs. A 10 mM solution of serine and imidazole was reacted in the same manner at 100-400C and analyzed in the same process as described above. Glycine, alanine, alpha- aminobutyric acid and beta-alanine were detected in the products. In these experiments the latter two non-proteinous amino acids obtained from temperature ranging from 200 to 300C.

In order to investigate the stability of amino acids in hydrothermal environments, 10 mM of alanine and beta-alanine solution were heated at 300-400C. It was suggested that beta-alanine is relatively more stable than the alanine. The present results suggest that omega-amino acids are relatively stable in SHSs and these types of amino acids might be molecular markers of hydrothermal reaction.

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