

Behavior of amino acids in siliceous ooze under hydrothermal conditions

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Since the stable presence of amino acids is a basic requirement for the existence of life, it is important to understand the physicochemical stability condition of amino acids (AAs) for a reasonable understanding of biomass around the deep-sea hydrothermal systems. In this study, stability of AAs in different marine sediments was evaluated under hydrothermal condition at various temperatures and hydrostatic pressures. The results of hydrothermal experiments, in which siliceous ooze samples were heated together with artificial seawater (3.5 % NaCl solution), are reported here. The results were compared with previously reported results based on carbonaceous ooze. Experiments on heating aqueous AAs but in absence of sediment were also conducted to check the effect of sediment on thermal stability of AAs.

Sample and artificial seawater mixture was heated in an air-tight vessel at the different temperature between 100 and 300 degree C. The liquid fraction was sampled at pre-decided intervals during 240 hrs of heating, after which the vessel was cooled to room temperature and reaction products were separated into liquid and solid fractions. The fractions were hydrolyzed with HCl at 110 degree C for 22 hrs. AAs were analyzed by the HPLC (Shimadzu LC-9A).

The total concentration of hydrolysable amino acids (THAAs) was 15.4 nmol/mg in the siliceous ooze. AAs in the artificial seawater were below detection limits. Changes in THAAs with time showed the largest difference between the two types of sediments heated at 150 degree C. THAAs in the case of carbonaceous ooze increased from 13.5 nmol/ml just after reaching at 150 degree C to 52.2 nmol/ml after 24 hrs, and 62.3 nmol/ml after 240 hrs. THAAs concentration in the case of siliceous ooze was 32.8 nmol/ml after 96 hrs, and drastically increased to 350.3 nmol/ml after 118 hrs and the final concentration was 444.2 nmol/ml after 240 hrs of heating at 150 degree C.

AAs were not detected in the final liquid fractions at 250 and 300 degree C, however, small amounts of AAs remained in the solid fractions. Concentration of THAAs remaining after the reaction at 250 and 300 degree C were higher in the siliceous ooze than in the carbonaceous ooze.

Methionine, serine, aspartic acid, leucine, alanine, glycine, glutamic acid and gamma-aminobutyric acid, which were selected as representative AAs were heated with the artificial seawater in a sealed glass ampoule at temperatures, 100, 150 and 250 degree C. AA concentration did not change much during 240 hrs of heating at 100 degree C. When heated at 150 degree C, the AA concentration decreased from 1295.1 nmol/ml (initial concentration) to 733.3 nmol/ml after 240 hrs reaction. The AA concentration in the starting solution used for the reaction at 250 degree C was 1178.3 nmol/ml, and became 1.2 nmol/ml after 240 hrs reaction. Our results proved that the aqueous AAs heated without sediment can hardly survive in high temperature hydrothermal solution.

Only glutamic acid concentration decreased during the reaction at 100 degree C. Glutamic acid, aspartic acid, gamma-aminobutyric acid and methionine were remarkably decomposed at 150 degree C. Glutamic acid, serine, glycine, methionine and gamma-aminobutyric acid barely survived when reacted at 250 degree C for 240 hrs. These results clearly differ from those when AAs are heated together with sediments at the same hydrothermal condition.

Results from our study suggested that AAs cannot survive in free form (aqueous phase) at higher temperatures, except when they occur in association with other inorganic or organic phase, most preferably in solid state.

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