Stability of amino acids in ocean sediment under simulated hydrothermal environments

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Many chemosynthetic organisms have been discovered in surroundings of hydrothermal vent and plume. Based on the discovery of chemosynthetic organisms in these surroundings, it has been expected that a biosphere of enormous volume may exist in the sub-seafloor hydrothermal systems. Deep sea floor sediments are large reservoirs of amino acids, which are fundamental organic compounds comprising organisms. In order to assess survival conditions of organisms under seafloor hydrothermal systems, it is important to understand stability of amino acids in the sediments at hydrothermal conditions. Behavior of acid-hydrolysable amino acids in ocean bottom sediment, which was mostly carbonaceous clay, was studied under hydrothermal conditions created in laboratory. The carbonaceous clay collected from the west of Hawaii was heated with artificial seawater (3 % NaCl solution) in an air-tight vessel for varying time and temperature ranges (at 100, 120, 150, 200, 250, 300 degrees C). After cooling, the reacted samples were separated into liquid and solid fractions. The separated samples were hydrolyzed with HCl at 110 degrees C for 22 hours. Amino acids in the hydrolyzed samples were analyzed using an HPLC (Shimadzu LC-9A).

The total hydrolysable amino acids (THAA) concentration in the starting sediment was 2.8 nmol/mg, and no amino acids in starting artificial seawater were detected. In the experiment at 100 degrees C, THAA content increased in the liquid fraction with time (from 7.6 nmol/ml just when the reaction temperature reached to 100 degrees C to 36.5 nmol/ml after 240 hours). At 120 degrees C also, THAA increased in the liquid with time. In contrast, in the experiment at 150 degrees C, THAA increased to 52.2 nmol/ml after 24 hours, and then moderately changed up to 62.3 nmol/ml (after 240 hours). In the experiment at 200 degrees C THAA concentration rose from 34.9 nmol/ml just after reaching at 200 degrees C to the maximum concentration of 49.1 nmol/ml after 9 hours. Then, the THAA gradually decreased to 18.6 nmol/ml at the end of the experiment after 240 hours. After 240 hours of reactions at 250 and 300 degrees C, no amino acids were detected in the liquid fraction.

The concentrations of THAA in solid fractions heated at 100, 150, and 300 degrees C were 2.0, 0.5 and 0.02 nmol/mg, respectively. A decrease in THAA with increasing temperature is clearly demonstrated in this experiment. At 250 and 300 degrees C, no amino acids were detected in the liquid fraction, however, some amino acids remained in the solid fraction. Amino acids in the solid fraction might be protected from thermal decomposition due to their complexation with clay minerals which did not allow amino acids to react sufficiently with artificial seawater.

The proportions of decomposed THAA (disappearance from both solid and liquid fractions) at 100, 150, 200 and 300 degrees C were 23.5, 62.7, 90.1 and 99.7 %, respectively. Decomposition rate of amino acids in experiments at 200 degrees C increased dramatically, therefore, the limits of amino acids stability against high temperature lie between 200 and 250 degrees C.

Judging from decomposition of each amino acid during hydrothermal experiments, amino acids were classified in order of their increasing thermal stability: (1) methionine, (2) arginine, threonine and serine, (3) aspartic acid, histidine, lysine, isoleucine and leucine, (4) alanine, valine and beta-alanine, (5) glycine, proline and phenylalanine, (6) glutamic acid and gamma-aminobutyric acid. However, all amino acids tended to decompose at temperatures above 200 degrees C.

The degree of decomposition of amino acids in both solid and liquid fractions increased with temperature. The organic matter like amino acid compounds in dissolved form is not stable at temperatures of 250 degrees C and above. Therefore, it is proposed that viable organic matter hardly survive in the hydrothermal systems at temperatures higher than 250 degrees C.