

## Pressure effect on amino acids in siliceous ooze in simulated seafloor hydrothermal environment

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Densely microbial population and biomolecules have been discovered around seafloor hydrothermal vent field, causing expectation of extensive sub-seafloor biosphere. We have estimated stable condition of alpha-amino acids and non-protein amino acids, which were essential for living organisms, under experimental hydrothermal conditions. The previous experiments using the siliceous and calcareous oozes revealed that the chemical compositions of sediment and reacted solution played a controlling role on stability of amino acids (AAs) under hydrothermal condition. In this study, pressure the hydrothermal experiment under subseafloor pressure has been performed at 100-200 deg C to constrain the effect of pressure on the stability of AAs in the siliceous ooze.

The siliceous ooze and artificial seawater (3.5 percent NaCl solution) were reacted in a titanium pressure vessel at different temperatures between 100 and 200 deg C and 30 MPa for 120 hours. After the each run, reaction products were separated into liquid and solid fractions. The fractions were hydrolyzed with HCl at 110 deg C for 22 hours. 17 kinds of alpha-AAs and non-protein AAs were analyzed by the high performance liquid chromatography (Waters 2695).

Total concentration of hydrolysable amino acids (THAAs) in the starting siliceous ooze was 15.4 nmol/mg, and no AAs were detected in the primary artificial seawater. THAAs in the siliceous ooze after reaction at 30 MPa and 100, 150 and 200 deg C were 9.4, 2.3 and 1.0 nmol/mg, respectively, while, the THAAs in the siliceous ooze reacted at the hydrostatic pressure at those temperatures were 13.5, 5.8 and 1.6 nmol/mg. Higher decreasing rate of the THAAs at elevated temperature and at 30 MPa than that at hydrostatic pressure indicates the decreasing stability of AAs at elevated pressure.

Dissolved THAAs after reaction at 100, 150 and 200 deg C and 30 MPa were 212, 253 and 51 nmol/mg, respectively, and those at hydrostatic pressure at the given temperatures were 145, 205 and 90 nmol/mg, respectively. At low 150 deg C, the dissolved THAAs were higher at 30 MPa than at hydrostatic pressure, while, those at 200 deg C were higher at hydrostatic pressure than 30 MPa. Thus, the dissolution and decomposition rates of AAs are higher at the higher pressure conditions.

AAs, except serine, glycine, proline and beta-alanine, were more stably present in the siliceous ooze under hydrostatic pressure than 30 MPa. Based on the behaviors of AAs dissolved in the solution at different temperatures and pressures, 6 groups of AAs were identified; (1) AAs of which concentrations were maximum at 100 deg C, hydrostatic pressure and 30 MPa (aspartic acid and serine), (2) AAs of which concentrations were maximum at 100 deg C and hydrostatic pressure, and were maximum at 150 deg C and 30 MPa (histidine and lysine), (3) AA of which concentration was maximum at 100 deg C and 30 MPa, and was maximum at 150 deg C and hydrostatic pressure (proline), (4) AAs of which concentrations were maximum at 150 deg C, hydrostatic pressure and 30 MPa (glycine, isoleucine, phenylalanine and beta-alanine), (5) AAs of which concentrations were maximum at 150 deg C and hydrostatic pressure, and were maximum at 200 deg C and 30 MPa (alanine, valine and leucine), (6) AAs of which concentrations were maximum at 150 deg C and 30 MPa, and were maximum at 200 deg C and hydrostatic pressure (glutamic acid and gamma-aminobutyric acid). Therefore, it is suggested that AAs have each different effects of pressure on those decreasing from the sediment or dissolution into the solution at elevated temperature.

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