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The relationships pH and silica between stability of amino acids under seafloor hydrotheraml comndition.

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To evaluate the effect of pH and silica concentration on the thermal stability of amino acids (AAs) under submarine hydrothermal conditions, glycine, lysine, glutamic acid, serin, cystein and proline were heated in the 2.0nmol/mg NaCl solution of which the pH was controlled strongly acidic (initial pH:1.0), alkaline (initial pH:11.0) condition, and un-controlled (initial pH:5.3), which heated at 140 degrees C for 3-168hrs. The reacted solutions and solids were analyzed by HPLC.
The pH of non-controlled solution was 3.3 after 168hr reacted. serin was decomposed according to the first-order reaction kinetics to be approximately 71% of initial concentration. Polar neutral AAs such as serin would be thermally unstable, particularly the ones having hydroxyl group. Lysine was decomposed to be 69%. Non-polar neutral AAs, glycine, and glutamic acid of 14% and 18% were decomposed, respectively, and are rather stable than the above polar neutral AAs. The glutamic acid remains probably possible via formation of lactam to be stabilized as pyroglutamic acid. Alanin was not added in the starting solution, however, its concentration increased with time corresponding to be decomposition of serin; its concentration increased as high as 0.7nmol/mg after 168hr. The aranin must be stable at the tested temperature.
In the alkaline solution, serin was decomposed as well as in the un-controlled solution, and about 6 7% was decomposed after 168hr. While, 26 and 15% of lysine and glitamic, respectively, were decomposed, indicating that those AAs remained more than those in the pH non-controlled solution. The concentration of glycine slightly increased after the heating , and the 90% remained after 168hr. Although alanin was formed, its concentration was only 0.1nmol/mg after 168hr. Thus, the most serin would be transformed into glycine but not alanin.
In the acidic solution, serin was decomposed rapidly following the first-order reaction kinetic, and was not detected from the solution after 120hr. Alanin increased almost equally to the decomposed serin, indicating that the alanin was rapidly formed via transformation of serin. At alkaline pH, glycine was dominantly formed via decomposition of serin rather than alanin, decomposition and transformation routes of AAs would depend on pH of the solution. Then, glycine, lysine and glutamic acid were gradually decomposed following the first-order reaction kinetic. The decomposition rates of all the AAs are the fastest in the acidic solution. Thus, the AAs would be thermally more stable in alkaline solution than acidic solution. Also, the AAs would be more stable existing as anion than cation.
To evaluate the effect of dissolved silica on the stability of AAs, silica was added in the above three different solutions, and performed similar experiments. The concentration of dissolved silica increased with time in acidic and alkaline solutions, and the concentrations after 168hr were 1908. 4mg/L and 292.6mg/L respectively. On the other hands, the concentration of dissolved silisa is 28. 6mg/L in the un-controlled solution. After 168hr, glycine, lycine and glutamic acid in the acidic and alkaline solutions remained 5~10% more than in the solutions. However, the decomposition rate of the AAs didn't change in the un-controlled solution. The dissolved silica must decrease the decomposition rate of AAs, especially in the alkaline solution, probably due to the 6 times high concentration of dissolved silica protected more AAs.
Our results suggest that the natural seafloor hydrothermal solutions, which contains abundant

dissolved silica, provide suitable chemical environment for AAs to remain in the higher temperature condition than the low silica containing solution. Especially, the hydrothermal systems having alkaline solution, e.g., which is formed via serpentinization of peridptite, must be chemical environments to keep AAs than the common hydrothermal systems venting acidic hydrothermal solution.

Keywords: seafloor hydrothermal system, dessolved silica, amino acids, origin of life,
alkaline hydrothermal solution