

The kinetic effects of silica on the transformation of amino acids

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A new hypothesis of coupled dehydration-polymerization in the hydrous silica - amino acids systems for the first chemical evolution of life was tested by some experiments.

The polymerization reaction was kinetically favored by the presence of silica.

Chert around submarine hydrothermal systems is one of possible geochemical environments of the first primitive life. Hydrated amorphous silica is abundant colloidal material in low temperature aquatic environments and has high surface area and surface active sites for chemical sorption and reactions. Its dehydration reaction proceeds spontaneously with a low to moderate heat energy sources (20-200°C). Considering that amino acids cannot be polymerized spontaneously, the presence of silica can lower the free energy of overall polymerization reactions. Dehydration reactions of hydrous amorphous inorganic minerals such as silica can thus be expected to catalyze dehydration-polymerization of primitive organic molecules such as amino acids into precursors of bio-molecules (proteins). Therefore, we propose here a new working hypothesis of possible geochemical mechanism for the origin of life: coupled dehydration-polymerization-crystallization in the hydrous silica - amino acids systems.

In order to test this hypothesis, we conducted hydrothermal interaction experiments between silica and amino acids. L-threonine (Thr)(0.1mol/l) with and without silica gel were heated at 70 to 150 °C for up to 16 days. After the experiments, the solution was filtered and analyzed by ATR-IR spectroscopy and HPLC.

In order to determine the concentrations of amino acids in solution, we have conducted both ATR-IR and HPLC analyses. The concentration of Thr was first determined by the peak height of 1360 cm⁻¹ band on the ATR-IR spectra. The triplicate ATR analyses on standard solutions showed a good linearity of the calibration line based on this 1360 cm⁻¹ band intensity. The concentration of Thr determined by this ATR calibration line can be fairly well correlated with that by HPLC. Therefore both the ATR and HPLC analyses can be used to determine Thr concentrations remaining in solution during the experiments.

The decreases of Thr in solutions were plotted against the reaction time. The semi-logarithmic plot showed a quasi-linear decrease indicating the first order reaction. The gradients of fitted lines gave reaction rate constants. The rate constants were changed by the presence of silica.

Film-like products were found on solution surfaces of several experimental runs. They are formed faster at higher temperatures and with the presence of silica. In order to quantify the kinetics of film formation, the time period for the first appearance of the film was taken as the half-life time, as a first approximation. By assuming the first order reaction for this film formation, the half-life can be converted to rate constants. They are plotted in an Arrhenius diagram. The film formation rates between 150 and 120 °C are faster with the presence of silica. The tentative activation energy values for the film formation were about 70 and 40 kJ/mol without and with silica, respectively. Although the first appearance time was not well checked for the experiments at low temperatures with silica runs, the present rates show the lowest rates. Therefore the activation energy value of about 40 kJ/mol for the film formation with silica will be somewhat overestimated. In any case, it is clear that the activation energy is lower in the presence of silica. This means that the film formation will become much easier for lower temperatures by the presence of silica. The polymerization reaction can therefore be favored by the presence of silica and supports our working hypothesis.

It should be noted that the polymerization reaction occurs rather quickly at these moderate temperature conditions.