

## Pressure dependence of peptide formation in solid-state: Implications for the origin of life under the deep crust

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Peptide formation is one the essential and mandatory reaction to promote Chemical Evolution for the origin of life. However, it has been uncertain as to which geological condition was suitable for the peptide formation. The hypothesis concerning the origin of life in a hydrothermal system was proposed and different types of deep-sea hydrothermal vents as a part of submarine volcanism are considered to be continuous flow reactors for abiotic synthesis of peptides. On the other hand, polymerization of the amino acids into peptides is unfavorable in the presence of liquid water at all temperatures. Even if some efficient mechanism for peptide synthesis existed, these peptides would be rapidly hydrolysed back to free amino acids at the high temperature of the vents.

If the mixture of amino acids were buried several kilometers beneath the surface of the earth, the temperature would be high enough so that peptides might be formed; nevertheless they would be turned to tar in the thousands or millions of years it would take to erode away the overlying material. Nakazawa proposed a hypothesis that peptide formation proceeded in the upper crust. The feature of crust is high-pressure, high-temperature, and dry conditions. Pressure makes organic materials remain in the solid phase at higher temperatures by suppressing melting or decomposition. Therefore, we attempted the solid-state polymerization of amino acids at high-pressure and high-temperature conditions to synthesize the peptide and clarified the pressure dependence of peptide formation.

Experiments were conducted in a test-tube-type autoclave using gold-tube reactors. Before use, the gold-tube reactors were washed in nitric acid and annealed at 900 C. Solid glycine was weighed and placed into the gold-tubes. The tubes were sealed by electric arc welding method. Multiple experiments were run at elevated pressures (5 to 100 MPa) and held at 150 C for 1 to 8 days.

Glycine peptides were identified and quantified by high performance liquid chromatography (HPLC). Each capsule was opened carefully and mobile phase was added to extract the oligopeptides from the product. Liquid phases were separated by the centrifugal method. The reaction yields were determined as percentage of the reactant converted to the reaction product. Oligopeptides more than hexamer were additionally identified by the detection of the molecular ion by liquid chromatography mass spectrometry (LC-MS).

Products were colored, grading from white (at 100 MPa) up to a deep brown (at 5 to 15 MPa). A HPLC chromatogram of the products indicated at least six oligomers: di-, tri-, tetra-, penta-, and hexaglycine. We also identified hepta-, octa-, and nonaglycine with LC-MS. These highly polymerized peptides were preferentially formed at 25 to 100 MPa. On the other hand, polymerization of glycine proceeded to only pentamer at 5 to 15 MPa. The oligomerization and the yields of each oligomer were increased with pressure and the duration of the experiment. This suggests that there is pressure dependence of peptide formation in solid-state. Pressure is effective to obtain longer peptide from amino acid.

In addition, sample gold tubes were expanded in volume with pressure, implying the production of gas phase. Decarboxylation and deamination are the main pathway of decomposition of amino acids. CO<sub>2</sub> and NH<sub>3</sub> would be produced as the gas phase. Therefore, pressure would also prevent decomposition of amino acid.

These results from this study support the theory that Chemical Evolution could happen in deep Earth environments, such as inside of upper crust.