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Stability of amino acids and peptides during diagenesis on the early Earth

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Formation of amino acids and their polymerized compounds (i.e., peptides) is an essential process for the origin of life. Since peptide formation from amino acid monomers is an endothermic reaction, which thermodynamically favors to proceed under higher temperature conditions, submarine hydrothermal systems have been proposed to provide suitable environments for the polymerization of amino acids and origin of life on the early Earth (e.g., Imai et al., 1999). However, lifetime of peptides in submarine hydrothermal environments is expected to be very short (< a few hours), because of rapid hydrolysis of peptides and decomposition of amino acids under high temperature aqueous conditions (Miller and Bada, 1988). Therefore, we alternatively hypothesize that sub-seafloor sedimentary environments, where sediments are dehydrated at moderate temperature and pressure (e.g., 150 degree C, 200 MPa) during diagenesis, are much more feasible for the polymerization of amino acids (Nakazawa et al., 1993; Ohara et al., 2007). To test the hypothesis, we conducted a series of amino acid polymerization experiments using a belt-type press. About 150 mg of amino acid powders (glycine, alanine, or valine) were sealed in a gold capsule, and placed at high pressure (1 -5.5 GPa) and temperature (180 - 400 degree C) for 2 - 24 hours. Although the experimental conditions were much higher in both temperature and pressure than natural diagenetic conditions, we aimed to investigate the effects of temperature and pressure in a wide range on the stability of amino acids and peptides. After the experiments, yields of residual amino acids and produced peptides were analyzed by LC/MS (Liquid Chromatography/Mass Spectroscopy). Elemental ratios (i.e., H/C, O/C, and N/C) of the run products were determined using an EA (Elemental Analyzer).

The results showed that all three amino acids were polymerized up to 5-mer under the experimental conditions. At a fixed temperature (e.g., 250 degree C), increasing pressure increased the yields of peptides as well as residual amino acids, though it was thermodynamically predicated to decrease the yield of peptides. This indicates that amino acids and peptides were prevented from decomposing to gaseous species (e.g., CO_2, NH_3) at the high pressures. On the other hand, increasing temperature from 250 to 400 degree C decreased the yield of amino acids and peptides at a fixed pressure and elapsed time (e.g., 2.5 GPa, 2 hours), indicating that peptide and amino acids may not persist under such high temperature conditions, even at the high pressures. Elemental analyses of the experimental products showed that products with a low yield of the residual amino acid significantly decreased in the N/C ratios, while they showed a slight increase in the O/C ratios, suggesting that $NH_3$was released during the decomposition of amino acids. Thus, deaminization is the key process to determine the stability of amino acids and peptides. Our study suggests that sub-seafloor sedimentary environments, subjecting to diagenesis, are more feasible for the polymerization of amino acids, than sea-floor hydrothermal environments, because of the greater stability of amino acids and peptides.

References

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