

高温高圧下でのメチオニン重合に対するグリシン及びその分解物の影響: 海洋堆積物内における化学進化の可能性 Effects of glycine and its decomposition products on polymerization of methionine under high temperature and pressure

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It is widely believed that abiotic polymerization of amino acids is an important process for the formation of the first life. Several geological settings have been proposed as the place for the polymerization: sub-marine hydrothermal vents (Imai et al., 1999), tidal flats (Lahav et al., 1978), and marine sediments (Nakazawa et al., 1993). A unique point of the marine sediment is its pressurized conditions. Previous studies have suggested the importance of pressurized conditions for the production of longer peptides (Ohara et al., 2007; Otake et al., 2011; Furukawa et al., 2012). These previous studies also indicate that the reactivity of each amino acid is widely different, leading to skepticism about the formation of peptides composed of plural amino acids. In this study, we investigated oligomerization of methionine and glycine under the conditions of high temperature and high pressure (at 175°C, 150 MPa, and 0-96 hours).

Methionine and glycine were used for representatives of each low and high reactive amino acid, respectively. Starting materials were solid methionine or solid methionine mixed with solid glycine, water, aqueous ammonia, or ammonium hydrogen carbonate. The additives other than glycine (water, aqueous ammonia, and ammonium hydrogen carbonate) are simulated decomposition products of glycine. Ammonium hydrogen carbonate decompose at about 60°C and yields ammonia, carbon dioxide, and water. For each starting material, 0.43 mmol of methionine were used. The amounts of each additive were 0.43 mmol. Each starting material was sealed into a gold tube of 25 mm length and 5.5mm diameter. Then, high temperature and pressure conditions were applied using a test-tube-type autoclave system. After these experiments, amino acids and their oligomers were extracted into aqueous solution from the experimental products and analyzed with a high performance liquid chromatograph connected to a mass spectrometer (LC/MS).

In all experiments, methionine decomposed with elapsed time. Peptides longer than di-methionine were not formed in experiments without the additives. On the other hand, methionine was oligomerized to di-methionine, tri-methionine and methionine diketopiperazine in the experiments with additives. Methionyl-glycine and glycy-methionine were also produced in experiments containing such additives. The rates of methionine decomposition and methionine-peptide formation were increased in experiments with additives. These rates were especially increased in samples containing aqueous ammonia, and ammonium hydrogen carbonate, suggesting that ammonia promote both the production rates of peptides and the decomposition reactions of methionine. The difference in reaction rates might have been caused by the difference in pH as suggested in a previous study (Sakata et al., 2010). When these results are applied to diagenesis in Hadean marine sediments, these results suggest that amino acids of lower reactivity may have been activated by amino acids of higher reactivity and might have produced peptides composed of plural amino acids.