

Effects of glycine and its decomposition products on polymerization of methionine under high temperature and pressure

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Polymerization of amino acids is an essential process for the origin of life. Several geological settings have been proposed as the place for the polymerization: sub-marine hydrothermal vent (Imai *et al.*, 1999), tidal flats (Lahav *et al.*, 1978), and marine sediments (Nakazawa *et al.*, 1993). Previous studies suggest the importance of the marine sediments to produce longer peptides (Ohara *et al.*, 2007; Otake *et al.*, 2011). These previous studies suggest that the reactivity of each amino acid is widely different. This may lead to skepticism about the formation of peptides composed of plural amino acids. However, there has been no experiment that investigated the oligomerization of plural amino acids. In this study, we investigated polymerization of methionine under the conditions of high temperature and high pressure (at 175°C, 150 MPa, 0-96 hours).

Starting materials were solid methionine and solid methionine with solid glycine, water, aqueous ammonia, or ammonium hydrogen carbonate. The additives in the starting materials other than glycine (water, aqueous ammonia, and ammonium hydrogen carbonate) are simulating 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 additives 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. 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).

Methionine was polymerized to di-methionine, tri-methionine and methionine diketopiperazine in experiments adding water, ammonia, ammonium hydrogen carbonate, and glycine. On the other hand, peptides other than di-methionine were not formed in experiments using methionine alone. Methionyl-glycine and glycy-methionine were produced in experiments containing each additive. In all experiments, methionine decomposed with reaction time. In experiments with additives, reaction rates of methionine decomposition and methionine-peptide formation were increased. These rates were especially increased in samples containing aqueous ammonia, and ammonium hydrogen carbonate, suggesting that ammonia and carbon dioxide promote the production rates of peptides and decomposition reactions of methionine. Compared with previous study (Ohara *et al.*, 2007), these results indicate that the reaction rate of methionine peptide formation was far lower than that of glycine. However, this rate was increased with addition of glycine. The present results also suggest that decomposition products of glycine especially ammonia and carbon dioxide increased the reaction rate of methionine.

When these results are applied to diagenesis in Hadean marine sediments, these results suggest that amino acids of low reactivity may be activated by amino acids of high reactivity and produced peptides composed of both amino acids.