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# Effects of metal ions (Ca2+, Mg2+, Zn2+, Cu2+) and pH on the formation and decomposition rates of di- and tripeptides

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Introduction: Recent finding of the serpentinization-driven deep-sea vent systems producing basic fluids, such as the Lost City hydrothermal field (Kelley et al. 2005) and the south Chamorro seamount (Hulme et al. 2010), has improved our understanding that submarine basic seepages are plausible environments for the origin and evolution of life in the early Earth (Russell, 2003). In our previous study, it was revealed that the dimerization of glycine (Gly) in aqueous solution reached the maximum rate in basic solution at pH 9.8 and 150$^o$C (Sakata et al., 2010), supporting Russell's hypothesis. However, the effects of metal ions on peptide formation under basic pH condition have not been well investigated. In this study, the heating experiments of Gly solution containing $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$ or $Cu^{2+}$ were conducted under various pH conditions, in order to evaluate the effects of metal ions on the formation and decomposition rates ($k_n$) of glycylglycine (GlyGly), glycylglylcylglycine (GlyGlyGly) and diketopiperadine (DKP).

Experimental: Aqueous solutions of 100 mM Gly, 100 mM Gly containing with 5, 200 and 400 mM $CaCl_2$, 5 mM $MgCl_2$, 5 mM $ZnCl_2$, and 5 mM $CuCl_2$, respectively, were prepared. Each solution was adjusted to acidic (pH = 2.2 ˜ 2.3), neutral (pH = 4.5 ˜ 6.0) and basic (pH = 9.8 ˜ 9.9). The solutions containing $CuCl_2$ were adjusted to pH = 3.4 and 9.8. Half milliliter of each solution in a pyrex glass tube was replaced with Ar gas and sealed under vacuum. These samples were heated at 140oC for 1 to 74 days. After heating, the samples were 10 times diluted and 100 micro liters of each solution was analyzed by High Performance Liquid Chromatography (HPLC). In this experiment, the six reaction pathways were considered: 2 Gly to GlyGly ($k_1$), GlyGly to 2 Gly ($k_{-1}$), GlyGly to DKP ($k_2$), DKP to GlyGly ($k_{-2}$), Gly + GlyGly to GlyGlyGly ($k_3$) and GlyGlyGly to Gly + GlyGly ($k_{-3}$). The rate constants were determined by fitting the changes of the concentrations of Gly, GlyGly, GlyGlyGly and DKP with increasing heating time using the least-squares method.

Results and discussion: The concentrations of GlyGly in the aqueous solutions of Gly containing $Ca^{2+}$, $Mg^{2+}$ and $Zn^{2+}$ under any pH condition, respectively, were lower than those without metal ions. The concentration of GlyGly decreased with increasing concentrations of $Ca^{2+}$. In the aqueous solutions of Gly containing $Cu^{2+}$, the concentration of GlyGly was higher at basic pH than those without metal ions, while it was lower at acidic pH. GlyGlyGly was yielded only in the solutions containing $Cu^{2+}$, and it was the most abundant at basic pH. Under the basic pH, the concentrations of DKP in the solutions containing any metal ion were lower than those in the solution of Gly only. All the rate constants ($k_1$, $k_{-1}$, $k_2$ and $k_{-2}$) for the aqueous solutions of Gly containing $Ca^{2+}$, $Mg^{2+}$ and $Zn^{2+}$ (5 mM) at any pH were lower than those for the solution without metal ions. The result indicates that $Ca^{2+}$, $Mg^{2+}$ and $Zn^{2+}$ inhibit the formation of GlyGly and DKP. For the aqueous solution of Gly containing $Cu^{2+}$, $k_1$ and $k_{-1}$ showed high values and $k_2$ and $k_{-2}$ showed low values compared to those without metal ions. Thus, $Cu^{2+}$ promotes the reactions between Gly and GlyGly while it inhibits the reactions between GlyGly and DKP. In the solutions containing $Cu^{2+}$, the values of $k_3$ and $k_{-3}$ were higher at basic pH than those at acidic pH. Such differences in the formation and decomposition rates of di- and tripeptides due to the variety of metal ions can be caused by the steric effects of metal complexes of glycine.

References:

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