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Decomposition and peptide formation of glycine on oxide and mineral surface under dry and wet conditions

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Peptide formation is an important process of the chemical evolution of precursor life on the primitive earth. It has been believed that sediments were good environment to proceed the chemical evolution, since mineral surface promoted oligomerization of amino acids and other biomolecules. In this study, the thermal behavior of amino acid adsorbed on minerals surface dry and wet condition was observed to evaluate the role of minerals for oligomerization.

Glycine (Gly) was adsorbed on alumina, amorphous silica and montmorillonite in 0.1 M solution. After drying, those were heated at 150 degree C for 3-288 hrs under wet and dry condition in glass ampoules. Gly and peptides were desorbed from mineral surface by 0.1 M $CaCl_2$ and the amounts of Gly remained and synthesized peptides were determined using HPLC.

The amount of Gly remaining on minerals exponentially decreased with heating time; 20 to 48 % Gly remained on mineral surface under dry condition after 288 hrs, and 59 to 73% under wet condition. 70% and 98% of Gly remained after heating without minerals under the dry and wet conditions, respectively. Minerals would not be protectors of amino acid but good catalysts to promote Gly reaction. Kinetic calculation indicates that the reaction rate of amino acids on mineral surface is 1.5-6 times faster under dry condition than wet condition. Since the decomposition of amino acids under wet condition was more slowly than under dry condition, dehydration would be the most dominant reaction under dry condition. Water inhabits Gly reaction under high temperature condition. The three types of peptide: diketopiperazine (DKP), diglycine (Gly_2) and triglycine (Gly_3) were detected in the system including montmorillonite heated under dry condition and reference solution. Peptides were not formed when amino acid adsorbed on alumina and silica was heated both in dry and wet conditions, probably because the concentration of peptide on aluminia and silica surface was too low. The 15.57% of Gly monomer became peptides on montmorillonite under dry condition, and the most abundant product was DKP (10.03%). On the other hand, only 0.5% of Gly became DKP and Gly_2 were yielded in the solution without minerals. Thus, the peptides are accumulated more under the dry condition than hydrothermal condition, and the montmorillonite is a good catalyst.

Water was added to montmorillonite system after heating at dry and 150 degree C condition (dry/wet condition) for 168 hrs to check the change of stability of peptide synthesized and Gly monomer before and after the hydrolysis. 11.17% of DKP remained after heating in dry condition, while only 1.54 % of DKP remained in dry/wet condition. Decomposition rates of Gly_2 and Gly_3were lower than that of DKP in those systems. The water added in the system promoted hydrolysis of DKP and Gly monomer, and destabilized those on the montmorillonite surface. The DKP on the montmorillonite would decomposed by hydroxyl ion, which was generated on mineral surface by the reaction with water. The existence of excessive water and hydroxyl ion is obstacle to condense DKP and elongate to form longer peptide. The maintaining of thermal dry condition is important to form and condense DKP on clay mineral surface.The condensation of DKP would be important as the first step of chemical evolution of life. If so, dry condition and existence of clay minerals would be essential factors to proceed the chemical evolution of precursor life on the primitive earth.

Keywords: peptide formation, dry sediment, glycine, clay mineral, chemical evolution, diketopiperazine