

## Formation of glycine from carboxylic acid and ammonia by shock conditions: Implication to chemical evolution in primitive oceans

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Origins of amino acids on the early Earth have been debated by many investigators. Previous literatures indicate that intensive impacts of extraterrestrial objects had occurred during 3.8-4.0 billion years ago. These impacts seem to have delivered and produced prebiotic organic compounds including amino acids, amines and carboxylic acids as well as ammonia [1, 2]. However, the variety of biomolecules experimentally formed in the simulation of these processes was limited compared with that of the protein-constituent amino acids. In this study, we focused on the low-molecular-weight organic compounds (LOC) such as amines and carboxylic acids supplied by one impact process. LOC must have experienced further shock wave due to successive impacts in oceans. We demonstrated impact experiments on a solution of formic acid and ammonia to investigate whether amino acids form from LOC by oceanic impacts on the early Earth.

Shock-recovery experiments were performed with a single-stage propellant gun using a sample container. Starting material is a mixture of <sup>13</sup>C-formic acid and ammonia. After the impact experiments, soluble organic compounds were extracted into water. Then amines and amino acids were analyzed with liquid chromatography-mass spectrometry. Glycine, methylamine and ethylamine whose carbons are composed of <sup>13</sup>C were identified in all of the samples. The amounts of glycine were almost constant regardless of the impact velocity (0.7-0.8 km/s). The amounts of produced amines increased depending on the impact velocity. These results suggest that shock wave converts a LOC into larger-molecular-weight organic compounds including an amino acid. The successive impacts might have contributed to chemical evolution providing variety in biomolecules on the prebiotic Earth.

[1] Cronin and Pizzarello *et al.* (1988), *Meteorites and the Early Solar System*, pp. 819-857. [2] Furukawa *et al.* (2009), *Nature Geosci.*, **2**, 62-66.

## Removal Mechanisms of Silicate in the Wastewater using Aluminum Hydroxide Coprecipitation Method

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This study investigated removal mechanisms of silicate in the wastewater using aluminum hydroxide coprecipitation method. To investigate detailed silicate uptake mechanism during coprecipitation with aluminum hydroxide, adsorption process and coprecipitation process were distinguished exactly in this study [1].

In adsorption experiment, aluminum hydroxide was previously prepared at pH 9 and combined with silicate solution while pH was strictly controlled at pH 9. All sorption isotherms of silicate in adsorption experiments indicated BET like unsaturation type. Especially, dominant removal mechanisms changed from simple layer adsorption to another sorption phenomena, which was equivalent to multi-layer adsorption when Si/Al molar ratio was 2-5. XRD analysis represented the precipitation of kaolinite, which suggested that silicate uptake during adsorption experiment using aluminum hydroxide consisted of two kinds of mechanisms; one was surface complexation of silicate with aluminum hydroxide and another was precipitation of kaolinite. Results from zeta potential measurement and FT-IR analysis supported these suggestion about silicate uptake mechanism. However, in adsorption experiments, residual concentration of silicate in solution was higher than calculated value from chemical equilibrium of kaolinite precipitation. This results suggested dissolution of aluminum hydroxide to precipitate kaolinite required substantial time.

On the other hand, in coprecipitation experiments, alkaline solution consisted of aluminum and silicate ions was prepared and pH was dropped to 9. In this case, residual silicate concentration gave close agreement with calculated value from chemical equilibrium of kaolinite precipitation. This results suggested coprecipitation process was more appropriate for silicate removal than adsorption process because kaolinite could precipitate rapidly.

[1] C.Tokoro, D. Haraguchi, *Journal of MMIJ* 127(2011), pp. 26-31.