# 学位論文要旨

Experimental simulations of reactions by meteorite marine impact: Implications for chemical evolutions of amino acids present in early oceans and the origin of life on the Earth
（隕石海洋衝突による化学反応の実験的考察：
初期地球におけるアミノ酸の化学進化と生命の起源への応用）

氏　名　梅田　悠平

Prebiotic oceans are predicted to have contained abundant amino acids, and to be subjected to meteorite impacts, especially during the late heavy bombardment (LHB). It is so far unknown how meteorite impacts affected amino acids in the early oceans. In this thesis, we focused on the products and effects by such shock reactions, what occurs in aqueous solutions containing simple amino acids such as glycine and alanine under high-pressure and -temperature extreme conditions, and how they occur. In addition, we discussed what is important for chemical evolution such as polymerization and dimerization of amino acids. Also, we examined possible reactions between water−mineral−amino acids under meteorite marine impacts from experimental results in this study. We carried out shock recovery experiments with using a propellant gun, meteorite analogue materials and simple organic materials. A metallic flyer plate with a plastic body was accelerated by explosive, and impacted at ultra high velocity to a sample container. Then, starting materials (meteorite analogues and simple organic materials in solution) embedded in the sample container were subjected to extreme high-pressure and -temperature conditions by propagating a shock wave.

Firstly, we discuss about the stabilities and chemical reactions of amino acids in water to simulate meteorite marine impacts. We describe the results of the selected liquid chromatographs (LC/MS) and discusses about the behavior and possibility on the chemical evolution of glycine and alanine in oceans under various impact conditions. The results revealed that both amino acids survived partially in early ocean through meteorite impacts, that part of glycine changed into alanine, and that large amounts of methylamine and ethylamine were formed. Furthermore, the formation of n-butylamine, detected only in the samples recovered from the solutions with additional nitrogen and carbon sources of ammonia and benzene, suggests that chemical reactions to form new biomolecules can proceed through marine impacts. Methylamine and ethylamine from glycine and alanine increased considerably in the presence of hematite rather than olivine under similar impact conditions.

Secondary, we focused on recovered solid samples to investigate reaction traces among olivine, amino acids and water and new products by shock wave. The microstructural observations for shocked minerals were carried out by a scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectrometry (EDX). The analytical results on shocked products in the recovered sample

showed (i) morphological changes of olivine to fiber and bamboo shoot-like crystals, to pulverized grains, and features of lumpy surfaces affected by hot water and (ii) the formation of carbon-rich substances derived from amino acids. Furthermore, we tried the functional group analysis for carbon-rich substances by using scanning transmission X-ray microscopy (STXM) to investigate the structure and elemental composition, and the cross-section observation and the elementary mapping for reaction boundaries between water−mineral−amino acids by using scanning transmission electron microscope (STEM) with EDX. The analytical results of these analyses indicated (a) the dissolution of the rim of olivine grains, (b) carbon-bearing bonds such as C=C, COOH, and $CO_3$ in carbon-rich substances, and (c) carbon-rich substances formed from a part of amino acids into dissolved olivine.

Finally, we carried out shock recovery experiments for mixtures of copper nitride ($Cu_3N$), carbon powder (graphite), and water with and without iron powder in order to demonstrate the synthesize of HCN from inorganic carbon. After experiments, cyanide ions ($CN^-$) in recovered solutions were analyzed by post-column ion chromatography. Analytical results indicated (i) the yield of $CN^-$ increased with increasing the initial iron amount, (ii) yields of $CN^-$ increased with increasing the initial carbon amount, and (iii) the yield of $CN^-$ increased with increasing impact velocity. As further investigation, we carried out shock recovery experiments on aqueous solutions of ammonium formate and formamide immersed in the pressed olivine powders to examine the formation of biomolecules from various HCN-bearing solutions. After experiments, biomolecules in recovered solutions were analyzed by high-performance hybrid mass spectrometry. Analytical results indicated the new peaks as products correspond to several biomolecules (amino acids, amino acid polymers, carboxylic acids, nucleobases, sugars, and cyclic peptides).

Through whole present study, these results suggest that amino acids present in early oceans can contribute further to impact-induced reactions, implying that impact energy plays a potential role in the prebiotic formation of various biomolecules, although the reactions are complicated and depend upon the chemical environments as well. HCN were also formed from such reactions simultaneously, which contribute to formation of several organic compounds under meteorite marine impacts condition. In addition, fine-grained olivine in meteorites might have morphologically changed and shock-induced chemical reactions might have been enhanced so that amino acids related to the origin of life may have transformed to carbon-rich substances by impacts. Also, a part of olivine grains would dissolve, and incorporate carbon-rich substances and nano-metal particles formed by shock reaction, which might play important role to concentrate organics on mineral surface for further chemical evolution. The present study suggested that shock energies by meteorite marine impacts should have great effects on not only the prebiotic chemistry but also the chemical evolution of simple biomolecules and the interaction between meteorite and ocean on early Earth.