

Comet impacts as a driving force of glycine oligomerization.

K. Mimura¹ and H. Sugahara¹, ¹Graduate School of Environmental Studies, Nagoya Univ., Nagoya 464-8601, Japan
(mimura@eps.nagoya-u.ac.jp, sugahara.haruna@e.mbox.nagoya-u.ac.jp)

Introduction: Abiotic peptide synthesis is a key step in the chemical evolution that led to the emergence of life. Peptides are not only building blocks of life but probably also played an important role as a catalyst to form biomolecules on the primitive Earth. Several studies have proposed plausible energy sources for abiotic peptide synthesis on the early Earth, such as heating by volcanic activity [1] and ultraviolet radiation [2]. An alternative approach has been to examine peptide synthesis using condensation reagents [3] or from other starting materials such as amino acid amides [4].

In this study, we examine the process of comet collision as a source of peptides on the early Earth. Comets are known to contain abundant organic materials including amino acids [5] and impact shock can cause reactions that transform these simple organic materials into more complicated ones [6]. These features suggest the formation of peptides could be associated with comet impact shocks [7]. However, this process has been largely overlooked in previous literature concerning peptide synthesis on the early Earth.

Here we report the results of shock experiments using frozen mixture of glycine, water ice, and silicate at cryogenic conditions that successfully reproduce the conditions in comet impacts.

Experimental: We used a mixture of glycine, water ice, and olivine as a starting material. Glycine is one of protein amino acids and abundant in carbonaceous chondrites. The mixing ratio was amino acid/water ice/olivine = 0.1/0.8/1.0 (wt/wt/wt). A container carrying the starting material was placed in liquid nitrogen (77 K) and subjected to shock using a vertical propellant gun. After shocked samples were recovered from containers, peptides were extracted from the samples and separated into a linear peptide (dipeptides and tripeptides) fraction and a cyclic peptide (diketopiperazines) fraction using a cation exchange column. After derivatization, the samples were analyzed by gas chromatograph-mass spectrometer.

Results and Discussions: Diglycine, triglycine, and glycine-diketopiperazine were identified in the shocked glycine samples by comparison of their retention times and mass fragmental patterns with those of purchased standard materials. No peptide was detected in shocked samples below 4.8 GPa, indicating that the detected peptides were not contaminated during the experimental process. The yields of diglycine and triglycine show an initial increase with increasing shock

shock pressure up to values of 3% and 0.3%, respectively, at 20.6 GPa. This increase is followed by a decline to 1% and 0.2% at 26.3 GPa. The yield of glycine-diketopiperazine increases with increasing shock pressure up to a value of 0.1% at 26.3 GPa.

The yields of linear peptides were higher than those of cyclic peptide in the pressure range of this study. The formation of linear peptides is extremely important to produce long chains promoting chemical evolution. In contrast, the formation of cyclic peptides retards further growth of peptide chains due to their lower reactivity [8]. Where peptides are formed by intermolecular condensation, the formation of linear peptides is thermodynamically less favored compared to cyclic peptides [9]. Thus, heating solutions of amino acids leads to the synthesis of large amounts of cyclic diketopiperazines [1]. In contrast, shock reactions of glycine in cryogenic conditions disfavor intramolecular condensation and lead to preferential synthesis of linear peptides that can combine to form more complex organic compounds. This result of our study is in contrast with the result of shock experiments on aqueous amino acids at room temperature by Blank *et al.* (2001) [7]. They reported that the amount of synthesized cyclic peptides was comparable to that of linear peptides. Thus, the cryogenic condition at impact shock might be a key for the predominant synthesis of linear peptides.

Our study suggests that comet impacts can readily account for the oligomerization of glycine to form the precursors of life on the early Earth. Furthermore, since comet impacts are ubiquitous phenomenon in the solar system, they probably play an important role in organic chemical evolution on other extraterrestrial bodies, especially icy satellites.

References: [1] Harada K. and Fox S. (1958) *J. Am. Chem. Soc.* 80, 2694-2697. [2] Tanaka M. et al. (2008) *Radiat. Phys. Chem.* 77, 1164-1168. [3] Huber C. and Wächtershäuser G. (1998) *Science* 281, 670-672. [4] Oró J. and Guidry C. L. (1960) *Nature* 186, 156-157. [5] Elsila J. E. et al. (2009) *Meteorit. Planet. Sci.* 44, 1323-1330. [6] Furukawa Y. et al. (2009) *Nature Geosci.* 2, 62-66. [7] Blank J. G. et al. (2001) *Orig. Life Evol. Biosph.* 31, 15-51. [8] Kawamura K. et al. (2009) *Adv. Space Res.* 44, 267-275. [9] Streitwieser A. et al. (1998) *Introduction to organic chemistry 4th ed.* 949-1003.