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Peptide synthesis triggered by comet impacts: A possible method for peptide delivery to the early Earth and icy satellites

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ABSTRACT

We performed shock experiments simulating natural comet impacts in an attempt to examine the role that comet impacts play in peptide synthesis. In the present study, we selected a mixture of alanine (DL-alanine), water ice, and silicate (forsterite) to make a starting material for the experiments. The shock experiments were conducted under cryogenic conditions (77 K), and the shock pressure range achieved in the experiments was 4.8–25.8 GPa. The results show that alanine is oligomerized into peptides up to tripeptides due to the impact shock. The synthesized peptides were racemic, indicating that there was no enantioselective synthesis of peptides from racemic amino acids due to the impact shock. We also found that the yield of linear peptides was a magnitude higher than those of cyclic diketopiperazine. Furthermore, we estimated the amount of cometary-derived peptides to the early Earth based on two models (the Lunar Crating model and the Nice model) during the Late Heavy Bombardment (LHB) using our experimental data. The estimation based on the Lunar Crating model gave 3×10^9 mol of dialanine, 4×10^7 mol of trialanine, and 3×10^8 mol of alanine-diketopiperazine. Those based on the Nice model, in which the main impactor of LHB is comets, gave 6×10^{10} mol of dialanine, 1×10^9 mol of trialanine, and 8×10^9 mol of alanine-diketopiperazine. The estimated amounts were comparable to those originating from terrestrial sources (Cleaves, H.J., Aubrey, A.D., Bada, J.L. [2009]. Orig. Life Evol. Biosph. 39, 109–126). Our results indicate that comet impacts played an important role in chemical evolution as a supplier of linear peptides, which are important for further chemical evolution on the early Earth. Our study also highlights the importance of icy satellites, which were formed by comet accumulation, as prime targets for missions searching for extraterrestrial life.

1. Introduction

Chemical evolution from simple molecules to increasingly more complex organic molecules is a preliminary step in the origins of life. The production of polymers is an essential step in the development of catalytic replication. One of the important polymer formations in chemical evolution is abiotic peptide synthesis (e.g., Yanagawa et al., 1990; Rode, 1999). Peptides are essential building blocks of life and are also thought to have played an important role as catalysts in the formation of other biomolecules on the early Earth. For example, some polypeptides are known to catalyze oligomerization of nucleotides, which can lead to the development of genetic material (Barbier et al., 1993). Some chiral dipeptides are known to catalyze the stereoselective synthesis of biomolecules (Pizzarello and Weber, 2010). This process may be responsible for the homochirality of biomolecules, which is a distinctive feature of terrestrial life.

Numerous studies have proposed possible pathways for abiotic peptide synthesis on the early Earth, such as oligomerization from activated amino acid derivatives (e.g., Leuches, 1906; Oró and Guidry, 1960; Deming, 2006), adsorption of amino acids onto mineral surfaces combining with various activation agents (e.g., Bernal, 1951; Flores and Leckie, 1973; Huber and Wächtershäuser, 1998; Leman et al., 2004), and irradiation of thin films of amino acids with energy from sources such as ultraviolet light (Simakov et al., 1996; Tanaka et al., 2008) or high-energy protons (6.6 MeV) (Simakov et al., 1997). Other researchers have also proposed heating and quenching cycles that act on amino acid solutions at submarine hydrothermal vents as a plausible mechanism for peptide synthesis on the early Earth (e.g., Corliss et al., 1981; Shock, 1992; Imai et al., 1999; Lemke et al., 2009).

Recently, it has been reported that comet impacts could be considered an alternative pathway for peptide synthesis on the early

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Earth (Blank et al., 2001; Sugahara and Mimura, 2014a). Blank et al. (2001) performed shock experiments on amino acid solutions at room temperature to produce peptides up to dimers. Sugahara and Mimura (2014a) performed shock experiments under cryogenic conditions, simulating comet impacts, and demonstrated that the amino acid glycine was oligomerized into peptides up to triglycine due to the impact shock. We also showed that cryogenic conditions during comet impacts might be an important prerequisite for the synthesis of predominantly linear peptides, as opposed to cyclic diketopiperazine. However, it was a preliminary study that only tested glycine, which is the simplest amino acid. Glycine is a unique amino acid because it has a hydrogen atom as its side chain; many other common amino acids have an alkyl chain instead. Because the side chain determines the chemical properties of the amino acid, it is necessary to examine whether the previous result of oligomerization of amino acids (glycine) via impact shock under cryogenic conditions is applicable to other complex amino acids.

In the present study, we chose alanine as the starting amino acid, conducted shock experiments under cryogenic conditions, and successfully reproduced the conditions during comet impacts. Alanine, which was used in the present study, substitutes the alpha hydrogen of glycine with a methyl group (R = $-CH_3$) and is the simplest amino acid that has an alkyl group as the side chain with a chiral center. The purpose of this study is to determine whether amino acid oligomerization due to impact shock is a universal phenomenon. Furthermore, we estimated the amount of peptides that were synthesized and delivered by comet impacts to the early Earth based on our experimental data and several models of the Late Heavy Bombardment.

2. Materials and methods

2.1. Starting materials

We prepared a mixture, composed of an amino acid (alanine), water ice, and silicate (forsterite) as the starting material. Although alanine has not yet been found in comets and the only amino acid that has been detected in comets is glycine (Elsila et al., 2009), alanine is an abundant amino acid in carbonaceous chondrites (e.g., Botta et al., 2007). It is grouped into the biologically important protein amino acids, which also includes glycine. The general formula of amino acids is NH_2–CH(R)–COOH, and the side chain(R) defines their chemical properties. The side chain of alanine is a methyl group (R = $-CH_3$), while glycine has a hydrogen atom (R = –H). In addition, unlike glycine, alanine has enantiomers because its α-carbon bonds to four different functional groups. Thus, alanine is the simplest chiral amino acid. Because alanine exists as a racemic mixture in carbonaceous chondrites (Pizzarello and Cronin, 2000), we chose DL-alanine (Kishida Chemical, >99.0% purity) for the experiments. The mixing ratio for our study was alanine/water ice/forsterite = 0.1/0.8/1.0 by weight (for the precise concentration of the amino acid, see Table 1). This ratio is comparable to the starting material used in the experiments on glycine by Sugahara and Mimura (2014a), which was based on the composition of interstellar dust (Greenberg and Mendoza-Gómez, 1992; Greenberg and Li, 1999). The use of forsterite as a representative silicate of comets is because it is one of major components in comets (e.g., Tomeoka et al., 2008). To prepare the starting material, alanine was dissolved in Milli-Q water (UV-sterilized Milli-Q water) and then mixed with forsterite. The forsterite used in the experiment was an industrially synthesized material (Marusu Glaze), and the grain size ranged from 0.3 μm to 1.5 μm. The forsterite was preheated at 450 °C for 4 h to remove any remaining organic material before use. Then, the mixtures were sealed in capsules (Fig. 1B) and frozen in a freezer. The volume of starting mixture in the capsule was very small (approximately 0.01 cm^3), thus the mixtures froze quickly and the amino acid content was distributed homogenously in the form of hydrated ions.

2.2. Shock recovery experiments

Our shock experiment procedures were adapted from our established methods, as reported in a previous study (Mimura et al., 2003; Sugahara and Mimura, 2014a). A vertical propellant gun was used to launch a projectile into a target placed in a vacuum chamber (1–10 Pa) at the desired velocity (Fig. 1A). The final velocity of the projectile just before reaching the target was optically measured using a laser. The velocity range achievable by this gun is 300–1800 m/s. The projectile consists of a flyer plate made of stainless steel (SUS 304) and a polycarbonate sabot. The flyer plate impacts the target assembly and produces a planar shock wave. The target assembly consists of three components, including a capsule, a capsule holder and a momentum trap (Fig. 1B). All of the components are made of stainless steel (SUS 304). The capsule is composed of a plug and a cap. The plug has a pit that measures 4 mm in diameter and 0.8 mm in depth. The starting material was placed in the pit of the plug and encapsulated within the cap. Prior to use, the plug and cap were carefully cleaned via ultrasonic cleaning in Milli-Q water, distilled methanol and distilled dichloromethane to avoid contamination by any organic materials.

For the shock experiments performed at cryogenic temperatures, the target assembly was placed in liquid nitrogen (77 K), which was retained in a container of polystyrene foam and set in the vacuum chamber of the gun. We measured the temperature record of the target assembly, while the chamber was under vacuum (Fig. 2). As shown in Fig. 2, the temperature did not rise above 77 K during the experiments while under vacuum. In the experiments, the impact shock was given to the target approximately 11 min after the vacuum was initially applied, and during this time, the temperature did not rise above 77 K.

After the shock experiments, the shocked samples were mechanically opened using a lathe machine. This procedure was conducted carefully using refrigerants to ensure that the samples were not heated.

2.3. Chemical analyzes

After the shock experiments, the recovered samples were dried, homogenized using an agate mortar and stored in a freezer prior to analysis. The homogenized dry samples were divided into two portions for further analysis. The abundances of amino acids and peptides were normalized to the dry weight of the samples. The procedures used for the chemical analysis of the shocked samples are based on work performed by Shimoyama and Ogasawara (2002). The detailed experimental procedures are described in Sugahara and Mimura (2014a) and briefly explained here.

Alanine was extracted from each dried shocked sample using hot Milli-Q water (110 °C). A Norvaline (Sigma–Aldrich) solution was added to the sample solution as an internal standard after the extraction. The extracted solution was recovered via centrifugation and then dried. The alanine in the dried samples was esterified using 1.25 M HCl–isopropanol (Sigma–Aldrich) and then trifluoroacylated using trifluoroacetic anhydride (TFAA) (Tokyo Chemical Industry). The final TFA-ALA-OiPr ester was recovered via liquid–liquid extraction using a 10% NaCl solution and distilled dichloromethane. The dichloromethane fraction was analyzed using a gas chromatograph-flame ionization detector (GC-FID) equipped with a fused silica capillary column: HP-5