Formation, Alteration and Delivery of Exogenous High Molecular Weight Organic Compounds: Objectives of the Tanpopo Mission from the Point of View of Chemical Evolution

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A wide variety of organic compounds have been detected in such extraterrestrial bodies as carbonaceous chondrites and comets. Amino acids have been confirmed in extracts from carbonaceous chondrites and cometary dusts. It was suggested that these organics were formed in quite cold environments. We irradiated possible interstellar media, such as a frozen mixture of methanol, ammonia and water, with high-energy particles. Amino acid precursors with high molecular weights were detected in the irradiated products. Such complex amino acid precursors are much more stable than free amino acids against radiation, and heat.

It is suggested that IDPs brought much more organics than meteorites and comets. However, characteristics of organic compounds in IDPs are little known, since they have been collected only in terrestrial biosphere. We are planning the Tanpopo Mission, where IDPs would be collected in aerogel equipped on the Exposure Facility of the International Space Station. In addition, amino acids and their relating compounds would be exposed to space environments to see their possible alteration processes.

Key Words: Amino acid precursors, space dusts, the Tanpopo Mission, extraterrestrial organic compounds, High molecular weight

1. Introduction

Since Miller’s historical spark discharge experiment in 1953 [1], a great number of experiments have been reported to study possible abiotic formation of bioorganic compounds. In earlier studies, strongly reducing gas mixtures such as a mixture of methane, ammonia and water were used as starting materials (“simulated primitive Earth atmospheres”). It is suggested, however, that the primitive atmosphere of the Earth was not strongly reduced, but only slightly reduced: Carbon dioxide, carbon monoxide, nitrogen and water were among major constituents of the primitive Earth atmosphere [2]. It is not so easy to form bioorganic compounds from the slightly reduced gases by such major energies as ultraviolet light, spark discharge and heat.

A wide variety of organic compounds were found in such interstellar materials as carbonaceous chondrites and comets, and the relevance between them and terrestrial origins of life is discussed. It was suggested that meteoritic and cometary organic compounds were synthesized in quite cold environments such as in ice mantles of interstellar dusts (ISDs) in dense clouds [3]. In the Greenberg scenario [4], organic compounds were formed in ice mantles of ISDs in dense clouds, were processed by UV light, were included in comets and parent bodies of meteorites in the solar system, and were delivered to the primitive Earth by comets and meteorites.

It was suggested that interplanetary dusts (IDPs) brought much more organics than meteorites and comets to the primitive Earth [5]. Characteristics of organic compounds in IDPs are, however, little known since they have been collected only in terrestrial biosphere.

We are planning the Tanpopo Mission, where IDPs would be collected in aerogel placed on the Japanese Experimental Module / Exposure Facility (JEM/EF) of the International Space Station (ISS) [6]. In addition, amino acids and their relating compounds would be exposed to space environments to see their possible alteration processes in the interplanetary space.

Here we report some preliminary results for the preparation of the mission, including possible formation and alteration of organic compounds in interstellar and interplanetary environments, and describe scientific objectives of the Tanpopo mission from the point of view of chemical evolution and origins of life.

2. Possible formation of complex precursors of amino acids in interstellar environments

2.1. Formation of amino acid precursors in simulated ISD ice mantles by proton and UV irradiation

Light from stars does not penetrate into the dense clouds, which makes inner dense clouds as cold as 10-20 K, and most
molecules there are frozen onto ISDs to form ice mantles (Fig. 1). High-energy cosmic rays can go through the dense clouds, and ultraviolet light is generated when cosmic rays interact with molecules. Thus cosmic rays and secondary ultraviolet light are possible energy sources for the reactions in ice mantles of ISDs. Kobayashi et al. [7] showed that several amino acids were detected in the hydrolyzed products when ice mixtures of carbon monoxide, ammonia and water was irradiated with high energy protons at 10 - 15 K. Formation of amino acid precursors were also reported in other experiments where ices simulating ISDs made in cryostats were irradiated either protons or ultraviolet light. It was difficult, however, to discuss the formation rate of amino acids in ISDs or to characterize the amino acid precursors before hydrolysis since the only limited amount of amino acid precursors were obtained in these experiments.

2.2. Characterization of complex amino acid precursors formed from possible interstellar molecules

In order to discuss the energy yield of amino acid precursors, we chose a mixture of methanol, ammonia and water (molar ratio: 1:1:2.8) as a starting material of irradiation experiments, because (i) all of them are found in ISD ice mantles as major constituents, and (ii) it is easy to make a large quantity of ice.

We performed Heavy ions irradiation by using “HIMAC” accelerator in National Institute of Radiological Sciences (Chiba, Japan). Such ions as helium (150 MeV/u), carbon (290 MeV/u), neon (400 MeV/u) and argon (500 MeV/u) were irradiated to the solid (77 K) or liquid (ambient) mixture of methanol, ammonia and water. Fifty gram each of the mixture was irradiated with heavy ions at the dose rate of 250 - 4800 Gy/h. Total dose was 700 - 15800 Gy, and total energy deposit was 2.2 x 10^{20} - 4.9 x 10^{21} eV [8].

After individual irradiation experiments, an aliquot of the irradiation products was hydrolyzed with 6 M HCl at 383 K for 24 hours. Amino acids in the hydrolyzed and unhydrolyzed fraction were analyzed with an ion exchange high performance liquid chromatography (HPLC) system where a post-column derivatization with o-phthalaldehyde and N-acetyl-L-cystein was applied, and/or gas chromatography / mass spectrometry (GC/MS) after derivatization with ethyl chloroformate and heptafluorobuthanol.

Figure 2 shows typical HPLC chromatograms of the heavy ions irradiation products after acid-hydrolysis. A wide variety of protein amino acids such as glycine, alanine, aspartic acid and non-protein amino acids such as β-alanine, α- and γ-aminobutyric acid were detected. Formation of amino acids was confirmed by GC/MS, where amino acids such as alanine were racemic mixture. In the unhydrolyzed fraction, only small amount of glycine was detected. It showed that not free amino acids, but amino acid precursors were formed during irradiation. Amino acid precursors were also formed by γ-irradiation of a frozen mixture of methanol, ammonia and water [9].

Gel filtration chromatogram of the heavy ions irradiation products showed that the amino acid precursors have large molecular weights of ca. 2300. Pyrolysis of the product gave a wide variety of compounds including polyaromatic hydrocarbons (naphthalene), heterocyclic compounds (pyridine, pyrimidine), and amides (benzonitrile). The complex organic compounds with large molecular weights are stable against heat, UV light and radiation. Figure 3 shows recovery of glycine when free glycine solution and aqueous solution of the proton irradiation product were irrigated with γ-rays from 60Co. Abiottiely formed complex precursors of glycine (“CAW”) was much more...
4. A novel scenario of chemical evolution from interstellar complex organic compounds to terrestrial life

Miller reported that hydrogen cyanide (HCN) and formaldehyde (HCHO) are two most important primary products in the product of spark discharge in a mixture of methane, ammonia and water [11]. Amino acids can be formed from hydrogen cyanide, aldehydes and ammonia via aminonitriles, which is known as the Strecker synthesis. Oro found that adenine was formed in concentrated hydrogen cyanide solution [12]. These experimental results led to the idea that biological monomers like amino acids and bases are formed from small molecules like cyanides and aldehydes in aqueous solution. Then it was supposed that the next stage of chemical evolution proceeded from biological monomers to oligomers.

The conventional scenario with the stepwise reactions has been popular since it can be expressed in the form of simple chemical equations. This scenario, however, has defects: Each of the steps required high concentration (ca. 1 mol L\(^{-1}\)) of the starting chemicals. Each reaction had side reactions, and the products often have a large number of isomers. Abiotic formation of oligonucleotides is especially difficult since at least four steps are required: Formation of bases, formation of sugars, formation of nucleosides from bases and sugars, formation of nucleotides from nucleosides and phosphates, and oligomerization of nucleosides. Yield of each step are usually as low as a few percent together with many other non-biological isomers. Another problem is that biological monomers (especially amino acids and sugars) are quite unstable against heat, UV and radiation, which may prevent their accumulation in primitive sea.

We would like to propose an alternate scenario, which was hinted by the fact that complex organic compounds can be formed easily in simulated planetary and interstellar environments. Complex organic compounds have been detected in carbonaceous chondrites, comets and in Titan. Laboratory experiments under simulated planetary or interstellar conditions gave complex organic compounds with molecular weights of thousands. They could provide biological monomers after hydrolysis, and they are much more stable than free monomers against heat and radiation.

Complex organic compounds formed in interstellar space was incorporated into meteorites and comets when the solar system was born, and delivered to the Earth around when stable ocean was formed in the surface of the Earth. Some of them had some (but quite low) functions like catalytic abilities. We would like to name it Garakuta molecules: Garakuta is a Japanese term meaning goods with low performance. The Garakuta molecules could provide biological monomers like amino acids. The Garakuta World could evolve itself by using the molecules such as amino acids and nucleic acid bases to have higher performance.

5. The Tanpopo Mission

We are planning a space experiments named Tanpopo, where space dusts would be collected in aerogel equipped on the Exposure Facility of the International Space Station. In addition, organic compounds and microorganisms would be exposed to space environments to see their survivability and possible alteration processes in the interplanetary space. These space experiments were designed to test the hypothesis of interplanetary transfer of microbes and delivery of organic compounds by IDPs [13]. Here we discuss the scientific objectives of the Tanpopo Mission from the point of view of chemical evolution, and preliminary results of the ground simulation for them.

5.1. Collection of space dusts and analysis of organic compounds in them

A wide variety of organic compounds have been found in such carbonaceous chondrites [14] and comets [15]. It was suggested that these extraterrestrial organic compounds were important sources for the first biosphere on the Earth. Chyba and Sagan estimated that interplanetary dusts (IDPs) brought much more organic carbons to the primitive Earth than meteorites and comets [5]. In addition, organic compounds in IDPs could be delivered to the Earth less destructive while those in comets and meteorites could be destroyed on their impacts. However IDPs have been collected only in terrestrial biosphere, and there is high probability of terrestrial contamination to them. Thus it would be of great importance that they would be collected in space to examine their intrinsic organic molecules.

In the Tanpopo Mission, IDPs will be collected on the Japanese Experimental Module / Exposed Facility (JEM/EF) of the International Space Station (ISS). Since IDPs are moving at ultra high velocity (ca. 10 km/s), we are going to use ultra-low density (ca. 0.01 g/cm\(^3\)) aerogel to capture them. Aerogel has been used to collect materials in space, including return of cometary dusts by the Stardust mission [16].

After exposure of the aerogel on JEM/EF for 1 year or more, it will be returned to the Earth, and analyzed the captured dusts together with their tracks. In order to determine amino
acid precursors, aerogel with impact tracks and terminals will be digested with 5 M HF - 0.1 M HCl mixed acid at 383 K for 24 h, hydrolyzed with 6 M HCl at 383 K for 24 h, desalted, and then analyzed with HPLC with two-dimensional HPLC system with a chiral column. It is expected that femtomole level of amino acid enantiomers can be determined.  

\[ \alpha\text{-Aminoisoobutyric acid and isovaline are two of the major non-protein amino acids found in carbonaceous chondrites, and would be the best candidates to be detected, since it would be quite difficult to reduce contamination of protein amino acids such as glycine and alanine.} \]

Complex organic compounds in the captured dusts and tracks will be characterized with microscopic spectrometric techniques including synchrotron based x-ray absorption near edge spectroscopy (XANES) combined with scanning transmission X-ray microscopy (STXM).

We are performing simulation experiments by using the two-stage light-gas gun at ISAS / JAXA to evaluate the present aerogel system (Fig. 3).

5.2. Exposure of organic compounds to the space environment

Our simulation experiments suggested that complex organic molecules containing amino acid precursors were formed in ice mantles of ISDs in dense clouds (see chapter 2). They would be altered by cosmic rays and ultraviolet light before they were incorporated in parent bodies of meteorites and/or comets. They were again altered in the Solar System small bodies. IDPs seem to have been made from the small bodies, and organic compounds in IDPs were irradiated with cosmic rays and strong solar ultraviolet light before fallen into the Earth.

Organic compounds in inner part of comets and meteorites are safe from UV light, but organics in IDPs are fully irradiated with strong solar UV as well as high-energy particles near Earth orbit. IDPs could bring extraterrestrial organic compounds including amino acids and/or amino acid precursors. It is of interest to examine how these organic compounds in IDPs alter or survive in actual space environments.

In the Tanpopo Mission, organic compounds will be exposed on ISS-JEM/EF. The exposure unit is set next to the aerogel unit. We are planning to expose organic samples including (i) glycine, (ii) hydantoin (a precursor of glycine), (iii) isovaline, (iv) 5-ethyl-5-methyl hydantoin (a precursor of isovaline) and (v) complex amino acid precursors synthesized from possible interstellar molecules. The complex amino acid precursors are synthesized by proton irradiation of a mixture of carbon monoxide, ammonia and water [9]. These samples will be labeled with stable isotope (\( ^{13}C \)) to discriminate terrestrial contamination after recovery. All the samples will be covered with MgF\(_2\) window, which allows solar UV/VUV light (\( \lambda > 120 \) nm) pass through. After exposure for 1 year or more on ISS-JEM/EF, the exposure unit will be returned to the Earth, and samples in the unit were subjected to analysis. Amino acid analysis after hydrolysis and characterization by XANES will be included in the analytical schemes.

In prior to the space experiments, stability of each sample against UV and radiation was tested on ground. Ground simulation experiments using \( \gamma \)-rays and UV light showed complex precursors were much more stable than free amino acids [10]. The present exposure experiment together with the capture experiment (see section 5.1) will give us an idea how extraterrestrial organics were delivered to the Earth in prior to the generation of the first life on the Earth.

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