**Japan Geoscience Union Meeting 2011**
(May 22-27 2011 at Makuhari, Chiba, Japan)


BAO001-P01 Room:Convention Hall Time:May 23 14:00-16:30

# Development of a LC/MS method to analyze simple sugars: an approach to investigate ribose formations on the early Earth

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Ribose is considered to be one of the difficult molecules to synthesize on the early Earth. Formose reactions with either boric or phosphoric acids have been reported as reactions to produce ribose. However, those reaction pathway and necessary conditions are still uncertainbecause analytical methods of products from the formose reaction are unavailable. Therefore, in this study, we have developed a method to analyze polymerization products of formaldehyde and their complex with borate ion using liquid chromatography-mass spectrometry (LC/MS). Small sugars (glyceraldehyde (C3), erythrose (C4), and D-ribose (C5)) and a complex of D-ribose and boric acid were used as representatives of polymerization products of formaldehyde. In order to increase the ionization efficiency of these samples, a mixture of chloroform and methanol was added as an ionization agent into the mobile phase between the LC and the MS. Tow negative modes, electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), were adopted for the ionization of these samples. In addition, two types of hydrophilic interaction chromatography (HILIC) columns and a ligand exchange column were used in the LC for the separation of these sugars and ribose-borate complex.

The ionization efficiencies of these sugars and ribose-borate complex were increased by adding the ionization agent in most cases. These sugars ionization modes were not determined either ESI or APCI. Among these three columns, the ligand exchange column was most effective for the separation of the sugars. However, the separation between ribose and ribose-borate complex could not achieve by the column.

Using these methods, we analyzed the polymerization products of glyceraldehyde reacted each other under highly alkaline conditions with or without sodium borate. The method was successful for the analysis of the residual glyceraldehyde. The results showed that decomposition of glyceraldehyde were more significant in the sample free from borate. This result suggests that borate ion improves the stability of glyceraldehydes. On the other hand, the peaks of other sugars were not apparent because of their low yields and the high background counts. All results indicate the usefulness of the newly developed method for studies of prebiotic ribose formation.

Keywords: LC/MS, Ribose, Formose reaction, Borate

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# Formation of Amino acids in non-reducing gas mixtures

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Introduction

It was suggested that the terrestrial atmosphere at the time of the generation of life was non-reducing gas dominated carbon dioxide and nitrogen. It was widely believed that organic compounds such as amino acids are not formed effectively from neutral gas mixtures. In 2008, however, Cleaves pointed out that low yield of amino acids from non-reducing gases previously reported was due to be oxidation of amino acids to nitrosamines by nitrate/nitrite during acid hydrolysis: He reported that the yield of amino acids was greatly increased when ascorbic acid was added to the discharge samples as an antioxidant before acid hydrolysis, However, it was not clear that amino acids were produced merely by spark discharges or not. In addition, the precursors of amino acids by the spark discharges have been unknown. We analyzed organic compounds synthesized by spark discharges in neutral gas mixtures, and examined possible formation pathways of amino acids.

Experimantal

A mixture of 300 Torr of carbon dioxide and 300 Torr of nitrogen was added to a 1.6 L flask with 40 mL of water, and sparks were fired between two tungsten electrodes for 24 hours. Organic compounds such as carboxylic acids in the products were analyzed by capillary electrophoresis. Amino acids were analyzed by HPLC and GC/MS after acid hydrolysis in 6 M HCl at 120$^{o}$C for 24 h with or without ascorbic acid. A mixture of pyruvic acid, nitric acid and ascorbic acid was heated at 65$^{o}$C for 4 days to examine formation of amino acid since it was previously reported that keto acids were formed from neutral gas mixtures by spark discharge.

Result & Discussion

Formaldehyde, formic acid, ammonia and nitric acid were detected in the spark discharge products. After acid hydrolysis with ascorbic acid, Gly, Ala and beta-Ala were detected, while no amino acids were detected without ascorbic acid. After acid hydrolysis of heated products from a mixture of pyruvic acid, nitric acid and ascorbic acid, a large amount of Gly and trace of aspartic acid and beta-Ala were formed. This result indicates that amino acids may be formed from reaction between some spark discharge products such as keto acids with ascorbic acid. In order to test this hypothesis, we are going to perform spark discharge in a gas mixture with $^{13}$C-Labelled carbon dioxide.

Keywords: Amino acids, Prebiotic synthesis, Spark discharge, Neutral atmosphere

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# Optical properties in UV-visible regions and production rate of organic haze on early Earth

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Standard models of solar evolution predict that the Sun was ˜25% less luminous at 3.8 Ga (Newman and Rood, 1977). If we assume that the atmosphere had a transmittance similar to the present, the average early Archean surface temperature would have been below the freezing point of water. However, the geologic record suggests that liquid water was present by at least 3.5 Ga and probably by 4.0 Ga (Sagan and Mullen, 1972, Schopf and Barghoorn, 1967). Thus, additional, strong greenhouse effects are required to make the early Earth habitable.

Sagan and Chyba (1997) argued that organic haze, such as that formed in Titan's atmosphere composed of N2 and CH4 (McKay et al., 1991), would have produced from CH4 photolysis in early Earth's atmosphere. Such early Earth haze might have shielded NH3 sufficiently that NH3 resupply rates were able to maintain surface temperatures above the freezing point (Sagan and Chyba, 1997; Wolf and Toon, 2010). However, the validity of the UV shielding hypothesis strongly depends on the optical property and production rate of organic haze formed in early Earth's atmosphere composed of N2, CO2, and CH4 (Pavlov et al., 2001).

Here, we investigate optical properties of photochemical haze on early Earth by laboratory experiments of haze production using a UV lamp from gas mixtures of N2, CH4, and CO2. Although a few laboratory experiments of haze production in early Earth's atmosphere has been conducted previously (Trainer et al., 2006), there is no experimental study to measure refractive indices of organic haze continuously from the UV to near-IR regions. In addition, the previous experiments used a deuterium lamp (Trainer et al., 2006), which has the wavelength peak at 160 nm. In this study, we use a UV lamp system using an electric discharge of H2/He gas mixtures, which produces a UV emission with the wavelength peak at 121.6 nm (i.e., Ly-alpha line) similar to the solar UV radiation. Based on spectroscopic ellipsometry, we obtain refractive indices and production rates of haze formed from various gas compositions. We also analyze intermediate gas products with a quadrupole mass spectroscopy. By comparing our results with those of the previously studies on Titan haze (Khare et al., 1984) and on early Earth haze (Hasenkopf et al., 2010), organic haze formed by our experiments has small imaginary refractive index. These results indicate that the optical depth of the organic haze is thin at the UV wavelengths, suggesting that the UV shielding by organic haze on the early Earth may have been less effective than previously thought.

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BAO001-P04 Room:Convention Hall Time:May 23 14:00-16:30

# Stability of Bioorganic Compounds in the Exposed Facility of the International Space Station

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A wide variety of organic compounds including amino acid precursors have been detected in such extraterrestrial bodies as carbonaceous chondrites and comets. It was suggested that these organics were formed in quite cold environments. We irradiated frozen mixtures of possible constituents of ice mantles of interstellar dust particles including water, methanol and ammonia with high-energy heavy ions from HIMAC, National Institute of Radiological Science, Japan. Amino acid precursors with complex structures were detected whose molecular weights are up to a few thousands. Such complex amino acid precursors are much stronger than free amino acids against radiation. Such organics could have been incorporated in solar system small bodies after the formation of the solar system and delivered to the primitive Earth.

Possible carriers of such organics are meteorites, comets and interplanetary dust particles (IDPs) that were formed from comets and meteorites. It is suggested that IDPs brought much more organics than meteorites and comets. However, nature of organics in IDPs is little known, since they have been collected only in terrestrial biosphere.

We are planning a space experiments named Tanpopo, 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 in the interplanetary space. We will report some preliminary results for the preparation of the mission including the capture of amino acid-containing particles at high velocity with ultra-low density aerogel. In addition, we irradiated amino acids (isovaline, etc.), simple precursor of amino acids (5, 5-ethylmethylhydantoin, etc.), and complex precursor of amino acids (CAW: proton irradiation product from a mixture of carbon monoxide, ammonia and water) with high energy heavy ions from HIMAC and with ultraviolet light from a deuterium lamp in order to test the stability of extraterrestrial organic compounds in space.

Keywords: Tanpopo Mission, amino acids, space dusts, cosmic rays, ultraviolet light

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# The microbe capture experiment in space: Fluorescence microscopic detection of microbes captured by aerogel

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Microbes have been collected at the altitude up to about 70 km in the sampling experiment done by several groups[1]. We have also collected high altitude microbes, by using an airplane and balloons[2][3][4][5]. We collected new deinococcal strains (*Deinococcus aetherius* and *Deinococcus aerius*) and several strains of spore-forming bacilli from stratosphere[2][4][5]. On the other hand, "Panspermia" hypothesis, where terrestrial life is originated from outside of Earth, has been proposed[6][7]. Recent report suggesting existence of the possible microbe fossils in the meteorite of Mars origin opened the serious debate on the possibility of migration of life embedded in meteorites (and cosmic dusts)[8][9]. If we were able to find terrestrial microbes in space, it would endose the possibility that the terrestrial life can travel between astronomical bodies.

We proposed a mission "Tanpopo: Astrobiology Exposure and Micrometeoroid Capture Experiments" to evaluate possible interplanetary migration of microbes, organic compounds and meteoroids on Japan Experimental Module of the International Space Station (ISS)[10]. Two of six sub themes in this mission are directly related to interplanetary migration of microbes. One is the direct capturing experiment of microbes (probably within the particles of clay) in space by the exposed ultra-low density aerogel. Another is the exposure experiment to examine survivability of the microbes in harsh space environment. They will tell us the possibility of interplanetary migration of microbes (life) from Earth to outside of Earth (or vise versa).

In this report, we will report whether aerogel that have been used for the collection of space debris and cosmic dusts can be used for microbe sampling in space. We will discuss how captured particles by aerogel can be detected with DNA-specific fluorescence dye, and how to distinguish microbes from other materials (i.e. aerogel and particles such as clay). The surface of microparticles captured by aerogel is often vitrified. The non-specific fluorescent light is often observed from vitrified materials. Therefore, we need to distinguish fluorescent light of stained microbes from that of spectral characteristics of vitrified materials and bleaching rate are going to be need to distinguish stained microbes with DNA-specific fluorescence dye and other materials such as clay and aerogel. We simulated the high-speed collision of micro-particles to the aerogel with the two stage light gas gun (ca. 4 km/s). The micro-particles containing dried cells of *Deinococcus radiodurans* mixed with clay material were used for the collision experiment, and the captured particles, which was stained after collision experiment, were observed with a fluorescence microscope. This experiment suggests that the captured microbes can be detected and be distinguished from clay materials.

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Keywords: Panspermia, Tanpopo, Astrobiology, Aerogel, fluorescence dye

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# Microbes-capturing experiment in ”Tanpopo” mission on ISS -Toward the detection of captured microbes in space by microbi

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Terrestrial life may fly off into outer space by volcanic eruption meteorological impacts, and so on. Microbes have been collected from high altitude up to 70 km since 1936 [1]. We also isolated microbes at high altitude up to 35 km using an airplane and balloons. The two isolates of these microbes are new deinococcal species, one of which shows higher UV ray tolerance than Deinococcus radiodurans [2,3]. On the other hand, panspermia hypothesis for origin of life on Earth suggests that the life or precursor materials of life came from space [4,5]. But this hypothesis can be subjected to several criticisms [6,7]. If microbes were to exist at the high altitude of low earth orbit (400 km), it would endorse the possibility of interplanetary migration of terrestrial life. We proposed the ”Tanpopo” mission to examine interplanetary migration of microbes and organic compounds on Japan Experimental Module (JEM) of the International Space Station (ISS) [8]. We will capture micro-particles including microbes and micro-meteoroids at the altitude of ISS orbit (400 km) with ultra low-density aerogel exposed to space for a given period of time.

After retrieving the aerogel, we will investigate captured microparticles and tracks followed by microbiological, organic chemical and mineralogical analyses. Captured particles will be analyzed after the initial curation of the aerogel and tracks. Particles potentially containing microbes will be used for PCR amplification of small subunit (SSU) rRNA gene followed by DNA sequencing. Comparison between the determined sequences and known SSU rRNA gene sequences of terrestrial organisms will suggest the origin and properties of the organism. The density of microbes at the ISS altitude might be quite low, and microbe cell number on each captured particle may be quite limited. Therefore, it is necessary to establish the effective PCR procedure for quite small amount of DNA template in the presence of other materials such as clay and aerogel. We will report current status of the PCR identification of microbes from test samples. The PCR conditions to amplify SSU rRNA gene from quite small number of cells and quite low concentration of genomic DNA with/without clay and aerogel are examined.

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Keywords: Astrobiology, limited environment, panspermia hypothesis, development of basic methods, orgin of life on earth

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# Chemical signature of Antarctic Marimo and Antractic soils

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A great number of Antarctic Marimo that is mainly composed with cyanophyta and green algae are developing in the low-salinity lake (Skallen Oike) in Antarctica. In order to study chemical and biological characteristics, the Antarctic Marimo sample was characterized by amino acid analysis and by fluorescence microscopy. Antarctic soil samples in Skallen Oike and other areas in Antarctica were also chemically characterized.These samples were collected near Showa Station during the 49th Japanese Antarctic exploration mission in 2006-7.

Outer part and inner part of the Antarctic Marimo was sampled, and observed by fluorescence microscopy. The inner part sample showed stronger fluorescence due to autofluorescence of chlorophylls. There are little difference in amino acid concentration and composition between the inner and the outer parts. Amino acids in Antarctic soil samples are positively correlated with alkaline phosphatase acitivity, which suggested that these parameters reflect biological activity in soils. Characteristics of amino acids and phosphatases in Skallen Oike soil and Antarctic Marimo will be compared in order to study the roles of Antarctic Marimo in the environments.

Keywords: Antarctic, Antarctic Marimo, soil, microscopic fluorometry, amino acid