Japan Geoscience Union Meeting 2013
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Theoretical investigation on the absorption spectrum of photosystem for the biomarker of extrasolar planets

Masahiko Taguchi[1], Yu Komatsu[1], Akimasa Sato[1], Mitsuo Shoji[1*], Megumi Kayanuma[2], Katsumasa Kamiya[1], Kenji Shiraishi[1], Kazuhiro Yabana[1], Masayuki Umemura[1]

[1]Graduate School of Pure and Applied Science, University of Tsukuba, [2]Department of Computer Science, University of Tsukuba

Over 800 extrasolar planets have been discovered, and more than 20,000 candidates have been detected. Planets in habitable zone have been observed, and the discovery of Earth-like planets is expected. Great attentions have been paid to the detection of life in extrasolar planets. For the detection, various indices have been proposed as biomarkers. One of the indicators is red edge[1], which is a characteristic steep gradient observed in the near-infrared region of around 750 nm in plant's reflection spectra [2]. In fact, red edge can be observed in the reflection spectrum of the Earth via the Moon (earthshine [3]). Since red edge is affected by many factors, its pricise predictions is not simple. However, a leaf chlorophyll absorption is thought to be the major factor of red edge [2].

On Earth, photosynthetic organisms have evolved through the collection of sunlight. On the other hand for the extrasolar planets, whose surrounding space environment has different spectrum from their primary star, photosystems should be different in many parts, such as pigment types and arrangements even though the environment is similar to the Earth.

Before predictions of biomakers of extrasolar planets, we examine the basic characters of chlorophylls in photosystems. It is also important for the study of the diverse photosystems on Earth. Chlorophylls are concentrated in a chloroplast, and form pigments-protein complexes in the photochemical systems.

The purpose of this research is to characterize the absorption spectrum of chlorophylls in a photosystem. First of all, we calculated the absorption spectrum of the pigment in methanol using DFT based polarization continuum model (PCM) method, and confirmed the validity of our calculation method. Then, quantum mechanics/molecular mechanics (QM/MM) calculations were performed for the absorption spectrums of the photosystem. Each chlorophyll was included in the QM region. We found that the absorption wavelengths are shifted about +10 nm by the effects of the protein environment. Similar influence was observed by the effect of amino acid coordination to the central Mg ion in the chlorophyll. These calculated results indicate a fine modulation character of the adsorption wavelength for the photosystem. This character is important for photosystems in extrasolar planets as well as in extreme conditions on Earth.

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Keywords: biomarker, extrasolar planet, photosystem, QM/MM, absorption spectrum

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Experimental studies on abiotic formation of amino acid precursors from interstellar media by cosmic rays

Midori Eto[1*], Takuto Okabe[1], Takeo Kaneko[1], Yumiko Obayashi[1], Hitoshi Fukuda[2], Yoshiyuki Oguri[2], Satoshi Yoshida[3], Kensei Kobayashi[1]

[1]Yokohama National University, [2]Tokyo Institute of Technology, [3]National Institute of Radiological Sciences

Various organic compounds including amino acid precursors have been found in extraterrestrial bodies such as meteorites and comets, and their relevance to the origin of life are discussed. It has been suggested that these extraterrestrial organics were formed in interstellar media in dense clouds. In the present study, we examined possible formation of amino acid precursors from interstellar media by irradiation of high-energy protons or heavy ions.

Carbon monoxide (350 Torr), ammonia (350 Torr) and liquid water (5 mL) was put in a Pyrex tube, and the gas mixture was irradiated with 2.5 MeV protons from a Tandem accelerator (Tokyo Institute of Technology). Total electric quantity irradiated was 1 - 4 mC, and the products were hereafter referred to as CAW. Gas mixtures of carbon monoxide (350 Torr) and ammonia (87.5 - 350 Torr) were also irradiated with 2 mC of 2.5 MeV protons, and the products were referred to as CA. A mixture of methanol, ammonia and water (molar ratio was 1:1:2.8) was irradiated with heavy ions (290 MeV/u carbon ions, or 500 MeV/u argon ions) from HIMAC, NIRS, Japan. Total irradiation dose was 1.5 - 15 kGy, and the products were referred to as MeAW. All the irradiated products were acid-hydrolyzed and then were subjected to amino acid analysis by HPLC and/or GC/MS.

When the gas mixture was irradiated with protons, white mist was formed in the gas phase that suggested that high molecular weight organic compounds were produced in the gas phase by the action of high-energy protons. The products dissolved water yielded a wide variety of amino acids after acid-hydrolysis. In all the CAW and CA products, glycine was predominant, followed by aspartic acid, serine, alpha-aminobutyric acid and beta-alanine. Yield of each amino acid was proportionate to the total electric quantity (or the total dose to the gas mixture). Heterocyclic compounds including uracil were also identified in CAW. MeAW also yielded glycine and other amino acids after acid-hydrolysis, but the yield of amino acids was not proportionate to the total dose.

The facts that solid products (mist) were formed in the gas mixture by proton irradiation and that the amino acid yield were proportionate to the dose showed that high molecular weight amino acid precursors were formed directly from the gas mixtures. Further study including irradiation to simulated interstellar ices will be done to examine possible formation mechanisms of amino acid precursors in space.

Keywords: cosmic rays, interstellar media, amino acid precursors, proton irradiation, origins of life, heavy ions

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Preliminary examination plan and subsequent analytical procedure of captured samples by aerogel in the Tanpopo mission

Kyoko Okudaira[1*], Akihiko Yamagishi[2], Hajime Yano[3], Hikaru Yabuta[4], Makoto Tabata[3], Shin-ichi Yokobori[2], Eiichi Imai[5], Kensei Kobayashi[6], Hajime Mita[7], Hideyuki Kawai[8], Masumi Higashide[3], Satoshi Sasaki[9], Tanpopo WG[3]

[1]The University of Aizu, [2]Tokyo University of Pharmacy and Life Science, [3]JAXA, [4]Osaka University, [5]Nagaoka University of Technology, [6]Yokohama National University, [7]Fukuoka Institute of Technology, [8]Chiba University, [9]Tokyo University of Technology

The Tanpopo mission is a Japanese astrobiological experiment which will be conducted on the Japanese Experiment Module (JEM) of the International Space Station (ISS) [1]. The Tanpopo mission consists of several subthemes: 1) capture of microbes in space, 2) exposure of microbes in space, 3) exposure of organic compounds in space, 4) capture of organic compounds (in micrometeoroids) in space, 5) evaluation of ultra low-density aerogel developed for the Tanpopo mission, and 6) capture of space debris at the ISS orbit (approximately 400 km altitude).

Here, we overview Preliminary Examination Team (PET) analysis and subsequent analytical procedure of aerogel samples for the mission, i.e. analyses for the subthemes 1, 3, 5, and 6 described above. Silica aerogel with 0.01 g cm^{-3} density supported by higher density aerogel [2] will be used to capture micrometeoroid and space debris at LEO. Captured particles and their penetration tracks will be offered for various analyses after retrieval to Earth. These samples will be analyzed for mineralogical, organic and microbiological characteristics.

In this paper, current status of Tanpopo-Aerogel-PET preparation will be introduced. In Preliminary Examination (PE), Curation team covers the receipt of retrieved samples (Sample Aerogel Panels), sample catalog preparation for data archiving and sample storage. Whole documentation team deals with penetration track mapping, penetration track measurement (e.g. incoming angle, track depth and track volume) and evaluation of aerogel as a capture medium. Processing team prepares keystones and quickstones (small pieces of aerogel) containing particles and their penetration tracks for allocation to researchers. After preliminary characterization, the samples (tracks and/or particles in keystones/quickstomes) will be properly processed in accordance with a request by each sub team for the subsequent detailed analyses.

Aerogel panels attached to zenith (space)-facing side will be allocated mainly to Organic and Inorganic Sub-Teams, and ones attached to ram-facing side (facing east) to both Debris and Microbe (terrestrial origin) Sub-Teams, while ones facing north to all Sub-Teams. We plan to preserve basically one of each aerogel panel for storage in the scope of future analyses and possible provision to researchers.

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Keywords: Tanpopo mission, International Space Station, Silica aerogel, Micrometeoroid, Space debris, Curation

Japan Geoscience Union Meeting 2013
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Analysis of amino acids in small particles captured with aerogel

Taka Kogawa[1*], Yuko Kawaguchi[2], Kyoko Okudaira[3], Hajime Mita[4], Makoto Tabata[5], Eiichi Imai[6], Sunao Hasegawa[5], Hideyuki Kawai[7], Hajime Yano[5], Hirofumi Hashimoto[5], Shin-ichi Yokobori[2], Akihiko Yamagishi[2], Yumiko Obayashi[1], Takeo Kaneko[1], Kensei Kobayashi[1]

[1]Yokohama National University, [2]Tokyo University of Pharmacy and Life Science, [3]Aizu University, [4]Fukuoka Institute of Technology, [5]JAXA/ISAS, [6]Nagaoka University of Technology, [7]Chiba University

Amino acids have been detected in such extraterrestrial bodies as carbonaceous chondrites and comets, and their relevance to the origin of life on the Earth is discussed. We are planning a space experiment named the Tanpopo Mission, where several experiments including capture of space dusts and exposure of organic compounds and microorganisms. As to the capture experiments, several aerogel blocks will be attached on several faces of an integrated experimental rack that will be placed on JEM/EF of ISS. High-speed dusts will make tracks in the aerogel. After recovering them to the Earth, we will separate each track with a terminal grain, and will apply to chemical analysis, including microscopic techniques (FT-IR, STXM-XANES, etc.) and amino acid enantiomers analysis after acid hydrolysis.

Amino acid is one of the main target molecules to be found in the capture experiments. We have tested whether hypervelocity dusts can be trapped in aerogel by using a two-stage light gas gun equipped in JAXA/ISAS. Samples such as amino acids adsorbed to porous silica gel and powder of Murchison meteorite were shot out at 4 - 6 km/s, and were captured in an aerogel to see whether organics could be recovered in the terminal grains or tracks. The aerogel block containing tracks of high-velocity particles was digested with HF-HNO, in a Teflon container. The digested solution was then acid-hydrolyzed with 6 M HCl, was desalted with a solid-state extraction column (MonoSpin SCX), and amino acids were determined by cation-exchange HPLC after post-column derivatization for fluorometric detection.

It is of quite importance to reduce amino acids in a procedural blank. The current situation in reducing the procedural blank will be presented.

Keywords: the Tanpopo Mission, interplanetary dust particles, small particles, microorganisms, aerogel, amino acids

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Synthesis of an amino acid from carboxylic acid and ammonia with shock wave

Chizuka Suzuki[1*], Yoshihiro Furukawa[1], Takamichi Kobayashi[2], Toshimori Sekine[3], Takeshi Kakegawa[1]

[1]Graduate School of Science, Tohoku University, [2]National Institute for Materials Science, [3]Graduate School of Science, Hiroshima University

Proteins are composed of twenty kinds of amino acids and are essential biomolecules for life on the Earth. Therefore, origins of amino acids on the early Earth have been an important concern. Many previous studies indicate that the late heavy bombardment (LHB) of extraterrestrial objects had occurred during 3.8-4.0 billion years ago. These impacts might have delivered and produced prebiotic organic compounds including amino acids, amines, and carboxylic acids as well as ammonia (Cronin and Pizzarello et al., 1988; Furukawa et al. 2009). However, the number of biomolecule by these processes was limited number of amino acids among protein-constituent amino acids. The organic compounds supplied by the impacts of extraterrestrial objects to the oceans must have experienced further impacts, because the LHB is a successive impact event. In this study, we demonstrated shock-recovery experiments on a solution of formic acid and ammonia to investigate whether amino acids form from low molecular weight organic compounds by oceanic impacts on the early Earth.

Shock-recovery experiments were performed with a single-stage propellant gun using an improved sample container. Starting material is a mixture of 13C-formic acid and ammonia. After the impact experiments, soluble organic compounds were extracted into water and then amines and amino acids were analyzed with liquid chromatography-mass spectrometer (LC/MS). Glycine, methylamine and ethylamine whose carbons are composed of 13C were identified in all of the samples. The amounts of glycine were almost constant regardless of the impact velocity (0.7-0.8 km/s). The amounts of produced amines increased depending on the impact velocity. The present results suggest that shock wave converts a low molecular weight organic compound to larger molecular weight organic compounds. The successive impacts might have contributed to chemical evolution providing variety in biomolecules on the prebiotic Earth.

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Enantiomer-specific isotope analysis (ESIA): D- and L-amino acids by biotic and abiotic processes

Yoshinori Takano[1*]

[1]JAMSTEC

Introduction

The one-handedness of terrestrial L-amino acids in proteins and in D-sugars of DNA and RNA are primary formation, structure and function of biopolymers for life on the Earth. Recently D-alanine has been recognized as a physiologically essential enantiomer for microbial growth and metabolic maintenance. The cell wall of domain Bacteria, especially for Gram-positive Bacteria, consists of a thick and uniform peptidoglycan layer that includes D-amino acids. Laboratory studies of the degradation of peptidoglycan showed it to decompose more slowly than proteins, indicating semi-labile compounds in nature. We have developed an analytical method to determine the ESIA of individual amino acid enantiomers and revealed nitrogen isotopic hetero- and homogeneity for D-alanine and L-alanine in terms of microbial processes in domain Bacteria and chemical processes in organic symmetric synthesis.

Experimental

The nitrogen isotopic composition of the individual amino acids was determined using a gas chromatograph/combustion/isotope ratio mass spectrometer (GC/C/IRMS) with a ThermoFinnigan Delta Plus XP combined with an Agilent Technologies 6890N GC and an Ultra-2 capillary column. Novel derivatization of amino acid diastereomers by optically active (R)-(-)-2-butanol or (S)-(+)-2-butanol with pivaloyl chloride produces N-pivaloyl-(R,S)-2-butyl esters (NP/2Bu) of the amino acid diastereomers. The elution order of these compounds on the chromatogram can be switched by a designated esterification reaction. We used purified peptidoglycans from domain Bacteria (phylum Firmicutes and Actinobacteria; Enterococcus faecalis, Staphylococcus aureus, Staphylococcus staphylolyticus, Lactobacillus acidophilus, Bacillus subtilis, Micrococcus luteus and Streptomyces sp.), (pseudo)-peptidoglycan from domain Archaea (Methanobacterium sp.), cell walls from domain Eukarya (Saccharomyces cerevisiae). Racemic D- and L-alanine were synthesized by a nucleophilic substitution 1 (SN1) reaction via an intermediate carbocation formed between alpha-bromopropionic acid (as amino acid racemic precursors) and aqueous ammonia.

Results and Discussion

The nitrogen isotopic difference of peptidoglycan defined as Delta15ND-L in bacteria, representative gram-positive phylum Firmicutes and Actinobacteria, tended to be 15N-depleted in D-alanine, suggesting that heterogeneous components are mainly controlled by enzymatic pathways prior to formation of the bacterial cell wall. Alanine racemase (Enzyme Commission, EC; 5.1.1.1) that interconvert L-alanine to D-alanine, one of isomerases for chiral amino acids, previously indentified in a biosynthetic pathway, participates in crucial enzymatic reaction to form D-alanine before D-alanine-D-alanine ligase (EC; 6.3.2.4) pathway in peptidoglycan metabolism. In contrast, the Delta15ND-L of racemic alanine in the chemical pathway during the nucleophilic substitution reaction between 2-bromopropionic acid and ammonia showed infinitely homogeneous components for each enantiomers. We present recent preliminary results in terms of abiotic geochemical samples for ESIA.

References

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Effects of glycine and its decomposition products on polymerization of methionine under high temperature and pressure

Rui Huang[1*], Yoshihiro Furukawa[1], Takeshi Kakegawa[1]

[1]Graduate school of Science, Tohoku University

It is widely believed that abiotic polymerization of amino acids is an important process for the formation of the first life. Several geological settings have been proposed as the place for the polymerization: sub-marine hydrothermal vents (Imai et al., 1999), tidal flats (Lahav et al., 1978), and marine sediments (Nakazawa et al., 1993). A unique point of the marine sediment is its pressurized conditions. Previous studies have suggested the importance of pressurized conditions for the production of longer peptides (Ohara et al., 2007; Otake et al., 2011; Furukawa et al., 2012). These previous studies also indicate that the reactivity of each amino acid is widely different, leading to skepticism about the formation of peptides composed of plural amino acids. In this study, we investigated oligomerization of methionine and glycine under the conditions of high temperature and high pressure (at 175^{o}C, 150 MPa, and 0-96 hours).

Methionine and glycine were used for representatives of each low and high reactive amino acid, respectively. Starting materials were solid methionine or solid methionine mixed with solid glycine, water, aqueous ammonia, or ammonium hydrogen carbonate. The additives other than glycine (water, aqueous ammonia, and ammonium hydrogen carbonate) are simulated decomposition products of glycine. Ammonium hydrogen carbonate decompose at about 60^{o}C and yields ammonia, carbon dioxide, and water. For each starting material, 0.43 mmol of methionine were used. The amounts of each additive were 0.43 mmol. Each starting material was sealed into a gold tube of 25 mm length and 5.5mm diameter. Then, high temperature and pressure conditions were applied using a test-tube-type autoclave system. After these experiments, amino acids and their oligomers were extracted into aqueous solution from the experimental products and analyzed with a high performance liquid chromatograph connected to a mass spectrometer (LC/MS).

In all experiments, methionine decomposed with elapsed time. Peptides longer than di-methionine were not formed in experiments without the additives. On the other hand, methionine was oligomerized to di-methionine, tri-methionine and methionine diketopiperazine in the experiments with additives. Methionyl-glycine and glycyl-methionine were also produced in experiments containing such additives. The rates of methionine decomposition and methionine-peptide formation were increased in experiments with additives. These rates were especially increased in samples containing aqueous ammonia, and ammonium hydrogen carbonate, suggesting that ammonia promote both the production rates of peptides and the decomposition reactions of methionine. The difference in reaction rates might have been caused by the difference in pH as suggested in a previous study (Sakata et al., 2010). When these results are applied to diagenesis in Hadean marine sediments, these results suggest that amino acids of lower reactivity may have been activated by amino acids of higher reactivity and might have produced peptides composed of plural amino acids.

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Open system incubation experiments of glycine-montmorillonite-water mixture at high temperature and high pressure

Kentaro Oguchi[1*], FURUKAWA, Yoshihiro[1], KAKEGAWA, Takeshi[1]

[1]Graduate School of Science, Tohoku University

There are several theories as to the place where primordial protein formed. Most of studies assume that polymerization of amino acids occurred in oceanic environments. However, there is a difficulty in the oligomerization of amino acids in oceans where huge amount of water exit, because the oligomerization of amino acid is a dehydration reaction. To address this contradiction, a model that hypnotizes the oligomerization proceeded in oceanic sediments was proposed. The effects of pressure in this model have been investigated previously. Clay minerals play an important role for the accumulation of amino acids in this model. However, the effect of clay minerals remains unclear. Therefore, this study investigated the effects of a typical clay mineral on the oligomerization of amino acids in a simulated diagenetic condition.

Glycine (Gly) adsorbed on montmorillonite was compressed and heated at 90^{o}C and 9 MPa with a piston cylinder for 7 days using silica powder as a pressure medium. Samples were collected and divided into three sections (S1, S2, and C1). The S1 was the outermost part of the sample, which was composed of mainly silica. S2 was the part between S1 and C1. Most of the S2 sample was silica. C1, the part of the center of the sample, was composed of mainly montmorillonite. Gly and peptides in these three samples were extracted with ammonia water. The extracted solution were filtered and concentrated to analyze the amount of Gly and peptides with LC/MS. Results show that Gly, diketopiperazine of Gly (Gly_{DKP}), and Gly dimer (Gly_2) were detected from three samples. The amount of Gly_2 and Gly_{DKP} were higher in C1 than in S1 and S2. Therefore, montmorillonite was considered to be effective to form peptides.

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Effect of oxygen fugacity in chemical processes of alanine during oceanic impacts of meteorites

Yuhei Umeda[1*], Toshimori Sekine[1], Yoshihiro Furukawa[2], Takeshi Kakegawa[2], KOBAYASHI, Takamichi[3]

[1]Graduate School of Science, Hiroshima University, [2]Graduate School of Science, Tohoku University, [3]National Institute for Materials Science

The biomolecules on the Earth are thought either to have come from the extraterrestrial parts carried with flying meteorites or to have been formed on the Earth from the inorganic materials through given energy. From the standpoint to address the importance of impact energy, it is required to simulate experimentally the chemical reactions during impacts, because violent impacts may have occurred 3.8-4.0 Gyr ago to create biomolecules initially. It has been demonstrated that shock reactions between ocean and meteoritic constitutions can induce locally reduction environment to form bioorganic molecules such as amino acid (Nakazawa et al., 2005; Furukawa et al., 2009). We need to know possible processes how further chemical evolutions proceed by repeated impacts and how more complicated biomolecules are formed.

In this study, we carried out shock recovery experiments to investigate the chemical reactions of alanine in aqueous solutions and the effect of oxygen fugacity. Experiments were carried out with a propellant gun. We used alanine labeled by ^{13}C to distinguish products from contaminants. Sample of aqueous solution immersed in olivine or hematite powders, sealed in a stainless steel container, was used as a target. The sample space has air gap behind the sample. The powder, solution, and air correspond to meteorite, ocean, and atmosphere on early Earth, respectively. Two powders of olivine and hematite can keep the oxygen fugacity low and high during experiments, respectively. After shots, the steel containers, after cleaned, were immersed into liquid nitrogen for sample solution to be frozen and then we drilled on the impact surface to extract water-soluble components from the sample using pure water in a beaker. After that, water-soluble components were analyzed by LC/MS for four amino acids (glycine, alanine, valine, and phenylalanine) and four amines (methylamine, ethylamine, propylamine, and butylamine).

The results indicate the formation of decomposition products (glycine, methylamine, ethylamine, and propylamine) of alanine and butylamine as a new biomolecule. However, the results did not detect any formation of valine and phenylalanine those could be expected to form by reactions. Glycine and some amines were detected in samples under low oxygen fugacity, while these molecules were hardly detected in samples under high oxygen fugacity. Therefore, oxidative conditions are not preferable to the formation of biomolecules. On the other hand, the present experimental results suggest that the survival rate of alanine depends on pressure and temperature but that it is not dependent on oxygen fugacity. In applying the present results to actual meteorite impacts, the physical condition during impact is a key factor in chemical reactions, although it also must be taken into account the heterogeneous distribution of impact energy in an impact that may cause a significant effect on the chemical reactions.

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Diastereoisomeric excess of Ala-DKP during condensation of racemic-Ala on olivine under hydrothermal condition

Shigeshi Fuchida[1*], Hiroshi Naraoka[2], Harue Masuda[1]

[1]Faculty of Science, Osaka City University, [2]Department of Earth and Planetary Science, Kyusyu University

<Introduction>

When peptides are abiotically formed from amino acid monomers under thermal condition, cyclic dipeptides, diketopiperazine (DKP), are intensely dominant. DKP was defined as an obstacle for peptide elongation (Basiuk et al., 1990), while, Nagayama et al. (1990) supposed that the DKP was an effective intermediate phase to provide internal free energy necessary to form additional peptide bond. If DKP play as an intermediate phase, DKP formation must be important as the first step of chemical evolution of peptides continuing to life. Minerals promote the DKP formation under laboratory thermally condition (e.g., Bujdak and Rode, 1996; Meng et al., 2004); e.g., DKP formation would be promoted on olivine surface, where amino acid monomers are dehydrated and the olivine is hydrated (serpentinization). Diastereoisomeric DKPs (*cis/trans*) are formed, when chiral amino acids are dimerized. In this study, the diastereoisomeric excess (*de*) of DKP formed from the simplest chiral amino acid, alanine (Ala), was observed on the surface of olivine (during aqueous reaction with olivine) at 120 degree C for 8 days.

<Experiment>

DL-Ala powder was reacted with/without powdered olivine and a small amount of ultrapure water in sealed glass ampoules under Ar atmosphere. The ampoules were heated in a drying oven at 120 degree C for 1-8 days. After cooling at room temperature, the reacted product was suspended in 5 mL ultrapure water and the dissolved diastereoisomers of DKP were quantified using a high performance liquid chromatograph with UV detection.

<Result and Discussion>

When the DL-Ala was heated without olivine, 3.0 % DL-Ala transformed into DKPs. On the other hand, 12.2 % of Ala changed to DKPs when the olivine coexisted. Olivine would be a good catalyst for DKPs formation. The DKPs were not detected even if the olivine coexisted after heating for 8 days, when a small amount of water was not added. A small amount of water would play a role to break the strong bonds of Ala crystals and promote the DKP formation reaction.

When *de* ({[*cis* DKP] - [*trans* DKP]}/ {[*cis* DKP] + [*trans* DKP]} is defined, positive *de* means *cis* DKP excess. The *de* of DKP formed from the reaction without olivine heating for 8 days was +7.3 %. On the contrast, it was +16.3 % when reacted with olivine. It was reported that *trans* DKP is preferentially formed relative to *cis* DKP during recemic amino acid condensation, then the *de* gradually decreased with increasing reaction time (Naraoka and Harada, 1986). In this study, the *de* of DKP considerably increased when reacted with olivine. Olivine would be not only an efficient catalyst to promote the DKPs formation but also a determining factor on the selectivity of diastereoisomeric DKPs. Thus, serpentinization of ultramafic rock would have connection to DKP formation with regulation of peptide stereoisomers in the primitive ocean on planets.

Keywords: diketopiperadine, diastereoisomeric excess, olivine, alanine

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Effects of silicate on the decomposition rates of pentoses

Sakiko Nitta[1*], Yoshihiro Furukawa[1], Takeshi Kakegawa[1]

[1]Graduate School of Science, Tohoku University

RNA is considered as a very important molecule for the origin of life because RNA carries genetic information and several RNA catalyze biological reactions. Ribose is an essential constituent of RNA. Ribose as well as the other pentoses can be produced abiotically through formose reaction. However, ribose is the most unstable pentose among of the pentoses produced by the formose reaction. Therefor, stabilization of ribose has been very important issue. For the solution of this problem, a previous study proposed that pentoses including ribose are stabilized forming complexes with silicate. Because of technical difficulties, it has not been clear which pentoses are stabilized by silicate. This study adopted a new application of liquid chromatography-mass spectrometry for the pentose analysis. The method made it possible to determine the concentration of each uncomplexed pentose. Incubation experiments of aldopentoses, ribose, lyxose, xylose, and arabinose, with three concentration of silicate have conducted in this study. In silicate-free solution, ribose had the highest rate of decrease. The rate of decrease for all aldopentoses became smaller with the concentration of silicate. In particular, the rate of decrease for ribose was significantly decreased. This result shows that silicate stabilize aldopentoses, especially ribose. Silicate is common in all over the world as silicate minerals and might have been common on the early Earth. Therefore, the selective stabilization of ribose by silicate might have provided a mechanism for the selection of ribose as the sugar in RNA on the early Earth.

Keywords: RNA, silicate, ribose, pentose, liquid chromatography-mass spectrometry

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The mechanism that had formed the primitive liposome in the early Earth

Shinji Karasawa[1*]

[1]Miyagi National College of Technology: Professor emeritus

[Introduction]

Materials used for the experiment for investigation of first primitive liposome had existed in the early Earth. Bubbles were generated by injection of iron powder into carbonated water. The side chain of appropriate amino acid adsorbs on the surface of the membrane. So, the life of bubble became longer by injection of the appropriate amino acid, because thermal motion of the adsorbed amino acid is suppressed and degradation of peptide bond of the amino acid is suppressed. A primitive protein is synthesized by incorporating into the membrane. The bubble rise to surfaces of water, and it will burst at the surface. As the result of repeating of the bursts, the surface of water was covered with similar membrane. After stirring that water, the bubbles were generated again under atmosphere of CO_2. After some time, the vesicles that stayed long time at middle portion of the water between surface and bottom were generated. The vesicle must be produced at burst of the bubble. It is able to include the membrane and the water inside of it. This special vesicle with long life was made from the membrane and the amino acids.

[Experiments on effects of amino acid to the bubble made from carbonated water and iron]

By addition of amino acid, the life of bubble generated in carbonated water mixed with iron powder becomes longer and its number increases. Here, materials for these experiments are (a)carbonated water: 75 cc, (b)iron powder: 5g and (c)amino acid (glutamine: 143mg, valine: 36mg, leucine: 71mg, isoleucine: 36mg). After several days from the mixing, the bubbles and the substance that had floated on the surface of the water were dissolved in the water by stirring of the water. After this stirring, bubbles were generated again. Initially, the rises-up and the fall-down were repeated. After some time, there emerged the vesicle that stayed in middle portion of the water. At this case, the atmosphere was filled with CO_2.

[Theoretical understandings]

The reason why bubbles are generated by injection of iron powder into carbonated water is as follows. The iron atom reacts with the oxygen atom of the carbon dioxide because the electronegativity of carbon atom is larger than that of hydrogen atom. The free carbon atom released from oxygen reacts with the iron atom. The iron carbide that has been produced reacts with the water. As the result, the free carbon atoms and the free hydrogen atoms form the membrane of the bubble. If insoluble gas is generated in the water where suitable organic molecules exist, the appropriate molecules will be arranged at the interface of the gas. The bubble made of the membrane rises up to the surface. The bubble will soon burst at the surface. The organic molecule that had been organized membrane of the bubble will cover the surface of water. After that, following phenomenon takes place at the burst of the bubble. The closed vesicle that includes the membrane and the water inside is produced by the mechanism to form the bubble. The reason why a liposome is generated is as follows. Amino acid is soluble in water but not soluble in oil. Organic molecules exist in the membrane of the bubbles generated in carbonated water mixed with iron powder. Appropriate side chain of amino acid is able to adsorb on surface of the membrane. Thermal motion of the adsorbed amino acid is suppressed and degradation of the peptide bond of amino acids is suppressed. The amino acid molecules adsorbed to the membrane will be mutually linked by the peptide bond. Although the association of amino acid is sensitive to the environment, the bubble of which membrane incorporated with linked amino acids becomes robust. The number of vesicles with long life will be increased. The large number of vesicles makes possible to form complicate cell by using broken parts of the membrane as units of the organization. The closed vesicle is able to include plural of small liposome.

Keywords: bubble, membrane, amino acid, peptide bond, protein, liposome

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(May 19-24 2013 at Makuhari, Chiba, Japan)

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Stratospheric Microorganisms Collection Using a Balloon

Sohsuke Ohno[1*], Ko Ishibashi[1], Akihiko Yamagishi[2], Yuko Kawaguchi[2], Shota Nitahara[2], Takahiro Segawa[3], Gensuke Tokoro[4], Kazuya Yamanouchi[4], Yuko Ishikawa[5], Norimune Miyake[1], Masanori Kobayashi[1], Takafumi Matsui[1]

[1]Planetary Exploration Research Center, Chiba Institute of Technology, [2]Tokyo University of Pharmacy and Life Sciences, [3]National Institute of Polar Research, [4]aRigen Pharmaceuticals, Inc., [5]Nippon Biologicals, Inc.

The subject of this study is focused on the stratospheric microorganisms, which are important for assessing the chances and flux of biological transfer escaping from and/or entering into the earth. Some previous studies reported the presence of microbes captured in the stratosphere by balloon, aircraft or rocket experiments. The presence of radiation- and desiccation resistant microbes, such as Bacillus and Deinococcus, have been accepted, although stratospheric environment is harsh against the microorganisms. However, it is difficult to discuss about the dynamic behavior of the stratospheric microorganisms, the mechanism of its vertical transportation, and its lifetime, because the time of observations and the number of detected microorganisms are not sufficient. In this talk, we introduce the plan of the balloon experiment to collect stratospheric microorganisms using a newly developed capturing system.

Keywords: Astrobiology, Panspermia, Stratosphere, Balloon, Extremophile

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Evaluation of biological activity in extreme environments by phosphatase activity

Taihei Kurizuka[1*], Taka Kogawa[1], Yumiko Obayashi[1], Takeo Kaneko[1], Hajime Mita[2], Yoshitaka Yoshimura[3], Yoshinori Takano[4], Mari Ogawa[5], Kensei Kobayashi[1]

[1]Yokohama National University, [2]Fukuoka Institute of Technology, [3]Tamagawa University, [4]JAMSTEC, [5]Yasuda Women's University

Terrestrial organisms are widely distributed even in extreme environments such as submarine hydrothermal systems and Antarctica soils. In order to evaluate biological activities in such extreme environments, we analyzed phosphatase activity and amino acids in soils and rocks in extreme environments.

Antarctic soil samples were collected near Showa Station during the 49th Japanese Antarctic exploration mission in 2006-7. Reference samples used were surface soil collected in the campus of Yokohama National University. Sea sand after heated at 773 K was used as blank. Chimney samples were collected in South Mariana hydrothermal systems, the Pacific Ocean in 2003 in a part of the Archaean Park Project.

Phosphatase was extracted from solid samples with Tris buffer solution, and the enzymatic activity in the extract was fluorometrically assayed with 4-methylumberyferryl phosphate as a substrate. Thermal stability and temperature-dependence of phosphatase were examined. Amino acid concentration in the same sample was also determined.

Outer part of the chimney samples faced to cold seawater, while inner part of them faced to superheated hydrothermal fluid. The former showed phosphatase activity, but the latter did not. Phosphatase extracted from the outer chimney, however, showed higher optimum temperature than E-coli. Thus, it is suggested that phosphatase found in the inner chimney was of thermophiles origin. Some Antarctica soils showed phosphatase activity, and some of them showed poorer thermal stability than E. coli alkaline phosphatase. Soil sampled at Langhovde penguins rookeries showed high phosphatase activity, and their thermal stability was close to E. coli's. This suggested that major source of phosphatase found in the soil was of microorganisms living in penguins' bodies.

Various enzymes have been detected in extreme environments. Characterization of such enzymes would give us further information on organisms living there. It can be said that phosphatase activity is a good biosignature for extant life in extreme environments.

Keywords: phosphatase activity, biological activity, extreme environments, amino acids, Antarctica, submarine hydrothermal systems

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Analysis of C_{20}-C_{25} isoprenoidal diether of halophilic archaea-lipid content changes in the incubation

TANOUE, Ryo[1], Noriaki YAMAUCHI[2*]

[1]Dept. Earth and Planetari Sci., Grad. School Sci., Kyushu Univ., [2]Dept. Earth and Planetari Sci., Fac. Sci., Kyushu Univ.

Archaea lives in a relatively harsh condition such as submarine hydrothermal vents (high temperature, low pH), swamp mud (anaerobic), and salt marsh (high salt concentration). Their living condition, especially the high temperature and low pH may be thought to resemble to the environment of primitive earth. It is settled for the third domain of life for 16SrRNA phylogenic tree. So, it is important microorganisms for the tools to imagine the first living organisms on the earth. Archaea has a characteristic lipid which core is consisted from the glycerol and saturated isoprenoid with ether linkage. Among them, halophilic archaea lives in a salt marsh, saltpan and the environment at the high salt concentration. The main lipid core is the C_{20}-C_{20} isoprenoid diether (called archaeol, (**1**)). And characteristic C_{20}-C_{25} diether (**2**)), rarely seen in other archaea, is also existed at the core. 2 have a possibility of the biomarker for hyper saline environment. Thus, the easy analytical method of **1**and **2**were investigated toward the possibility of biomarker for hypersaline environment to the evaluation of living halophilic archaea around coastal region. For the reevaluation of the C_{20}-C_{25} diether as a biomarker for a hypersaline environment, analytical methods of isoprenoidal lipid-core produced by the halophilic archaea by ESI-MS was conducted. Further, the compositional change for **1** and **2**, which simultaneously produced by the microorganism were observed by the two halophilic archaea species.

The lipid content of thermophilc archaea adopt the harsh condition to make the single-layer C_{40} tetraether lipid and, further, the five membered ring structure were formed inside of the isoprenoidal lipid core with higher temperature. (This phenomenon has been applied to create a new index, TEX_{86}.) Further, cryophilic archaea, which lives in an Antarctic salt lake, changes the lipid content toward increasing the number of unsaturation in archaea with low temperature. For our preliminary experiment, lipid content changes with the incubation condition were observed from hypersaline neutral *N. pallidum* JCM 8980. Thus, content change with the incubation condition (temperature, pH, salt concentration) for other species were observed.

Alkaline hypersaline archaea Natronomonas pharaonis JCM 8858 has similar optimum condition other than optimum pH (8.5). Lipid core changes about the several pH, salt concentration, and temperature (normal condition, 300 ml medium contains casamino acids 4.5g, sodium citrate 0.9g, glutamate 0.75g, magnesium sulfate 0.75 g, potassium chloride 0.6 g, sodium chloride 60 g) were observed. The microorganism was incubated for ordinal 12 days (at the beginning of the stationary phase) and lipid were extracted, hydrolyzed, and purified to give the lipid core. The ratio of **1** and **2** were determined with the ESI-MS at the negative ion mode with the $CHCl_3$-containing solvent system for the observation of chloride-adduct ion.

The growth ratio was almost the same without the low temperature condition observed significant growth bunting. The lipid content of *N. pharaonis* previously reported was consisted to our result. Further, temperature increasing caused increasing of the content of **2** with the hypersaline archaea. For the pH change, optimal pH tends to increase **2**, and other pH decrease the content of **2**. Salt concentration is not seemed to affect to the content of the lipid core. Usually, Salt tolerance of halophilic archaea has been secured and the nature of the protein, high potassium concentration in the cytoplasm. However, a change of the contents of the lipid core with the temperature change is the same as *N. pallidum*, which is considered to the adaptation to temperature change in halophilic archaea. Similar experiment for alkaline halophilic archaea *Natronobacterium gregoryi* will be reported.

Keywords: halophilic, archaea, biomarker, hypersaline environment

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Mineralogical study of clastic sedimentary rocks in the 3.2 Ga Moodies Group, South Africa

Shohji Kawai[1*], Takeshi Kakegawa[1]

[1]Graduate School of Science, Tohoku University

It is important to investigate the timing of emergency of oxygenic phototrophs (i.e., cyanobacteria) on the early Earth. To approach this problem, Sakamoto (2012) studied chemical sedimentary rocks (Banded Iron Formation:BIF) deposited in shallow ocean environments in Moodies Group in the Barberton Greenstone Belt, South Africa (ca.3.2Ga). Sakamoto (2012) concluded that chromite in Moodies BIFs is a chemical precipitates from oxygenated 3.2 Ga ocean water. However, absence of knowledge of a clastic chromite creates ambiguity if Sakamoto's chromite was a real chemical precipitate. Therefore the objectives of this study is set: (1) to constrain paragenesis and find minerals formed under oxic environments in shallow water clastic sediments, (2) to determine the chemical compositions and occurrence of clastic chromite, and (3) to discuss microbial ecosystem through stable carbon isotopic compositions.

We collected of the Moodies Group from the under-ground mining site (Sheba mine). Chromite in the examined samples is rounded or angular and surrounded by fuchsite and Cr-bearing biotite, contrasting chemical precipitated euhedral chromite surrounded by magnetite. Mg# of clastic chromite is 0.012 to 0.043, which differs from Mg# of chemical precipitated chromite (Mg# = 0.000). Such contrast suggests that both detrital and chemical precipitated chromites are present in Moodies sedimentary rocks. Additionally, stable carbon isotopic compositions are within a range of organic matter produced by cyanobacteria. Overall results of this study indicated that presence of 3.2 Ga oxygenic shallow oceans in where cyanobacteria were active.