

系外惑星のバイオマーカーのための光合成光吸収についての理論的研究 Theoretical investigation on the absorption spectrum of photosystem for the biomarker of extrasolar planets

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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 precise 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 biomarkers 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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キーワード: バイオマーカー, 系外惑星, 光合成, 量子古典混合計算, 光吸収

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

宇宙線による星間物質からのアミノ酸前駆体生成の実験的検証 Experimental studies on abiotic formation of amino acid precursors from interstellar media by cosmic rays

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地球生命の誕生に用いられたアミノ酸などの有機物の起源として、隕石等による地球外有機物の供給が注目されている。隕石や彗星の有機物は太陽系生成前の分子雲環境下で、星間分子に宇宙線などにより生成した可能性が考えられている。本研究では、模擬星間物質（一酸化炭素・メタノール・アンモニア・水など）に東工大タンデム加速器からの陽子線、もしくは放医研 HIMAC からの重粒子線を照射し、生成物を加水分解の後、アミノ酸の定量を行った。出発物質の組成、照射条件などの違いによるアミノ酸生成量の違いを調べ、アミノ酸生成機構などを考察した。

キーワード: 宇宙線, 星間物質, アミノ酸前駆体, 陽子線照射, 生命の起源, 重粒子線

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

たんぽぽ計画エアロゲル試料の初期分析とその後の分析フロー

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

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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/quickstones) 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

エアロゲルで捕集した微小粒子中のアミノ酸分析法の検討 Analysis of amino acids in small particles captured with aerogel

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たんぽぽ計画においては、国際宇宙ステーション曝露部にエアロゲルを設置し、これで高速に飛来する惑星間塵などの微小粒子を捕集する予定である。これを地球に回収した後、アミノ酸分析等により微小粒子のキャラクタリゼーションを行うが、その予備実験として、二段式軽ガス銃を用いて射出した模擬宇宙塵をエアロゲルで捕集し、その分析を行った。エアロゲル中のアミノ酸ブランクの測定などを行い、実験計画の評価を行った。

キーワード: たんぽぽ計画, 惑星間塵, 微小粒子, 微生物, エアロゲル, アミノ酸

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

衝撃波を用いたカルボン酸およびアンモニアからのアミノ酸合成 Synthesis of an amino acid from carboxylic acid and ammonia with shock wave

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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.

D-型とL-型のアミノ酸の同位体化学：生物起源と非生物起源のシグナル識別法 Enantiomer-specific isotope analysis (ESIA): D- and L-amino acids by biotic and abiotic processes

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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 2-bromopropionic acid (as amino acid racemic precursors) and aqueous ammonia.

Results and Discussion

The nitrogen isotopic difference of peptidoglycan defined as $\delta^{15}\text{N-D-L}$ in bacteria, representative gram-positive phylum Firmicutes and Actinobacteria, tended to be $\delta^{15}\text{N}$ -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 identified 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 $\delta^{15}\text{N-D-L}$ 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.

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高温高圧下でのメチオニン重合に対するグリシン及びその分解物の影響: 海洋堆積物内における化学進化の可能性 Effects of glycine and its decomposition products on polymerization of methionine under high temperature and pressure

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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°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°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 glycy-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.

モンモリロナイト-グリシン-水混合物を用いた開放系における加圧加熱実験 Open system incubation experiments of glycine-montmorillonite-water mixture at high temperature and high pressure

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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°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 (Gly₂) were detected from three samples. The amount of Gly₂ and Gly_{DKP} were higher in C1 than in S1 and S2. Therefore, montmorillonite was considered to be effective to form peptides.

隕石海洋衝突によるアラニンの化学進化と酸素分圧の影響 Effect of oxygen fugacity in chemical processes of alanine during oceanic impacts of meteorites

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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 ¹³C 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.

熱水条件下における Ala-DKP 生成時におけるジアステレオマーの過剰とカンラン石の役割

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

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<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 $de = \frac{[cis\ DKP] - [trans\ DKP]}{[cis\ DKP] + [trans\ DKP]}$ 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 racemic 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: diketopiperazine, diastereoisomeric excess, olivine, alanine

五炭糖の分解速度に対するケイ酸の影響 Effects of silicate on the decomposition rates of pentoses

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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. Therefore, 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.

キーワード: RNA, ケイ酸塩, リボース, 五炭糖, 液体クロマトグラフ/質量分析計
Keywords: RNA, silicate, ribose, pentose, liquid chromatography-mass spectrometry

初期の地球において原始的なリポソームを生成したメカニズム The mechanism that had formed the primitive liposome in the early Earth

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【はじめに】

初期のリポソームの形成過程を探求する次ぎの実験に用いた物質は初期の地球には存在していた。炭酸水に鉄の微粉末を加えると気泡ができた。その気泡は、アミノ酸を加えると寿命が長くなり、その数が増えた。そこで、気泡の膜の表面にアミノ酸の側鎖が吸着して、吸着したアミノ酸の熱運動は抑制され、そのペプチド結合の分解が抑制されるとして最初のタンパク質が膜に組み込まれて生成されたと考えた。水中の気泡は浮上し、水面で破裂する。このことが繰り返されると水面が気泡と同じ膜で覆われる。そして、水底と水面の中間に層をなして停留する小胞が生成されることが観測された。この小胞は、水面で破裂する際に、その内部に膜および水を吸い込んで発生したと考えられる。本報告でこのような実験結果と原始のリポソームを発生するメカニズムを報告する。

【炭酸水に鉄粉を混ぜて発生する気泡に及ぼすアミノ酸の効果を実験】

鉄粉を炭酸水に混ぜて発生する気泡はアミノ酸を添加することにより、その寿命が長くなり、その存在の数が増加した。この実験で使われた物質は、炭酸水 75 cc、鉄粉 5g、アミノ酸（グルタミン:143mg、バリン:36mg、ロイシン:71mg、イソロイシン:36mg、）である。数日間にわたって生成された水面に浮かぶ物質は、攪拌すると水に溶解する。その攪拌の後で、雰囲気大気圧のCO₂で満たしていると再び鉄粉等の底質から気泡が生成される。生成された泡が水中を浮上し、水面で破裂して気泡を作る物質は水底に沈降する。そのような上昇と下降が繰り返されることが続いて、しばらくすると水の間部分に停留する小胞が現れ、その小胞は寿命が長く、時間経過に沿ってその数を増した。

【理論による理解】

炭酸水に鉄の微粉末を混入することにより気泡が生成される理由は次の通りである。炭素原子の電気陰性度が水素原子のそれよりも大きいので、鉄原子は、二酸化炭素の酸素原子と反応する。酸素から放出された炭素原子が電気陰性度の関係で鉄原子と反応し、生成された炭化鉄が水と反応する。その結果、遊離炭素原子と自由水素原子が発生して気泡を形成する。水に溶けない気体が水中で発生すると水中の有機分子が気泡の膜を組織する。気泡は浮上するが、水面に到達した気泡は破裂する。やがて、気泡の膜を構成する有機分子が水面を覆うようになる。

他方、アミノ酸は水に溶けて、油には溶けない。しかし、炭酸水に鉄粉を混ぜて発生する気泡の膜には有機分子が存在し、アミノ酸分子の側鎖には気泡や水面の膜の有機分子に吸着するものがある。膜に付着したアミノ酸の分子の熱運動は抑制され、アミノ酸分子相互間のペプチド結合の分解も抑制される。その会合状態は環境に敏感ではある。一種の原始的なタンパク質ともいえる会合物質が有機分子の膜に吸着して合成される。

会合分子を持つ膜を持つ気泡が水面で破裂すると、破裂する際に気泡を形成するメカニズムが作用して、水面の膜と水を内部に吸い込み、原始的なリポソームができる。この特殊な小胞は水面と水底の間に停留する。このアミノ酸分子が膜に組織されて寿命が長くなると、その小胞の個数が増加する。水面に浮かぶ膜の断片を単位として組織される複雑な小胞や複数のリポソームを飲み込んだ小胞もできる。このようなメカニズムで原始的なリポソームと初期のタンパク質が生成されるという仮説を実験結果に添えて報告する。

キーワード: 気泡, 膜, アミノ酸, ペプチド結合, タンパク質, リポソーム

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

気球による成層圏微生物捕集実験 Stratospheric Microorganisms Collection Using a Balloon

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本講演では、我々が計画している、大気球を使い成層圏中の微生物を採集する実験について紹介する。

キーワード: アストロバイオロジー, パンスペルミア, 成層圏, 気球, 極限環境微生物

Keywords: Astrobiology, Panspermia, Stratosphere, Balloon, Extremophile

ホスファターゼ活性を用いた極限環境生物活動評価 Evaluation of biological activity in extreme environments by phosphatase activity

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地球極限環境における生物活動評価にホスファターゼ活性を用いることを検討した。試料としては、南極土壌や海底熱水噴出孔チムニー等を用いた。ホスファターゼ活性は4-メチルウンベリフェリリン酸を基質とする蛍光法を用いた。同じ試料のアミノ酸濃度も定量した。ホスファターゼ活性値やアミノ酸濃度は、生物活動とよい相関を示した。試料から抽出したホスファターゼの熱安定性や活性の温度依存性を調べると、その環境での主要生物種の生息温度に依存する傾向がみられた。

キーワード: ホスファターゼ活性, 生物活動, 極限環境, アミノ酸, 南極, 海底熱水系

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

好塩性アーキアに特徴的な C₂₀-C₂₅ ジエーテルの分析? 幾つかの好塩性アーキアの生育環境による脂質成分変化 Analysis of C₂₀-C₂₅ isoprenoidal diether of halophilic archaea-lipid content changes in the incubation

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アーキア(古細菌)は、海底の熱水噴出口(高温, 低 pH), 底泥(無酸素), 塩田(高い塩濃度)といった他の生物の生育が困難な環境に多く存在する微生物で, 16SrRNA による分子系統樹や, 高温, 低 pH での生育が原始地球環境と類似すると想定されることなどから, 生命の起源を探る為のツールとして, 極めて重要な微生物である。好塩性アーキアは, 通常生物のグリセリンと脂肪酸がエステル結合したものでなくグリセリンとイソプレノイドと呼ばれる C₅ 単位が重合した C₂₀ の枝分かれ炭化水素がエーテル結合した C₂₀-C₂₀ ジエーテル(アーキオール)(1)が脂質の主成分である。さらに, 他の古細菌にはほとんど見られない特徴的な C₂₀-C₂₅ ジエーテル(2)が存在する。好塩性アーキアは岩塩や高塩濃度環境での存在が示されているので, C₂₀-C₂₅ ジエーテル脂質は高塩濃度環境としてのバイオマーカーとしての利用の可能性が考えられる。一方, 沿岸域生物圏でのバイオマス推定は例がなく, 従ってこういったごく“普通”の環境での好塩性アーキアがどの程度この生物圏に影響をおよぼしているのかは不明である。好塩性古細菌の環境耐性を考え, 本微生物のごく普通の沿岸域でバイオマス推定を, 脂質構造の特徴に注目し, 有機物の微量迅速分析という典型的な有機地球化学的手法で明らかにしたいと考えている。

さて, 好熱好酸性古細菌においては, テトラエーテル脂質に五員環化合物が存在し, 温度に対しては五員環の数と五員環化合物の割合が多くなるように変化することが特徴的で, これが高温耐性の一つとされる。また南極で発見された好冷性アーキアは, 脂質主成分は 1 であるが低温で二重結合を 1 の中間に持つような脂質の割合が増大することが示されている。すでに予備の実験で我々は *N. pallidum* JCM 8980 では 1 と 2 の存在比が培養条件により変化することを示唆する結果を得ているが一方アーキアの環境変化に対応する膜成分変化は極性基変化の影響が大きいとする説も有る。そこで, 好塩性古細菌の環境変化に対応するコア脂質部分の変化について 2 種の性質がやや異なる種について, 生育条件変化による脂質成分の変化を検討した。

微生物 *Natronomonas pharaonis* JCM 8858 は, 好アルカリ性古細菌で至適条件が pH 8.5 という特徴があり, その他(温度 37 °, NaCl 濃度は 20% 程度)は JCM 8980 とよく似た至適条件を持つ。この好塩性古細菌培地 300 ml (カザミノ酸 4.5 g, クエン酸ナトリウム 0.9 g, グルタミン酸 0.75 g, MgSO₄ · 7H₂O 0.75g, KCl 0.6 g, NaCl 20%) に, *N. pharaonis* を 1 ml 加え 12 日間培養し(この条件が定常期(またはその直前)というのを増殖曲線観察で確認), 遠心分離にて集菌, Bligh-Dyer 法にて脂質抽出の後溶媒を除いて, 3% HCl-MeOH, 引き続き 7 M NaOH を加えて加水分解した。得られた脂質コアはシリカゲルカラムクロマトグラフィーにて hexane, hexane-ethyl acetate (10:1), hexane-ethyl acetate (2:1) で精製, hexane-ethyl acetate (10:1) 溶出分(約 1~1.5 mg)を ESI-MS にて分析した。温度としては 27 度から 42 度, 温度 37 度でかつ pH を変化させるという条件で培養を行い, 脂質を分析した。まず, 低温(27 °)で増殖は著しく遅く, ほぼ 3 倍の日数を要した。その他でこのような著しい増殖度の変化は見られなかった。文献で報告されている 1 と 2 の存在比は本実験による ESI-MS 分析においてもほぼ確保されていた。さらに条件を変化させた場合, 高温で 2 の割合が増加する傾向にあった。一方 pH は至適条件でほぼ最大でその他は減少する傾向にあった。一般に好塩性古細菌の耐塩性は主にタンパク質の性質と, 細胞質内の高カリウム濃度で確保されていると言われているが, 温度環境の変化に対応する変化は *N. pallidum* と同様であり, 好塩性古細菌に一般的な温度変化への適応の一端ではないかと考えられる。現在さらに好アルカリ性の古細菌 *Natronobacterium gregoryi* の培養と脂質変化の研究を行っているのでこれについても報告予定である

キーワード: アーキア, バイオマーカー, ジエーテル脂質, 高塩濃度環境

Keywords: halophilic, archaea, biomarker, hypersaline environment

南アフリカバーバートン地域ムーディーズ層(32億年前)砕屑性堆積岩の鉱物学的研究

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

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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. 3.2 Ga). 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.