

高波長分解能赤外ヘテロダイン分光器を用いた火星大気中のメタン及び水蒸気同位体の検出
Methane and HD0/H2O in the Martian atmosphere studied by ultra-high spectral resolution

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The Mid-Infrared LAsEr Heterodyne Instrument (MILAHI), which operates onboard the dedicated Tohoku 60cm telescope (T60) at the summit of Mt. Haleakala, has been designed for investigating the trace gases (Methane, HD0/H2O, etc) in the terrestrial atmospheres, such as Mars and Venus. The limitation to detect such trace gases from the ground-based is mainly due to the difficulty of correcting the atmospheric absorptions in the Earth atmosphere. High spectral resolution of MILAHI (>10E6) enables to retrieve them without any ambiguity due to the reproduction of atmospheric spectra on Earth.

In this study, we focus on the detection of methane and HD0/H2O in the Martian atmosphere. As a local oscillator (LO), newly installed quantum cascade laser (QCL) nicely covers 7.7 micron wavelength for these molecules. It is the only IR heterodyne instrument that gives access to new spectral range as compared with previous instruments of this kind.

Because the facility/instrument is just becoming to be operational in these years, the first Mars campaign will be performed on Feb.-Mar. 2016, with large Doppler shift (~15 km/s) between Mars and Earth. Prediction of the radiative transfer model indicates that the determination with two- VSMOW precision could be obtained by 15-minute integration. Upper limit 100ppb of methane will also be determined by 32-hours integration.

Further continuous observations will help to constrain (i) the possibility of biological/geological activities in the current Martian atmosphere, and (ii) water cycle and its evolution on Mars.

キーワード：メタン、HD0/H2O、ヘテロダイン

Keywords: Methane, HD0/H2O, Heterodyne

Primordial Anorthositic Continent on Mars and Planetary Habitability

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The Moon has primordial continental crustal materials consisting of anorthosite. Anorthosite has been recently discovered on the Martian surface as well, with occurrence possibly extensive similar to the lunar-like global anorthosite crust [1]. A felsic primordial Martian crustal basement, in addition to anorthosite, may include andesite [2] and granite [3]. A key example of this may be the conglomeratic alluvial-fan materials of Peach Vallis in Gale crater which are interpreted to be representative of the ancient felsic crust [4] of Terra Cimmeria exposed by the Gale impact [5]. Terra Cimmeria is one of the ancient geological provinces of Mars, dated to be > 4.0 Ga based on impact crater statistics, stratigraphy, and magnetic data, which records major contractional, transtensional, and extensional tectonism [6]. In the case of the Earth, the occurrence of anorthosite is observed to be limited in the geological record, however, lunar and Martian surface geology indicates that anorthosite was likely more universal on the Earth as primordial continent during the first 600 million years after its formation. Difference in the presence of an anorthositic continent is due to the size of planet. The reason why the primordial continent of the Earth disappeared is explained by the strength and duration of mantle convection. On Mars, due to its size and relatively rapid heat loss, a proposed early phase (~>3.93 Ga) of plate tectonism shut down [7] before the primordial crust could be destroyed. The presence of a primordial continent is the essential and most significant factor as it determines the fate of the planet to be habitable or not. The key is to have limited amount of an initial ocean to emerge a significant extent of primordial continent at the surface, as well as to operate plate tectonics on the planet [8]. When this logic is applied to a super-Earth, it suggests that a primordial continent forms on the surface but that the continent is transported into the deep mantle due to strong mantle convection immediately following its formation. After the primordial continent disappears from the surface of the planet, the supply of nutrients necessary for life terminates. Even if a primordial ocean existed on the surface of a super-Earth, the ocean would disappear before life emerges. Therefore, there is very little chance for life to emerge on a super-Earth. Mars, on the other hand, may hold significant environmental information not only about extremely ancient Mars and the solar system, but also possible early life. References: [1] Carter, J., Poulet, F. (2013) *Nature Geoscience* 6, 1008-1012. [2] Bandfield, J.L. et al. (2000) *Science* 287, 1626-1630. [3] Wray, J.J. et al. (2013) *Nature Geoscience* 6, 1013-1017, doi:10.1038/ngeo1994. [4] Sautter, V. et al. (2015) *Nature Geoscience*, doi:10.1038/ngeo2474. [5] Anderson, R.C. et al. (2015) GSA Annual Meeting in Baltimore, Paper No. 203-11. [6] Dohm, J.M. et al., 2013. In "Mars Evolution, Geology, and Exploration", Nova Science Publishers, Inc., pgs. 1-34. [7] Baker, V.R. et al. (2007) In "Super-plumes: Beyond plate tectonics", Springer, p. 507-523. [8] Maruyama, S. et al., 2013. *Geoscience Frontiers* 4, 141-165.

Keywords: Mars, anorthosite, Earth, Moon, habitable trinity

窒素ガス中飛翔体衝突で発生する高温プルーム内で合成されるアミノ酸の分析（小惑星衝突模擬実験）

Analysis of amino acids synthesized in a gas plume by projectile-impact in nitrogen gas (Model experiment of asteroid's impacts)

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タイタンなど、大気を持つ衛星/惑星に小惑星が衝突した時、衝突により発生する高温ガスプルーム内で化学反応が起き、種々の有機物が合成され、地表に蓄積してきたと考えられる。この仮説を検証するため、2段階軽ガス銃を用いた、衝突合成実験を行っている。[1] 直径 7.1 mmのポリカーボネート弾を、秒速 7 km/sまで加速し、与圧室内のターゲットに衝突させる（ここに、与圧室内の窒素圧力は約 1 気圧、ターゲットは、直径 65 mmの鉄の前面に氷（氷+ヘキサ）を付加してある）。衝突直後に、ターゲット表面に高温プルームが発生し、10cm程度の大きさに成長する、約25 μ sの発光後、プルームの温度は低下し、消滅する。この時合成されたすす試料（多くの部粒子を含む）は、与圧室の内壁に堆積する。このすす試料を注意深く回収し、分析する。微粒子試料を高温純水で還流し、抽出液をダブル誘導化し、高速液体クロマトグラフで分析した。その結果、アミノ酸であるグリシン、アラニンを検出することができた。[2] 特に、氷+ヘキサ+鉄ターゲットを用いると、その合成量が増加した。1mgの試料に対し、グリシンが約 2 nmol 含まれていた。試料無しの場合の種々の不純物分析から、これらのアミノ酸は、衝突合成されたと言える。次に、微粒子試料を6 M HCl中、110°Cで24時間加水分解を行い、脱塩処理後、陽イオン交換液体クロマトグラフ分析を行った。[3] その結果、グリシン、アラニン、アスパラギン酸などのタンパク質アミノ酸や γ -アミノ酪酸などの非タンパク質アミノ酸が検出され、その量は加水分解前よりもはるかに多くなった。これはアミノ酸が前駆体の形で生成していることを示す。コンタミでないことを証明するために、アミノ酸のD/L比の測定を計画中である。現在、ガス条件、ターゲット条件を変えて、アミノ酸合成量がどのように変わるかを調べている。一方、FT-IR分析やTOF-MS分析においても、アミノ酸分子の存在を示す証拠を得ている。窒素大気を持つタイタン衛星に、大量の小惑星が衝突した歴史と今回の実験結果を考えると、タイタン表面には、アミノ酸がかなり蓄積しているのではないかと考えられる。参考文献：[1] T. Mieno, S. Hasegawa, "Production of carbon clusters by impact reaction using light-gas-gun in experiment modeling asteroid collision", Appl. Phys. Express 1(2008) 067006-1-3.[2] K. Okochi, T. Mieno, K. Kondo, S. Hasegawa, K. Kurosawa, "Possibility of Production of Amino Acids by Impact Reaction Using a Light-Gas Gun as a Simulation of Asteroid Impacts", Orig. Life Evol Biosph 45 (2015) 195-205.[3] T. Horiuchi, Y. Takano, K. Kobayashi, K. Marumo, J. Ishibashi, T. Urabe, "Amino acids in water samples from deep sea hydrothermal vents at Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean", Org. Geochem., 35 (2004) 1121-1128.

キーワード：小惑星衝突、タイタン、アミノ酸合成、高温ガスプルーム、ガス銃実験

Keywords: impact of asteroid, Titan, synthesis of amino acids, hot gas plume, gas gun experiment

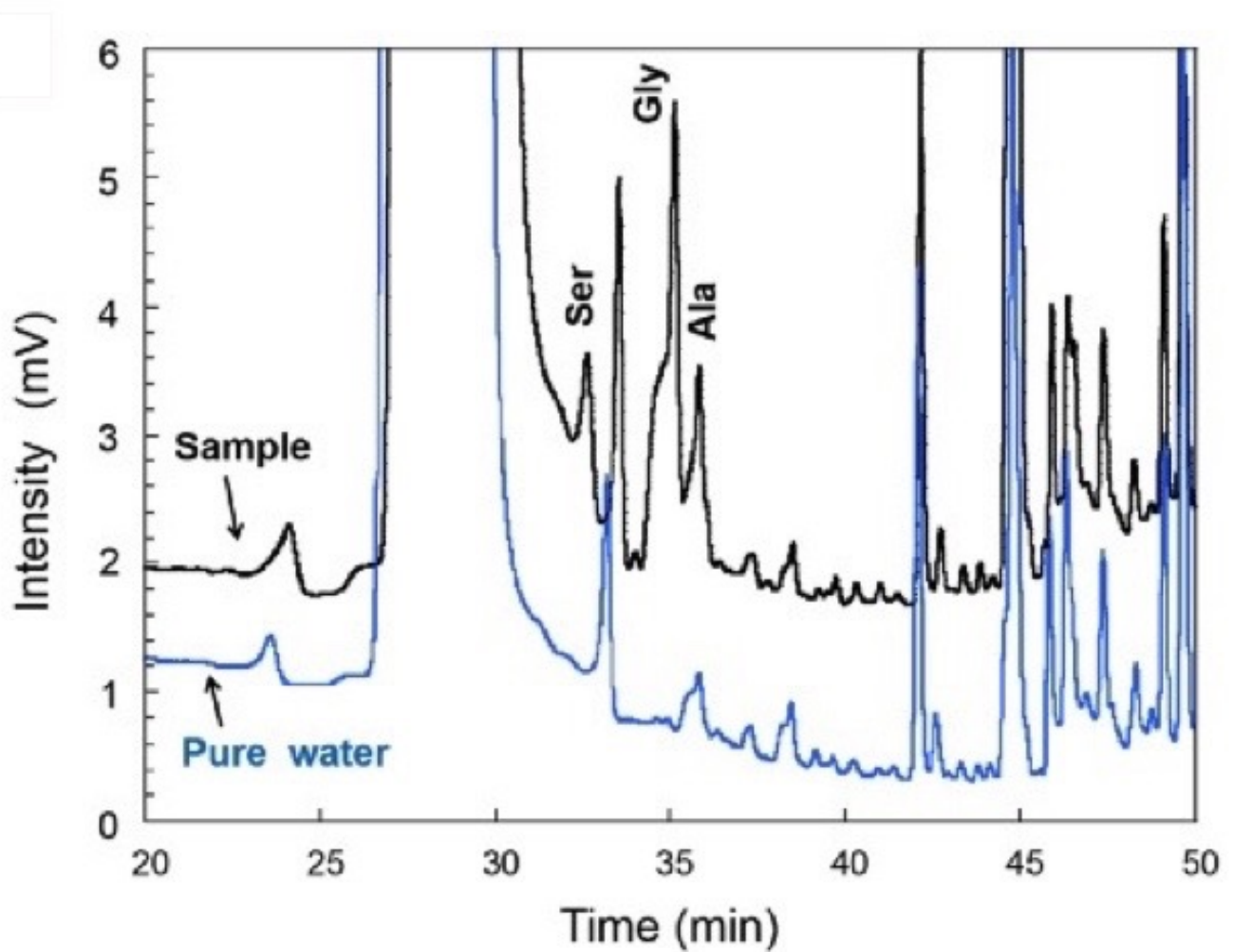


Fig. 1 HPLC chart of the sample refluxed by pure water and dabsylized, where the ice + hexane + iron target is used. The chart of dabsylized water is also shown. (quoted from ref. 2.)

粒子線照射による模擬星間塵アイスマントル中での超複雑アミノ酸前駆体生成
Formation of Super-complex Amino Acid Precursors in Interstellar Ice Analogues by
Particles Irradiation

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分子雲中の星間塵アイスマントル中での有機物生成の検証のため、メタノール・アンモニア・水の混合物を液体窒素中で凍結し、これに放射線医学総合研究所のHIMACからの290 MeV/u炭素線を照射した。生成物を加水分解するとグリシンなどのアミノ酸の生成が確認された。生成物（加水分解前後）をFT-IR, ESI-MSなどでキャラクタリゼーションを行った。また、比較として一酸化炭素、メタン、アンモニア、水の混合気体への陽子線照射も行い、結果の比較と、反応機構の推定を行った。以上の結果から、星間塵アイスマントル中で、宇宙線的作用により複雑な構造を有するアミノ酸前駆体が生成しうることが強く示唆された。

キーワード：星間塵アイスマントル、アミノ酸、超複雑有機物、宇宙線、重粒子線照射

Keywords: Ice mantles of interstellar dust particles, Amino acids, Super-complex organic molecules, Cosmic rays, Heavy ions bombardment

有機物・微生物の宇宙曝露と宇宙塵・微生物の捕集：たんぽぽ計画の進行状況

Current status of Tanpopo: Astrobiology Exposure and Micrometeoroid Capture Experiments at the Exposure Facility of ISS-JEM

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Tanpopo, a dandelion in Japanese, is a plant species whose seeds with floss are spread by wind. We proposed this mission to examine possible interplanetary migration of microbes, and organic compounds at the Exposure Facility of Japan Experimental Module (JEM: KIBO) of the International Space Station (ISS). The Tanpopo mission consists of six subthemes: Capture of microbes in space (Subtheme 1), exposure of microbes in space (Subtheme 2), analysis of organic compounds in interplanetary dust (Subtheme 3), exposure of organic compounds in space (Subtheme 4), measurement of space debris at the ISS orbit (Subtheme 5), and evaluation of ultra low-density aerogel developed for the Tanpopo mission (Subtheme 6). Exposure Panels for exposure of microbes and organic materials and Capture Panels for aerogel were launched on April 2015. The Panels were placed on the Exposed Experiment Handrail Attachment Mechanism (ExHAM) in the ISS. The ExHAM with Panels were placed on the Exposure Facility of KIBO (JEM) with the Japanese robotic arms through the airlock of KIBO. The trays and panels will be exposed for more than one year and will be retrieved and returned to the ground for the analyses.

キーワード：宇宙実験、国際宇宙ステーション、微生物、有機物、シリカエアロゲル

Keywords: Space experiment, International space station, Microbes, Organic compounds, Silica aerogel

THE FIRST YEAR OPERATION AND INITIAL SAMPLE ANALYSIS AND CURATION REHEARSALS OF THE TANPOPO ASTROBIOLOGY EXPERIMENTS

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Launched in April, 2015, the "TANPOPO" mission has beocme the first astrobiology space experiment of Japan. It aims to test various aspects of the "quasi-panspermia" hypothesis for exogenesis origin of life precursors and their interplanetary transport [1]. In May and November 2015, the first year samples were installed on two sets of the "ExHAM" pallet on the handrail of the ISS-Japan Experiment Module (JEM) Exposed Facility (EF) in the duration of 1-4 years. The TANPOPO experiment consists of following six sub-themes: 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.

In 2015-2019, the TANPOPO employs blocks of the the least dense aerogels among past space missions as 0.01 g/cc [2] on the Capture Panels (CP) that will be exposed and retrieved to capture impacting solid microparticles such as organic-bearing micrometeoroids and possible terrestrial particles in the low Earth orbit. By analyzing captured micrometeoroids in the CPs, one can learn what kinds of extra-terrestrial organic compounds inside micrometeoroids to be transported from parent bodies and how they may be altered in outer space. Also by evaluating retrieved samples of exposed terrestrial microbes and astronomical organic analogs on the exposure panels, one can investigate their survivals and alterations in the duration of interplanetary transport.

If microparticles of terrestrial origin are ever impacted into the CPs, one can prove that terrestrial microbes (e.g., aerosols embedding microbial colonies) may be present, even temporarily and in "freeze dry" form in the low earth orbit altitudes.

The TANPOPO-Initial Sample Analysis and Curation (ISAC) has been in its rehearsal since January 2016 and will be conducted by its Preliminary Examination Team (PET) as soon as the first samples will be returned to the Earth after summer of 2016.

The ISAC plan for CPs covers the receipt of retrieved samples, their initial inspection and documentation, processing and distribution of the samples for detailed analyses of each sub-theme, cataloging for data archiving and sample storage. For initial inspection and documentation, they will map and measure aerogel penetration tracks and captured particles (e.g., incoming angle, track depth and track volume) by the original keystone machine at ISAS clean room. Then they will process keystones containing microparticles to be inspected further and their penetration tracks for allocation to respective sub-theme researchers, in accordance with their requests for the subsequent detailed analyses within the first 100 days after the Earth sample return [3].

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Keywords: astrobiology, space experiment, micrometeoroids, panspermia, microbes

エアロゲルを用いた惑星間塵捕集時の有機物変性評価：衝突実験後のMurchison隕石のSTXM-XANES分析

STXM-XANES analyses of Murchison meteorite powders captured by aerogel after hypervelocity impacts: A potential implication of organic matter degradation for micrometeoroid collection experiments

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The ultralow-density silica aerogel (0.01 g/cm^3) has been developed at Chiba University [1], and is used as a dust capture medium in the Tanpopo mission that is an ongoing Japanese astrobiology space experiment at the Japanese Experiment Module (JEM) 'Kibo' on the International Space Station (ISS) [2]. One of the purposes of this mission is capturing micrometeoroids around the ISS orbit. The low-density aerogel is expected to reduce shock-degradation of materials by hypervelocity impacts (several kilometers per second), as previously used to capture the cometary dust particles from the Comet 81P/Wild 2 in the STARDUST mission [e.g. 3]. In order to evaluate potential degradation of the micrometeoroids by hypervelocity impact to the aerogel, we conducted the simulation experiments using a two-stage light-gas gun and Murchison meteorite as a micrometeoroid analog material. We conducted X-ray absorption near edge structure (XANES) analyses for the particles recovered from the impacts, using a scanning transmission X-ray microscopy (STXM).

Two-stage light-gas gun experiments were conducted at the Space Plasma Laboratory, ISAS/JAXA. We fired Murchison powder (micron-sized grains) into silica aerogels (0.01 g/cm^3) by shotgun method. In shot #399, 30-100 micron sized powder was fired at 4.4 km/s at a vacuum degree of 7.5 Pa, while in shot #1473, 37-60 micron sized powder was fired at 5.9 km/s at a vacuum degree of 9.5 Pa. Several grains of the Murchison meteorite manually extracted from the aerogel were embedded in sulfur separately, and sliced into 100 nm-thick sections with an ultramicrotome equipped with a diamond knife. Before analysis, the sections on the SiO-coated Cu TEM grids were mildly heated ($<100^\circ\text{C}$, $<15 \text{ min}$) until the sulfur sublimated off the grids. C-, N- and O-XANES analyses were performed for two grains from each shot (4 in total) using the STXM at beam line 5.3.2.2 in the Advanced Light Source, Lawrence Berkeley National Laboratory.

STXM images and elemental maps for C, N and O showed no clear evidences for surface degradation, nor differences between surface and interior of the sections of the Murchison grains after the experiments, although there were some heterogeneity of the elemental distributions and textures. Note that the heterogeneity of the elemental maps partially attribute to heterogeneity of the sample thickness that is mostly due to large porosity of this meteorite. The sizes of the analyzed ultramicrotomed sections that roughly represent the recovered grain sizes were in the range of 10 to 25 μm for shot #399, and in the range of 10 to 40 μm for #1473. The C-XANES were obtained at

least a few micrometer inside of the grains. The C-XANES spectra of the Murchison after the 4.4 km/s shot have organic features at 285.0 eV assigned to aromatic/alkene C=C, absorption at 286.7 eV is assigned to ketone C=O, absorption at 287.5 eV is assigned to aliphatic C-C, absorption at 288.7 eV is assigned to carboxyl O-C=O, but in the case of the 5.9 km/s shot, most of these features disappeared. All sections show abundant oxygen mainly from silicates with some contributions from organics, but show low nitrogen contents. The results indicate that the Murchison grains recovered after 4.4 km/s impact into the 0.01 g/cm³ aerogel seem generally intact, but the grains recovered after 5.9 km/s impact show drastic changes in organic structure. Although further discussion is required on the size effects, the threshold impact velocity for organic survivability might be between 4.4 and 5.9 km/s. At least, organic matter in micrometeoroids with entry velocity of ~4.4 km/s or less can survive from the impact to the 0.01 g/cm³ silica aerogel.

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キーワード：宇宙塵、たんぽぽ計画、STXM-XANES、炭素質コンドライト

Keywords: Micrometeoroids , Tanpopo mission, STXM-XANES, Carbonaceous chondrites

アラニンの25 °Cにおける圧力誘起オリゴペプチド生成

Pressure-induced formation of alanine oligopeptides at 25 °C

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Introduction

Oligomerization of amino acids can provide a clue to the origin of life because it is a fundamental step of protein synthesis. Under high pressure, increases of intermolecular interactions result in chemical reaction which cannot proceed under ambient condition. Oligomerization of amino acids was reported from experiments under high pressure and high temperature conditions simulating impact of comets, hydrothermal vents, diagenesis in sub-seafloor sedimentary environments (e.g., Sugahara and Mimura, 2015; Imai and Honda, 2010; Otake et al., 2011). In these experiments, both high pressure and high temperature are the important factors for amino acids oligomerization. However, it is unknown which factor is more efficient for forming oligomers. In this study, we focus on exclusive effect of high pressure on oligomerization reaction. We tested oligomerization of L-alanine under a room temperature and high-pressure condition. Fujimoto et al. (2015) reported pressure-induced oligomerization of L-alanine up to the trimer using GC-MS analysis (Fig 1). In the present study, we used LC-MSMS to detect higher oligomers.

Experimental procedures

All high-pressure experiments were carried out at 25 °C. Starting material was loaded in a high-pressure cell with three different conditions: wet, dry and solution (wet: L-Alanine powder with its saturated aqueous solution. dry: L-alanine powder. solution: saturated L-alanine aqueous solution.). Sample was compressed using a large-volume opposed-anvil apparatus or a "Kawai-type" multi-anvil apparatus. Experimental runs were conducted at pressures of approximately 5 GPa, 7 GPa, 9 GPa, 11 GPa, and 16 GPa using an opposed-anvil apparatus and 18 GPa and 23 GPa using a multi-anvil apparatus. After decompression to ambient pressure, run products were dissolved in pure water and analyzed using LC-MSMS.

Results and discussion

Alanine dimer was detected from all the run products. With increasing pressure, the yields of alanylalanine increased for each experimental condition (wet, dry, and solution). At pressures higher than 9 GPa, formation of alanine trimer was detected and the yield increased with pressure. These results are consistent with the results of Fujimoto et al. (2015). It is noteworthy that oligomerization of alanine occurred under water-coexisting conditions. In the pressure and temperature conditions applied in this study, water in the samples existed as ice VII, the oligomerization observed here was a solid-phase reaction. Higher oligomers were detected from the samples recovered from high pressure. Under the wet condition, the formed oligomers decreased with increasing the oligomer size and the largest oligomer detected was 8-mer.

This study revealed that oligomerization of amino acids occurs under high pressure at room temperature with existence of water as ice VII which is known to exist in the interiors of icy planets. This study proposes an interior of an icy planet as a new abiotic condition for oligomerization of amino acids.

キーワード：アミノ酸、高圧、オリゴマー化

Keywords: amino acids, high pressure, oligomerization

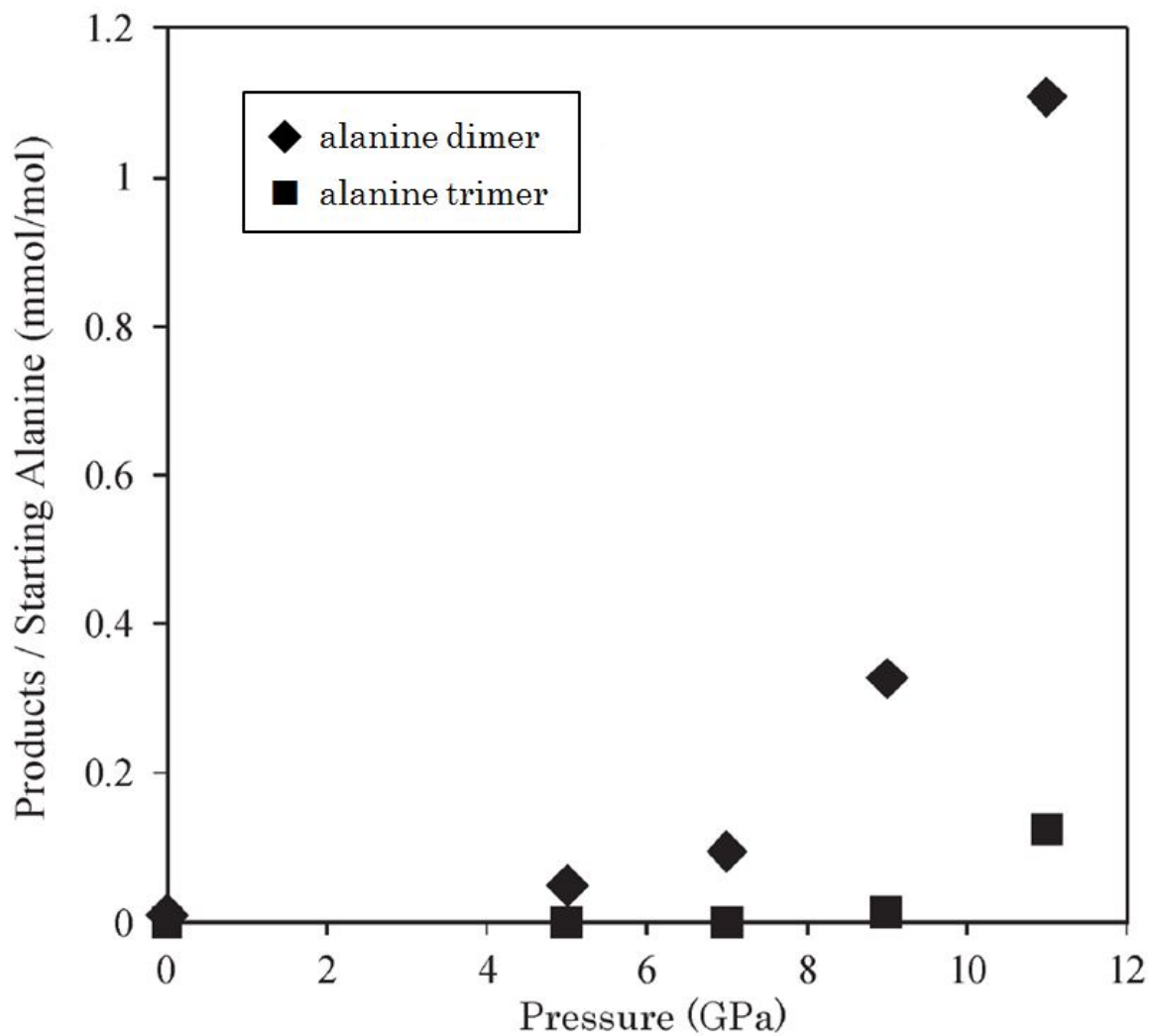


Fig. 1 Molar ratios of alanine dimer and trimer to starting alanine vs. pressure.
(Fujimoto et al., 2015)

放射線により誘起されるオリゴペプチドのエピ化反応

Epimerization of oligopeptides induced by radiation rays

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生命体を構成するタンパク質は翻訳直後にはL型という片手構造（ホモキラル）のアミノ酸から構成されている。化学進化の過程でタンパク質の元となるポリペプチドがホモキラルになった過程は解明されていない。多くの仮説が提示されているが、ポリペプチドの単量体であるアミノ酸の片手構造の生成を説明する仮説が多い。本研究ではアミノ酸からポリペプチドが生成する過程にあるオリゴペプチドの物性と反応性に注目した。特に、オリゴペプチドに γ 線や放電などの放射線が作用したときのエピ化反応が起こり得るか、さらに、エピ化反応の速度がジペプチドの構成比にどのような影響があるかを調べた。

鎖状および環状のアラニンジペプチド（Ala-Ala）の水溶液またはその結晶に γ 線（1-24 kGy）を照射し、アキラルまたはキラルカラムを装着したHPLCで反応液を分析した。鎖状L-Ala-L-AlaおよびD-Ala-L-Alaの1mMに γ 線を照射した溶液では分解とエピ化が同時に進行した。pH2の反応液を用いた場合には両者の分解速度定数には大きな違いは見られなかったが、L-Ala-L-Alaからの線量当たりのエピ化速度定数は 0.017 kGy^{-1} 、D-Ala-L-Alaからは 0.0033 kGy^{-1} となり差が見られた。これはホモキラルペプチドの方がヘテロキラルペプチドよりエピ化しやすい条件であり、ホモキラリティーの濃縮に適さないことが示唆された。しかしながら、環状ジペプチドを用いた反応ではヘテロキラルペプチドはホモキラルペプチドよりエピ化しやすいという結果が得られた。

キーワード：エピ化、オリゴペプチド、 γ 線

Keywords: epimerization, oligopeptides, gamma rays

生命のビッグバン：39.5億年以上前の特殊な有機分子構成

Big Bang of life: unique composition of organic molecules at >3.95 Ga

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The earliest life on Earth may have appeared at approximately 4.0 billion years ago (Ga) based on analyses of molecular clocks. However, there is no evidence of early life between 4.0 and 3.7 Ga. The type of the earliest life is also unknown. Here, we report that organic molecules derived from the earliest life have been detected from the oldest shallow-sea sedimentary rocks from Labrador, Canada, the age of which is >3.95 Ga. These molecules have two unique features: (1) branched alkanes (methyl- and ethyl-) and squalane exclusively dominate in these rocks; (2) *n*-alkanes and branched alkanes possess strong even-over-odd predominance in the number of carbons. These features have not been found in strata younger than 3.5 Ga. Among these molecules, it is difficult for squalane to be produced by non-biological processes. The dominance of squalane, which is derived from squalene, a constituent of archaeal lipid and precursor of both eukaryotic (sterol) and prokaryotic (hopanoid) lipids, suggests that this is a fundamental organic molecule of life common to all three domains, i.e., prokaryotes, archaea, and eukaryotes. This unique composition changed to a more normal composition between >3.95 Ga and 3.48 Ga. This change looks like dawn of the universe, i.e. Big Bang, because the unique type of life that occurred during this first short period of <0.5 billion years was followed by the current type of life that has persisted for >3.5 billion years. Giant impact of asteroids on Earth occurred between 4.03 and 3.85 Ga (Late Heavy Bombardment) evidenced by ages of impact craters of the moon. Those impacts could have eradicated the early life found in Labrador followed by emergence of the current type of life on Earth.

キーワード：初期生命、有機分子、後期重爆撃、始生代

Keywords: early life, organic molecules, Late Heavy Bombardment, Archean

ガンフリント層に多量に見いだされるパイロビチュメンが示す初期原生代地球環境
Significance of pyrobitumen in ca. 1.9 Ga Gunflint Formation: Unique feature of
Paleoproterozoic Earth?

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Occurrence of pyrobitumen has been known in Paleoproterozoic sedimentary rocks. However, their exact age, source rocks and extents have been constrained poorly. Here I report detailed description and new geochemical data of pyrobitumen in ca. 1.9 Ga Gunflint Formation. Pyrobitumen disseminated in oolitic carbonate, conglomerate and shale of Gunflint Formation. Some pyrobitumen occur as thin veins concordant with sedimentary bedding. These features suggest that large quantity of bitumen (or oil) introduced and disseminated in Gunflint sediments, when the sediments were still soft.

Carbon isotope compositions are much lighter than sedimentary organic matter, e.g., kerogen, in the same rocks. Kerogen in Gunflint Formation has a contrast compositions of pyrobitumen, suggesting that bitumen was generated elsewhere. Carbonaceous rocks are completely absent except Gunflint Formation in the studied area. This postulate bitumen (oil) generation and migration within Gunflint Formation.

Results of the present study suggest that (1) examined pyrobitumen is analogous to other Paleoproterozoic Shungite, (2) burial of organic matter were intensive even at 1.9 Ga, largely affecting C and N cycles of biosphere, (3) oil generation, migration, and solidification were most likely promoted by intensive Paleoproterozoic igneous activities. In particular, the combination of above (2) and (3) were unique to Paleoproterozoic Earth, largely contributing to remove atmospheric CO₂.

Evidence of various microbial activities was reported from Gunflint Formation. There exist a possibility that a part of the past geochemical and electron microscopic evidence were records of microbial activities in migrating oil, rather than representing activities of Paleoproterozoic marine microorganisms.

キーワード：初期原生代、パイロビチュメン、ガンフリント

Keywords: Paleoproterozoic, pyrobitumen, Gunflint

地球生命誕生の3段階モデル

3 step model for the emergence of first life

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生命の起源は、おそらく生物学者だけでは解けない問題だろう。この問題は、生物学のみならず、天文学、地球物理学、化学、地質学などを総動員した超学際研究によってのみ解明できるはずである。われわれは、地球史研究を通して、生命を育んだ器としての地球の歴史を、横軸46億年研究と特異点研究の2つの手法を利用して解明してきた。そこから導かれる生命誕生場はどのようなものであり、最初の生命はどのようなものだったのかをまとめたのが、地球生命誕生の3段階モデルである。本モデルでは、生命は、第一次生命体、第二次生命体を経て第三次生命体（原核生物）が誕生したことを提唱する。以下に、各段階における生命体について詳述する。

第一次生命体は、それぞれの個体そのものだけでは生存できなかったが、多数が外部共生することによって生き延びることが可能であった生物群だと考える。第一次生命体が持っていたワンセットの遺伝子をミニマム遺伝子と考える。おそらく、ミニマム遺伝子は約100個の遺伝子からなっており、「膜+代謝+自己複製」を可能にした。しかし、生存するためには細胞外共生をする必要があった。当時、ミニマム遺伝子の周囲には、この微小生態系の100倍以上の量のオルガネラ（現代のウイルスに酷似の状態）が存在していたが、これらの微小生態系が活動するためには、連続してエネルギーを供給することが必要で、当時の冥王代地球表層では太陽エネルギーが利用できなかった。その代わりに、地下の自然原子炉から供給される強力なエネルギーによって地表と間欠泉内部をつなぐ環境でのみ存在が可能だった。自然原子炉間欠泉は、熱湯が周期的に噴出するため、内部の温度は100°Cが上限となる。従って、高温によるRNAの損傷を受けることは少なかった。

間欠泉から地表に投げ出される第一次生命体は、地表に降り注ぐ原始太陽風（現在の1000倍の放射線）によって分解され死滅する。それによって、これらはタールと化す。冥王代表層環境の厚い大気（CO₂100気圧）が薄くなり、次第に太陽が顔をだし始めると、可視光（太陽エネルギー）を利用することができるようになった新しい生命（第2次生命体）が生まれる。これは地下の自然原子炉間欠泉で生まれた第一次生命体を基本とし、太陽からの弱い電磁エネルギーを利用するために、半導体（FeSなど）を利用した反応システムを創り出した。第一次生命体に引き続き、第二次生命体も無限に近い種類のアミノ酸の高次有機物からできるので、第二次生命体の多様性はさらに増加し、種類は無数にあったと考えられる。第二次生命体も細胞外共生していた。

原始海洋は猛毒（pH<1、超富重金属元素濃度、塩分濃度は現在の5-10倍）である。したがって、淡水をたたえる湖沼環境で生まれた第二生命体は、原始海洋に遭遇すると大量絶滅する。大陸内部のリフト帯の湖沼環境で生まれた生命体は、リフトが割けて海洋が浸入することによって大量絶滅を起こすことになる。このプロセスが何度も繰り返され、幾度となく第二次生命体は大量絶滅を経験する。一方、プレート運動によって、海洋の重金属は鉱床として硫黄とともに固定され、マントルプレートと共に沈み込むことによって海洋から取り除かれていった。更に、陸地の風化浸食運搬作用によって、細かく砕かれた大陸の岩石と海洋が反応することによって、海洋の中性化が進む。このように浄化されていった海洋にやがて適応した生命体は遺伝子の数を桁違いに増加して、細胞壁を作り、耐性強化した。これが真正細菌でシアノバクテリアの起源だと考えられる。

こうして、原始生物は、生き延びるための防御構造を、次々と発明して、遺伝子数を急増させた。理論的に可能なアミノ酸の種類はほぼ無限（10²⁰）に近いが、現代地球の生物は20種類のアミノ酸だけを使う。これは、第二次生命体が、無限に近い種類のアミノ酸を組み合わせたものであったが、猛毒海洋への適応戦略で淘汰された結果であろう。これが地球型生命体の起源である。

キーワード：生命の起源、三段階モデル、冥王代地球

Keywords: origin of life, three step model, Hadean earth

宇宙線によるタイタンソーリン生成に関する実験的研究

Laboratory simulations of Titan tholins formed by cosmic rays

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Titan is the largest moon of Saturn, which has a dense atmosphere mostly consisted of nitrogen and methane. It has been suggested that Titan's atmosphere is an analogue of that of primitive Earth, which is no more remained. Thus the study of the chemical evolution in Titan's atmosphere could give us many important suggestions, and it draws our special attention from the point of view of astrobiology.

Organic materials were detected in Titan's atmosphere. It indicates that an active organic chemistry occurs due to irradiation by solar UV light, Saturnian magnetospheric electrons and cosmic rays as energy sources. Many simulated experiments have been performed by using these energies. Complex organic materials produced in laboratory simulations have often been called tholins, which contain hydrocarbon, nitrile and heterocyclic aromatic moieties. Tholins could give amino acids after interaction with water.

Most laboratory works have simulated reactions in the higher atmosphere of Titan, where solar UV and Saturnian magnetospheric electrons are considered major energies. In the lower atmosphere, however, cosmic rays could have larger contribution than UV [1]. However, there is not many laboratory simulations using cosmic rays. Taniuchi et al. (2013) studied tholins formed by proton irradiation and the produced tholins were analyzed by SEM, AFM, pyrolysis GC/MS and MALDI-TOF-MS [2]. The tholins yielded a wide variety of amino acid precursors after acid hydrolysis, but the structures of amino acid precursors were little known. In this study, we irradiated gas mixtures simulating Titan atmosphere with high energy protons to investigate possible structures and formation mechanisms of tholins.

We prepared a 700 Torr (93 kPa) of gas mixture of nitrogen (95%) and methane (5%) as a simulated Titan tropospheric atmosphere: The pressure corresponds to that of Titan at an altitude of 10 km. The gas mixture was introduced to a Pyrex tube with a Havar foil window. KBr substrates were also placed in the Pyrex tube to sample the products including insoluble fractions. The gas mixtures were irradiated with protons from a Tandem accelerator at Tokyo Institute of Technology. After proton irradiation, KBr substrates were taken out of the tube and were subjected to FT-IR and XANES analysis. XANES analyses were carried at NewSUBARU synchrotron facility at University of Hyogo. The products on the inside Pyrex tube were collected with several kinds of solvents which has different polar character, and were analyzed by ESI-MS. An Aliquot recovered with each solvent was hydrolyzed and subjected to amino acid analysis by ion exchange HPLC.

ESI-MS indicated that tholins made by proton irradiation contained amino acid precursors such as hexamethylenetetramine. XANES and FT-IR analyses showed that the tholins contained amine groups and aliphatic moieties. No clear evidences of aromatic groups were observed. Characteristics of water soluble fraction of the tholins were difference from those of the whole tholins. Spectroscopic results showed that some O-containing groups in the whole tholins, which suggested that trace amount of water could have contaminated to the gas mixture at room temperature. We are now

designing the experiments at low temperature to avoid water vapor contamination.

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キーワード：アストロバイオロジー、タイタン、宇宙線、化学進化、ESI-MS、FT-IR

Keywords: Astrobiology, Titan, cosmic ray, chemical evolution, ESI-MS, FT-IR spectroscopy

火花放電・紫外線照射および陽子線照射による弱還元型模擬原始大気からのアミノ酸生成
 Amino acid formation from simulated mildly-reducing primitive atmospheres by spark discharges, UV irradiation and proton irradiation

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生命の誕生に先立ち、アミノ酸などの有機物が無生物的に生成したと考えられる。1953年、ミラーは、原始地球大気を模擬したCH₄、NH₃、H₂、H₂Oからなる強還元型混合気体に、雷を模擬した火花放電実験を行い、アミノ酸が無生物的に生成することを確認した[1]。しかし、現在では原始地球大気はこのような強還元型ではなく、N₂やCO₂などが主とし、これに少量の還元型ガス(CO、CH₄など)が加わった弱還元型大気であったことが示唆されている[2]。そこで本研究では、様々な混合比のN₂、CH₄、CO₂の混合気体に様々なエネルギーを与え、原始地球上でのアミノ酸生成の可能性について検討した。エネルギー源は、火花放電(雷を模擬)、陽子線(宇宙線を模擬)、紫外線の3種類を用いた。

出発物質として、N₂(50%)、CH₄(0-50%)、CO₂(バランス)の混合気体(全圧700 Torr)と、超純水5 mLを用いた。以下、各混合気体はCH₄比率で表す。

<火花放電実験> Pyrex製容器に混合気体700 Torrと超純水5 mLを入れ、テスラコイルを用いて1対のタングステン電極間で放電を12時間(1分間隔のON-OFFサイクルを24時間繰り返し)行った。全エネルギーは864 kJと試算された。

<陽子線照射実験> Pyrex製容器に混合気体700 Torrと超純水5 mLを入れ、タンデム加速器(東京工業大学)からの2.5 MeV陽子線を2 mC照射した。CH₄比率の低い、CH₄ 1%、CH₄ 0.5%などの実験も行った。全エネルギーは3.16 kJであった。

<紫外線照射実験> 石英窓のついたPyrex製容器に混合気体700 Torrと超純水5 mLを入れ、紫外線ランプ(浜松ホトニクスL1835)を用いて紫外線を12時間照射した。全エネルギーは136 Jと推定される。

放電もしくは照射後に、容器内の生成物(水溶液)を回収し、その一部を酸加水分解(6 M HCl中で110°C、24時間加熱)した後、陽イオン交換HPLC法(o-フタルアルデヒドとN-アセチル-L-システインによるポストカラム誘導体化-蛍光検出)を用いてアミノ酸の定量を行った。

どの実験生成物も、酸加水分解前はアミノ酸がほとんど検出されなかったが、酸加水分解後には、出発物質の組成により種々のアミノ酸の生成が確認できた。その中でグリシン(Gly)の生成量が最も多かったため、以後、加水分解後のGlyの生成量を中心に議論する。

火花放電実験では、CH₄比率10%以下ではGlyの生成は確認できなかったが、CH₄比率15%では少量(12.0 nmol)のGlyの生成が確認され、CH₄比率50%では最も多く(3.64×10⁴ nmol)のGlyが生成した。CH₄比率10%~15%間にアミノ酸生成の閾値があることが示唆された。

陽子線照射実験では、CH₄比率0.5%でもGlyが生成し(6.83 nmol)、基本的にCH₄比率が大きくなるほど生成量が増えた。CH₄比率50%でのGly生成量は1.53×10⁴ nmolであり、火花放電よりも低い、エネルギー収率は火花放電より高かった。火花放電とは異なり、CH₄濃度の閾値がないことが示唆された。

紫外線照射実験では、CH₄比率0%~30%ではアミノ酸の生成は確認できなかったが、CH₄比率40%、50%では極少量の生成が確認できた。ただし、これがコンタミネーションでないことを確認する必要がある。

以上から、与えるエネルギーによってアミノ酸生成の傾向が異なり、その反応機構が異なる可能性が示唆された。

実際の原始地球大気は弱還元型でCH₄比率は極めて低いと想定されるため、雷や紫外線をエネルギー源としたアミノ酸生成の可能性は低いと考えられるが、宇宙線であればアミノ酸前駆体が生成された可能性が高いと思われる。一方、紫外線単独では、弱還元型大気からのアミノ酸生成は困難であるが、原始地球に降り注いでいた紫外線のエネルギーフラックスは極めて高いため、紫外線と宇宙線や放電とのシナジー効果を検証する必要がある。

ある。

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キーワード：弱還元型原始大気、火花放電、陽子線照射、紫外線照射、アミノ酸

Keywords: mildly-reducing primitive atmospheres, spark discharge, proton irradiation, UV irradiation, amino acids

たんぽぽミッション機械式宇宙温度計による温度測定

Temperature Measurement with the Mechanical Space Thermometer for the Tanpopo Mission

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Temperature in the space is very interesting as astrobiology because it control the life and death of the creature in space environment. The mechanical thermometer using a bimetallic strip coil was developed for the Tanpopo mission. The Tanpopo mission is a multi-year passive exposure experiment for astrobiology exposure and micrometeoroid capture onboard the Exposed Experiment Handrail Attachment Mechanism (ExHAM) at the Japanese Experiment Module 'Kibo' (JEM) Exposed Facility (EF) on the International Space Station (ISS). The Tanpopo mission apparatuses were launched by the SpaceX-6 Dragon CRS-6 on April 14 2015, from the Cape Canaveral Air Force Station in the U.S.A. Since its microbial exposure experiment requires recording the maximum temperature that the Tanpopo exposure panel experiences, we have developed a mechanical thermometer with no electric power supplied from the ExHAM. At a given time and orbital position of the ISS, the thermometer indicator was video-imaged by the extravehicular video camera attached to the Kibo-EF and controlled from the ground. With these images analyzed, we were able to derive the temperatures of the Tanpopo exposure panels on the space pointing face of the ExHAM as shown in Fig.1. Nine times of observation of the thermometer was carried out in 2015. The maximum temperature was 26.4 ± 5 °C. Now this passive and mechanical thermometer is available to other space missions with no electric supplies required and thus highly expands the possibility of new extravehicular experiments and explorations for both human and robotic missions.

キーワード：国際宇宙ステーション、たんぽぽ、機械式宇宙温度計

Keywords: International Space Station, Tanpopo, Mechanical Space Thermometer

No.	Observation Time GMT (2015/D/T)	Sun Beta Angle (degree)	Max. Temp. (°C)	Min. Temp. (°C)
1	153/01:00 ~ 08:00	73.772 ~ 73.738	-8.8±5	-12.5±5
2	159/09:50 ~ 16:50	53.874 ~ 52.542	-11.1±5	-21.0±5
3	164/13:00 ~ 20:00	29.963 ~ 28.611	16.4±5	-0.6±5
4	170/21:00 ~ 171/06:00	1.747 ~ 0.179	17.5±5	-3.4±5
5	184/00:00 ~ 06:00	-28.325 ~ -28.170	23.9±5	-1.6±5
6	194/17:15 ~ 23:40	0.845 ~ -0.263	20.9±5	3.4±5
7	349/03:30 ~ 11:00	-15.081 ~ -16.486	26.4±5	6.9±5
8	355/11:40 ~ 18:00	-45.075 ~ -46.313	-8.9±5	-20.9±5
9	362/11:40 ~ 18:40	-73.652 ~ -74.172	-27.2±5	-35.3±5

Fig.1 Results of Temperature Measurement

模擬宇宙環境によって引き起こされる*Deinococcus radiodurans* R1内の*rpoB*遺伝子の解析
Analysis of mutations of *rpoB* gene in *Deinococcus radiodurans* R1 induced by simulated space conditions

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To investigate the microbial viability and their DNA damage, the radioresistant bacteria *Deinococcus* spp. have been exposed at Exposure Facility of International Space Station (ISS) in Tanpopo mission since May 2015 [1]. The Exposure Panels (EPs) harboring dried-deinococcal cells will return to the ground after about one-, two- and three-year exposure. We are going to analyze the survival rate and DNA damage of dried deinococcal cells using pulsed-field gel electrophoresis, quantitative-PCR and mutation assay. The antibiotics rifampicin binds the RNA polymerase β -subunit, which is encoded by *rpoB* gene, and inhibits the initial step of the transcription activity. Certain mutations in the *rpoB* gene confer rifampicin resistance [2]. Based on the above understanding, we will determine mutant frequency and the mutation spectrum for the *D. radiodurans* *rpoB* gene. From these mutation data, we will estimate major DNA damage induced by space environment. For this purpose, the mutagenic specificity of the *D. radiodurans* *rpoB* gene in simulated space conditions was investigated in this study.

The *D. radiodurans* R1 cell-suspension was dropped in the wells of aluminum plates ($\phi 20$ mm) and was dried under vacuum (vacuum-dried). The dried cells were exposed to vacuum ($< 10^{-5}$ torr) or UVC_{254nm} under the vacuum conditions. As a control, we analyzed the vacuum-dried cells without additional vacuum incubation. After exposure experiment, the cells were recovered from each well. inoculated to 10 ml of mTGE medium and cultured to show the OD_{590 nm} to be about 4. The cell suspension was plated on mTGE agar containing 50 μ g/ml of rifampicin to determine the number of rifampicin resistant colonies (Rif^R), and on mTGE agar without rifampicin to determine the total number of viable colonies.

The rifampicin-resistant mutant frequency of vacuum-dried cells was $1.3 (\pm 0.5) \times 10^{-8}$. The rifampicin-resistant mutant frequency of the *D. radiodurans* R1 wet cells has been shown to be about 1.5×10^{-8} [3]. The result suggests that the rifampicin-resistant mutant frequencies of vacuum-dried cells and wet cells are comparable for *D. radiodurans* R1. Further, we will report and discuss the rifampicin-resistant mutant frequency and mutation spectra in the *rpoB* gene of rifampicin-resistant cells following exposure to UVC_{254nm} and vacuum ($< 10^{-5}$ torr).

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キーワード：国際宇宙ステーション、たんぽぽ計画、突然変異

Keywords: ISS, Tanpopo mission, mutatuion

超好塩性アーキアが生産する脂質コア中の不飽和アーキオール誘導体の構造決定の試みと C_{20} - C_{25} ジエーテルの構造決定

Attempt to the structure determination of unsaturated archaeol derivatives characteristic for the halophilic archaea lipid-core produced at very high salt concentration

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アーキアは全て特徴的な脂質コアであるアーキオール (C_{20} イソプレノイドジエーテル) を持っている。さらに好塩性アーキアは5炭素長い C_{25} イソプレノイドを一つ持つ C_{25} - C_{20} ジエーテル(1)を生産する。これは C_{25} イソプレノイドがグリセロールの二級水酸基側 (C-2) に結合していることがすでに報告されている[1][2]。

アーキオールのイソプレノイドが二重結合を幾つか持つような誘導体の存在が、好熱性[3]および好冷性アーキア[4]で報告がされていた。近年Dawsonらは幾つかの超好塩性アーキアでは、アーキオールと C_{25} - C_{20} ジエーテルおよびその不飽和体 (例えば構造2が推定されている) が生産され、高塩分培養条件下で不飽和化合物の割合が増加することを報告した[5]。一方この文献では C_{25} - C_{20} ジエーテルでは構造3 (C_{25} イソプレノイドがグリセロールの一級水酸基側 (C-3)) が示されていた。なおこの構造3は彼ら以外の幾つかの文献でも散見される。私はこれまでアーキアおよびバクテリアにおけるジエーテル脂質の構造解析法の検討の過程で、不均等なジエーテルを持つ脂質コアの合成法を開発した[6]。そこで比較的容易に合成可能な1と2を合成し、構造解析から1の構造を確認するとともに、不飽和ジエーテルの構造推定を行うこととした。

現在1と2について合成を完了し、1についてはDawsonの報告している C_{25} - C_{20} ジエーテルとTMS化体のマススペクトルが完全に一致することを確認した。ここでこれまで培養微生物由来試料で得られた C_{25} - C_{20} ジエーテルはすべて1に相当する異性体であることを検証できた。また合成品2のTMS化体とDawsonの報告している化合物のマススペクトルを比較することで、不飽和ジエーテルの正確な構造が推定できるものと考えており、報告を予定している。

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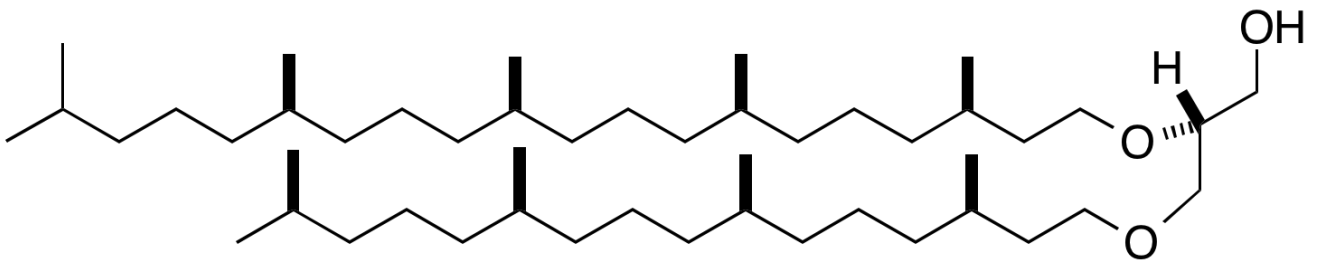
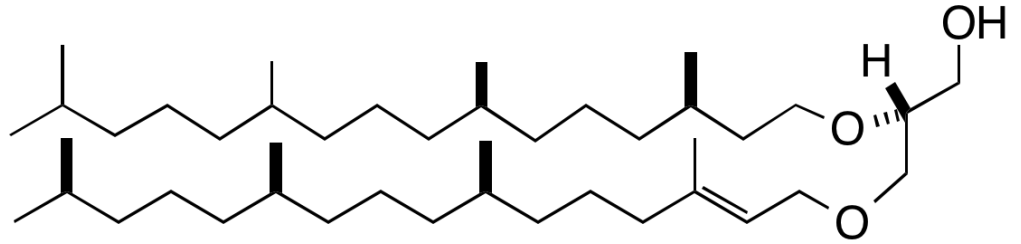
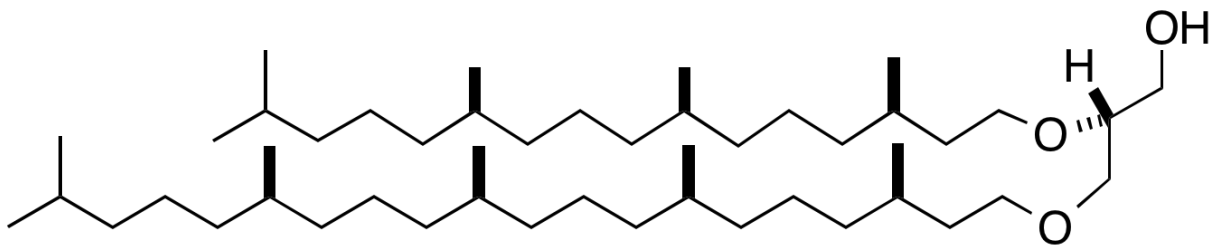
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キーワード：好塩性アーキア、脂質コア、構造決定

Keywords: halophilic archaea, lipid-core, structure determination

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