Japan Geoscience Union Meeting 2014
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宇宙ダスト上のアミノ酸生成過程についての理論的研究
Theoretical investigation of amino acid formations on interstellar dusts

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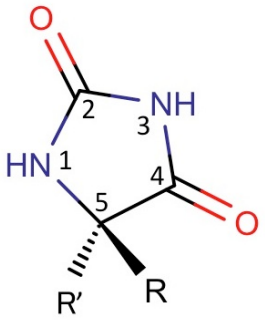
Molecular evolution in the interstellar space remains unsolved. Formations of molecules in space have been extensively studied by experiments and space observations. Formations of complex organic molecules are expected in the interstellar space. In fact, some amino acids were found in meteorites and amino acids were detected after UV irradiation of interstellar ice analogs.

In the amino acid formation in space, many precursors and molecular evolution pathways are expected. Among these possible pathways, it is very important to know the energy profiles and molecular structures in the major formation pathways. In this study, possible amino acid formation pathways are investigated by using accurate quantum chemistry methods at the density functional theory levels.

Two formation pathways of glycine and alanine were examined: (1) hydrolysis of aminoacetonitrile and (2) hydrolysis of hydantoin derivatives. In the aqueous solution model, Polarizable Continuum Model was used.

Calculated formation energy of glycine is the most stable in the formation pathway in vacuum and no excessively stable intermediates existed. In aqueous solution, hydantoin pathway was slightly unstabilized. In conclusion, glycine production is considered to be occured easily if the components exist. Similar trend is expected for the alanine production.



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ISS/JEM 曝露部利用実験たんぽぽ：宇宙塵捕集計画と地上実験
Cosmic dusts capture on the International Space Station: Progress of the ground-based experiment

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Introduction: Organic matter in interplanetary dust particles (IDPs) records the primitive chemical history in the early Solar System as well as it is thought to have delivered the building blocks of life to the early Earth (Chyba and Sagan, 1992). The Japanese Astrobiology working group, Tanpopo, is planning to collect the IDPs using a low-density silica aerogel (0.01 g/cm^3) (Tabata et al. 2011) on the International Space Station (Yamagishi et al. 2009). The mission has a great advantage that collection of the pristine IDPs without atmospheric entry heating and terrestrial contamination will be expected. One thing that has to be considered is a possible modification of the chemical composition of organic matter in IDPs upon their high velocity impact to the aerogel. This issue has been also concerned in the Stardust cometary dust sample return mission. Although the laboratory simulations have been conducted to study the alteration of minerals (Okudaira et al. 2004; Noguchi et al. 2007), the alteration of organics under a realistic condition has not been well understood. As a ground-based experiment, we have conducted a laboratory experiment of aerogel capture of Murchison meteorite powder at 4 km/s using a two-stage light gas gun, in order to evaluate the extent of modification of organic matter in the meteorite.

Experimental: The Murchison meteorite powder (˜500 ug) of a particle diameter of 30-100 um in a polycarbonate sabot was shot at ˜4 km/s using a two-stage light gas gun at JAXA/ISAS. The penetrations of the meteorite powder formed ˜70 tracks of ˜10 mm length in aerogel. Six terminal particles were extracted from the aerogel tracks using a tungsten needle and were pressed between two Al foils. The particles on the Al foils were analyzed by micro-Fourier transmission infrared (FTIR) spectroscopy at the beamline 43IR, Spring-8 and Osaka Univ., and micro-Raman spectroscopy at Osaka Univ. For a comparison, pre-shot Murchison meteorite powder was analyzed by these micro-spectrometers.

Results and discussion: The IR imaging detected the regions of absorptions of aliphatic carbons, CH3 at 2960cm^{-1} and CH2 at 2920cm^{-1} within the two Murchison terminal particles captured by aerogel. Thus, organic matter is survived through the high velocity impact at 4 km/s. The spectral intensities of aliphatic carbons in the terminal particles are slightly lower than those in the pre-shot Murchison meteorite. CH2/CH3 ratios obtained from the IR spectra of the terminal particles were 0.3 ? 3, while those of the pre-shot sample were 1.3 ? 2. The difference in the ratios may be reflected by modification of aliphatic chains of organic macromolecules in the meteorite, e.g., demethylation, methylation, or cracking, due to the high velocity impact heating. From the two terminal particles, D- and G- bands, which are derived from carbonaceous matter, were detected by micro-Raman analyses. Peak widths and positions of the two bands showed similar values to those for pre-shot Murchison meteorite. Thus, modification of aromatic structures after the aerogel capture is unlikely. Although relative amounts of organics were low in the four other terminal particles, this may be reflected by original heterogeneity of the meteorite.

キーワード: ISS/JEM 曝露部, 宇宙塵, 有機物, アストロバイオロジー, 生命の起源, エアロゲル
Keywords: International Space Station, Cosmic dusts, Organic matter, Astrobiology, Origin of life, Aerogel

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軽ガス銃を用いた小惑星衝突模擬実験によるアミノ酸合成の可能性
Possibility of production of amino acids by impact reaction using a light-gas gun as a simulation of asteroid impacts

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We are interested in the production process of amino acids in space. Especially, asteroids coming to Titan satellite have made impact reaction on the surface including nitrogen gas, water ice and methane. On the Titan surface, various material, produced by the impact reactions, have been stored under low temperature and dark condition. To do the simulation experiment, a JAXA 2-stage light-gas gun has been used. A projectile with 6.5km/s of speed hits a water + iron target in 1 atm of nitrogen gas, causing an impact reaction. Figure 1 shows a crater on the target. Figure 2 shows produced black soot which deposited onto the aluminum sheet. The samples produced are carefully collected and analyzed by HPLC, FTIR, TOF-MS. As a result of HPLC, peaks suggesting the existence of glycine and alanine in the samples produced were confirmed.
Keywords: impact reaction, gas gun, Titan, asteroid, amino acid, HPLC

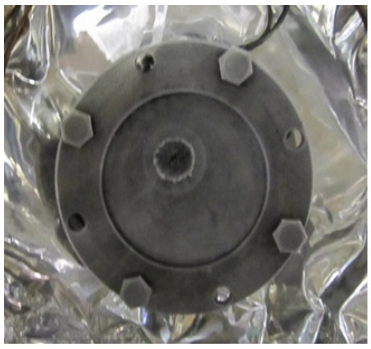

Fig.1 A crater on the target.

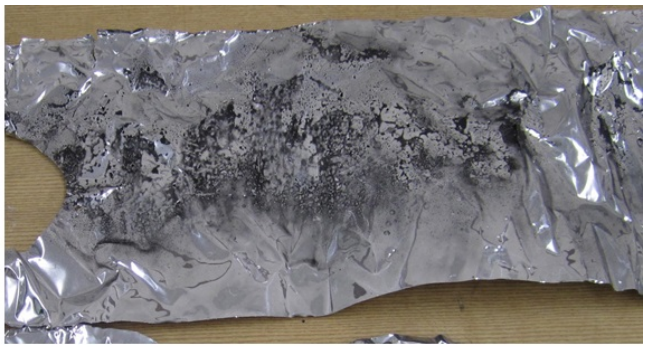

Fig.2 Produced black soot deposited onto the aluminum sheet.

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火花放電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 simulaed mildly-reducing primitive atmospheres by spark discharges and proton irradiation

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原始地球上での有機物の生成を考える上で，原始大気の組成，特にその酸化還元状態が重要である。Miller は，メタン，アンモニアを多く含む模擬原始大気中で火花放電を行い，アミノ酸の生成を確認した。しかし，今日では原始地球大気は，中性ないし弱還元型と考えられている。どの程度まで還元的であったならば，原始地球大気中でのアミノ酸生成が可能かを調べるため，種々の混合比の二酸化炭素，メタン，窒素，水蒸気の混合気体に火花放電，もしくは陽子線照射を行い，生成物中のアミノ酸の定量を行った。

火花放電の場合は，弱還元型（二酸化炭素：メタン=7:3) の場合でもアミノ酸生成が困難となったが，陽子線照射の場合はさらに還元性の弱い二酸化炭素：メタン=9.5:0.5 の場合でもアミノ酸が生成した。このことは，原始大気組成により，アミノ酸生成に必要なエネルギー源が異なることを示す。

キーワード: 弱還元型原始大気, 火花放電, 陽子線照射, 生命の起源, アミノ酸
Keywords: mildly-reducing primitive atmospheres, spark discharge, proton irradiation, origins of life, amino acids

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模擬海底熱水系におけるアミノ酸の安定性と反応
Stability and reactions of amino acids in simulated submarine hydrothermal systems

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1970 年代末の海底熱水噴出孔の発見は，生命起源研究に大きなインパクトを与えた。それまで，ミラーの実験などにより原始大気中での有機物生成の重要性が考えられていたが，惑星科学の進歩とともに，原始大気が強還元型でないと考えられるようになり，そのような環境下でのアミノ酸などの有機物の生成が限定的とみなされるようになったためである。海底熱水噴出孔では非還元的な地球を考えた場合でも局所的な強還元的な場を保持していると考えられ，有機物の生成・進化に有利と考えられた。さらに，マグマの熱による海水の加熱とそれが冷海水中に噴出することによる急冷，熱水中に溶け出した高濃度の金属イオンやシリカの触媒作用なども化学進化に有利に働くことが期待できる。

海底熱水噴出孔での有機物進化の研究のため，室内模擬実験が多数行われてきた。初期の実験では，閉鎖系のオートクレーブが用い，種々の試料をガスで加圧後に加熱し，その生成物を調べることが多かった。しかし，オートクレーブでは，海底熱水噴出孔の大きな特色である，加熱された海水の急冷（quenching）の効果を検証することができない。そこで，海底熱水系のよりよい模擬のため，種々のフローリアクターが考案された。

本研究では，海底熱水噴出孔での化学進化，特にアミノ酸の重合に関して，オートクレーブおよびフローリアクターを用い，それらの特性の比較とそれらの中でのアミノ酸重合物の生成の可能性の検証を行った。

キーワード: 海底熱水系, アミノ酸, 生命の起源, フローリアクター
Keywords: submarine hydrothermal systems, amino acids, origins of life, flow reactor

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メイラード・タイプ反応で生じる微小球状有機物の形態観察
Scanning electron microscopic observation of organic microspherules formed by Maillard-type reaction

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It has been suggested that organic microspherules played a role as a physical container to maintain catalytic molecules and their reaction intermediates at concentrations high enough to sustain catalysis in prebiotic chemistry on the early Earth (Weber, 2005). Experimental studies on the formation of organic microspherules from a variety of organic compounds, such as amino acids (Fox and Harada, 1958), gelatin and gum arabic (Oparin, 1976), organic extracts from meteorite (Deamer, 1985; Deamer and Pashley, 1989), interstellar organic analogue (Dworkin et al. 2001), fatty acids and polycyclic aromatic hydrocarbons (Groen et al. 2012), formaldehyde and ammonia (Cody et al. 2009; Kebukawa et al. 2013) have been reported. However, the formation process and stability of these organic microspherules have been unexplored. In this study, sizes, shapes, and distributions of organic microspherules formed during the progress of Maillard-type reaction of formaldehyde and ammonia were investigated.

Experimental:
Paraformaldehyde (120mg), glycolaldehyde (120mg), ammonium hydroxide (54ul), calcium hydroxide (30mg) in 2ml of water in a glass tube was heated at 50-90 degrees C for 71-720 hours. For comparison, the samples without ammonium hydroxide were heated under the same conditions. After heating, the sample solutions were centrifuged. The precipitated material were rinsed with 2N HCl to dissolve calcium, and dried at 50 degrees C to obtain organic solids. The organic solid samples were pressed on a indium plate, gold-coated, and observed by a scanning electron microscopy (SEM).

Results and discussion:
After several minutes in heating, all the sample solutions turned yellow and eventually turned brown to black. Organic solids were produced at 90 degrees C but 50 degrees C. The yields of organic solids from sample solutions with ammonia were 10 times higher than those without ammonia. The yields gradually increased during heating. While distorted-shaped aggregates are produced from the samples heated for 71-120 hours, micron-sized organic microspherules (0.4-4.0 um) were observed from those heated for 240-720 hours. The samples with ammonia show perfectly round shapes of microspherules. Some microspherules are large and oval in the sample heated for 480 hours. The sizes of the microspherules increased with heating time. Organic solids produced by the same reaction as this study's at 90 degrees C for 72 hours consist of approximately equal abundances of aromatic and aliphatic carbons (Kebukawa et al. 2013). This molecular composition could result in amphiphilicity that is related to formation of the stable microspherules observed in this study. Formaldehyde and ammonia are thought to have been commonly present on the early Earth, and thus the organic microspherules formed by these molecules which proceed polymerization efficiently under mild conditions, could have played a role as a precursor of prebiotic cell membrane.

Keywords: organic microspherules, Maillard reaction, prebiotic cell membrane

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DNA 蛍光色素を用いたエアロゲルに衝突した微生物の検出
Fluorescence imaging of microbe-containing micro-particles that had been shot from a two-stage light-gas gun into an ult

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KAWAGUCHI, Yuko[1*] ; SUGINO, Tomohiro[2] ; TABATA, Makoto[1] ; OKUDAIRA, Kyoko[3] ; IMAI, Eiichi[4] ; YANO, Hajime[1] ; HASEGAWA, Sunao[1] ; YABUTA, Hikaru[5] ; KOBAYASHI, Kensei[6] ; KAWAI, Hideyuki[7] ; MITA, Hajime[8] ; HASHIMOTO, Hirofumi[1] ; YOKOBORI, Shin-ichi[2] ; YAMAGISHI, Akihiko[2]

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We previously proposed an experiment (the Tanpopo mission) to capture microbes and organic compounds on the Japan Experimental Module of the International Space Station. An ultra low-density silica aerogel will be exposed to space for one year. After retrieving the aerogel, particle tracks and particles found in it will be visualized by fluorescence microscopy after staining it with a DNA-specific fluorescence dye. In preparation for this study, we simulated particle trapping in the aerogel so that methods could be developed to visualize the particles and their tracks. During the Tanpopo mission, particles that have an orbital velocity of about 8 km/s are expected to collide with the aerogel. To simulate these collisions, we shot *Deinococcus radiodurans*-containing Lucentite particles into an aerogel from a two-stage light-gas gun (acceleration 4.2 km/s). The shapes of the captured particles and their tracks and entrance holes were recorded with a microscope/camera system for further analysis. The size distribution of the captured particles was smaller than the original distribution, suggesting that the particles had fragmented. We were able to distinguish between microbial DNA and inorganic compounds after staining the aerogel with the DNA-specific fluorescence dye SYBR green I as the fluorescence of the stained DNA and the autofluorescence of the inorganic particles decay at different rates. The developed methods are suitable to determine if microbes exist at the International Space Station altitude.
Keywords: Aerogel, Space experiment, Hypervelocity impact experiment, DNA-specific fluorescence dye.

Keywords: Aerogel, Space experiment, Hypervelocity impact experiment, DNA-specific fluorescence dye

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酵素活性を利用した極限環境生命探査法の検討ーホスファターゼとカタラーゼー
Studies on life detection methods by using enzymatic activities: Phosphatase and Catalase

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南極，砂漠，火星などの極限環境における生命探査法として，ホスファターゼ活性やカタラーゼ活性を用いた酵素活性測定法を検討した。

キーワード: 極限環境, 火星, 生命探査, 酵素活性, ホスファターゼ, カタラーゼ
Keywords: extreme environments, Mars, life detection, enzymatic activities, phosphatase, catalase

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BAO01-P09 会場:3 階ポスター会場 時間:4 月 28 日 18:15-19:30

Molecular approach to the characterisation of Sri Lanka red rain cells
Molecular approach to the characterisation of Sri Lanka red rain cells

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The recent mysterious phenomenon that has attracted much attention is that of the red rain which fell in Polonnaruwa, Sri Lanka, on 13 November 2012. The microbial content in red rain shows generic similarities to that of the Indian red rain which fell in 2001. The morphological property of those microbes has been well documented [1,2]. Various microscopic analyses of our Sri Lankan red rain sample indicate that the defining red rain cells (RRC) exist in the presence of other microorganisms including diatoms. In our past paper, the ultrastructure of RRC shows that it is possibly a spore-form and so allowing them to thrive in the extreme upper biosphere conditions [3]. We also show the presence of uranium in the abnormally thick cell wall of RRCs.

In this report, we present the molecular approach to the characterisation of microbial communities in red rain and reveal the genus of RRCs. A beads-beating protocol is carried out for the efficient extraction of DNA and denaturing gradient gel electrophoresis (DGGE) for the analysis of microbial communities.

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キーワード: 赤い雨, 極限環境微生物, ポロンナルワ
Keywords: Red rain, Extremophile, Polonnaruwa

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縞状鉄鉱床の形成で最古の有機炭素を生成した機構
The mechanism that had formed the oldest organic carbon with the banded ironstone formations

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M. T. Rosing は約 38 億年前の縞状鉄鉱床が形成された時期に生成された西グリーンランドの堆積岩の中に最古の有機炭素を検出したと報告した [1]。その報告によれば、その堆積岩に含まれた 2~5 μ のグラファイトの微粒子の炭素同位体比 ($^{12}C/^{13}C$) の値が無機炭素のそれより大きい。ところが、連鎖反応を行う分子のシステムにより実現している光合成によって最古の有機炭素が生成されたとすることはできない。本報告において、著者は縞状鉄鉱床の形成によって生成された浮遊物に ^{12}C が少し多く取り込まれた仕組みを提案する。

炭酸水に鉄の微粉末を加えると、写真 1 に示すような現象が観察できる。水底の鉄の微粒子の表面に気泡ができて、その気泡が鉄の微粒子を水底から水面に浮上させる。炭素の電気陰性度は水素より大きいので、鉄の酸化によって、炭酸水の CO_2 から酸素が取り除かれる。自由になった炭素原子は電気陰性度のために鉄と分子間力で結びつき、浮遊物ができる [2]。浮遊物の鉄の原子は酸素と結合して酸化鉄となり、自由になった炭素原子が浮遊物の分子間結合を増強し、外界のエネルギーを得て有機物質が生成される。

約 38 億年前の地球の表面は酸化物や硫化物や炭酸塩などで覆われており、大気には多くの二酸化炭素ガスがあったが、海ができ、その海水温度もある程度の温度以下になり、大気中の二酸化炭素が海水に溶けるようになっていた。そのような状況において火山の噴火が頻繁に発生して多量の鉄の微粒子が放出されて、縞状鉄鉱床が形成された。他方、大気中の二酸化炭素の分子が頻繁に水面に衝突した。それが、分子間結合で構成された浮遊物に含まれた。浮遊物は水面で累積される。そこに、紫外線等によるエネルギーが外部から供給されて、浮遊物の中で有機分子の組織も形成された。やがて、それらが海底に沈殿して堆積した。こうして、大気の二酸化炭素に由来す ^{12}C 炭素同位体が西グリーンランドの堆積岩に取り込まれた。

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[**写真 1**] 炭酸水に鉄の微粉末を加えると気泡が発生し浮遊物ができて集積される様子 (左:作りおいた古いメッシュ#300 の鉄の微粉末、中央:作って新しいメッシュ#300 の鉄の微粉末、右:やや粒が大きいメシュ#200 の鉄の粉末)

キーワード: 38 億年前, 縞状鉄鉱床, 有機炭素, 二酸化炭素, 炭素同位体比
Keywords: 3.8 billion years ago, Banded iron formation, Organic carbon, Carbon dioxide, Carbon isotope ratio