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星間複雑有機物の太陽系環境下での変成と生命の起源
Alteration of interstellar complex organics in Solar system environments and its relevance to origins of life

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炭素質コンドライトや彗星中にアミノ酸（前駆体）を含む多様な有機物が検出され、それらと地球上での生命の誕生との関連が注目されている。分子雲環境を模した重粒子線照射実験により、模擬星間物質から高分子態アミノ酸前駆態が生成することが地上実験で確認されている。このような有機物が、太陽系形成後、太陽系環境下（隕石母天体や惑星間）で変成を受け、隕石・彗星有機物として地球にもたらされたというシナリオが考えられる。また、原始地球上に有機物を届けた媒体としては、微小な宇宙塵（惑星間塵）が重要であったことが示唆されている。惑星間塵中の有機物は、太陽紫外線等に曝露されることなどによりさらに変成を受けると考えられる。しかし、これまで惑星間塵は地球生物圏内で捕集された例はあるものの、その有機物に関する知見は少ない。われわれは、太陽系星間環境中での有機物の変成と、その有機物のキャラクタリゼーションのため、加速器等を用いた模擬実験を行った。また、宇宙環境下での惑星間塵等の採集と、有機物の宇宙環境下での変成を調べるため、宇宙ステーション曝露部を用いた実験（たんぽぽ計画）を計画中であるので、紹介する。

（１）地上実験：　たんぽぽ計画の準備も兼ねて、加速器をもちいた有機物の宇宙放射線や宇宙電磁波による変成を調べる実験を行っている。宇宙線の影響を調べるため、放射線医学総合研究所の重粒子加速器 HIMAC からの重粒子線（290 MeV/u の炭素線など）を照射する実験を行っている。さらに、宇宙環境で得られる広い波長範囲（X 線から赤外線まで）の白色光をアミノ酸関連分子に照射する実験を、兵庫県立大学の放射光施設ニュースバルで行うべく、準備中である。宇宙実験、および現在および過去の太陽系環境を考慮した地上実験により星間で生成した有機物から塵などにより供給された有機物への進化の過程と生命の誕生との関連を考察していく予定である。

（２）宇宙実験（たんぽぽ計画）：　たんぽぽ計画は、国際宇宙ステーションの日本実験モジュール (JEM) の曝露部を用い、高速で飛来する宇宙塵を極低密度のエアロゲルを用いて捕集し、微生物および有機物の分析を行うこと、微生物や有機物を宇宙環境に曝露すること、などを行う計画で、2012 年からの実施予定で準備が進んでいる。有機物に関しては、宇宙塵を捕集したエアロゲルから、宇宙塵を含むブロックを切り出し、加水分解後にアミノ酸を分析すること、および顕微分光法（STXM-XANES など）により塵中の有機物のキャラクタリゼーションを行う予定である。曝露資料としては、アミノ酸（イソバリンなど）や、その前駆態（ヒダントインなど）が候補に上がっている。

キーワード: アミノ酸前駆体, 星間複雑有機物, 生命の起源, 惑星間塵, たんぽぽ計画, 加速器実験
Keywords: amino acid precursors, interstellar complex organics, origins of life, interplanetary dust particles, Tanpopo mission, accelerator experiments

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高温高圧環境におけるバリンペプチド生成
Valine peptide formation under high temperature and high pressure conditions

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Peptide formation on the early Earth is an essential process for the origin of life. Heating experiments of compressed solid valine, one of the simplest amino acid having an alkyl side chain, were performed under various temperature (150-200^{o}C) and pressure (50-150 MPa) conditions up to 384 hours, in order to investigate how temperature and pressure affect the stability of valine and reaction rates of the peptide formation from valine monomers. The samples were enclosed in a gold tube and pressurized with a test-tube type autoclave using water as pressure medium. Produced peptides were analyzed by liquid chromatography-mass spectrometry (LC/MS). The recovered valine and decomposition products having amino groups were analyzed with a high performance liquid chromatography (HPLC) after the derivatization with a florescent reagent.

The run products contained linear peptides from dimmer to hexamer, cyclic dimmer, other amino acids, ammonia, and amines. The decomposition rates of starting valine at three different temperatures showed that the decomposition of the starting valine was very sensitive to the temperature change. Increasing temperature also accelerate the rates of both formation and decomposition of the linear peptides. On the other hand, the decomposition rates of valine and its peptides decreased with increasing pressure. The effect of pressure on production rates of valine peptides were very small, compared to that of temperature. Because the major decomposition products were ammonia and carbon dioxide, which were vapor or supercritical phase at the experimental conditions, pressure could suppress the degradation of valine and peptides by inhibiting their degassing reactions. The results of our experiments support a hypothesis that peptides were formed through diagenesis and suggest that pressure expand the stability of valine and the peptides under high temperature conditions. The present study also suggests that the typical diagenetic condition (up to 100^{o}C) is suitable for the high yield peptide formation in geological time scale. Polymerization of other amino acids, such as glycine and alanine, were also confirmed at different series of anhydrous experiments, suggesting a general importance of pressurized deep sediments for prebiotic peptide formations.

キーワード: アミノ酸, 重合, タンパク質, 生命の起源, 初期地球, 圧力
Keywords: amino acid, polymerization, protein, origin of life, early Earth, pressure

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Experimental and geological link for prebiotic peptide and ribose formation
Experimental and geological link for prebiotic peptide and ribose formation

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Controversy exists as to which geological environments were suitable for prebiotic organic formation. In this presentation, potential geological environments to form peptide and ribose will be discussed. Heat energy is necessary to promote polymerization of amino acids and then to form peptides. However, once-formed peptides easy break if heat energy suppresses and amounts of water exceed the peptide-equilibrated amounts. During diagenesis of deep marine sediments, where dehydration proceeds under high P and T conditions, may provide ideal environments for the peptide formation.

High pressure (150MPa) and temperature (up to 180C) experiments were performed in order to examine if daigenetic conditions are ideal for peptide formations. A mixture of glycine and alanine or a mixture of methionine and glycine was used as a starting material. Amounts of ammonia in reaction system increased with time, suggesting broke down of amino acids. On the other hand, amounts of glycylalanine, glycylglycylalanine glycylmethionine and methiolmethionine were high and exceed the amounts of glycine-5mers and alanine-4mers. The resuslts of the present study suggest that peptides composed of different amino acids has easily formed with high yields under high P and T conditions accompanied with high ammonia concentrations. Presence of ammonium-mica in Isua Supracrustal Belt in Greenland may suggest ammonia-rich diagenesis in ancient marine sediments, supporting the present experimental results.

For prebiotic ribose formation, stepwise reactions between borates and formaldehyde are suggested. Such interaction happens only under high borate concentrations. Borate-rich environments are often considered as unrealistic on the early Earth. However, tourmaline-rich garnets in sediment-protolith were found in Isua Supracrustal Belt. This finding suggests that borate-rich conditions were present during diagenesis of ancient marine sediments, and promises ribose formation during diagenesis.

キーワード: pre biotic, peptide, ribose, Isua
Keywords: prebiotic, peptide, ribose, Isua

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ナノバクテリア化石状ナノ組織の形成環境について
On the formation environment of the nano-bacteria fossil-like texture

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生命活動に関与する化石物質の特徴と生成環境は下記のようにまとめられる。
１）固体化した化石物質の形状は、液相からの固化時に曲線表面組織を示す。
２）固体化した化石物質の組成は、海水液相環境で陽イオン（Ca, Fe, Mg）が炭素を含む鉱物相である。地殻岩石層が関与して形成されると Si が含まれて複雑に変化する。
３）人工実験で液相のない宇宙真空環境での衝突試料では、主に不規則な破壊亀裂組織が生成されるが、液相が生成する大気環境での衝突試料は、曲面状組織に不規則な亀裂組織が形成されるのが特徴的である。
４）玖珂隕鉄中の溶融層のナノバクテリア状組織の組成が微細アカガネアイト組成である。
５）火星隕石のナノバクテリア組織は磁鉄鉱組成で炭酸塩相が共生しており、これはナノバクテリア状組織の真空衝突形成ではなく、共生する炭酸塩相が水分を含む大気環境下で陽イオン変化　(Ca, Mg, Fe) して形成されたことを示す。

キーワード: ナノ組織, 化石状, 生成環境, 液相, 炭酸塩, 不規則亀裂
Keywords: nano-texture, fossil-like, formation environment, fluid phase, carbonate, irregular cracking

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Life detection in Archean rocks: are stable isotopes reliable?
Life detection in Archean rocks: are stable isotopes reliable?

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Among signatures of ancient biological activity, stable isotopes of C, S, Fe and N hold an important place. Indeed, metabolic processes tend to produce different, and sometimes diagnostic, enrichment or depletion in certain isotopes. Large environmental and biological changes at the surface of the Earth, as those provoked or provoking the oxygenation of the primitive atmosphere are clearly imprinted in the C, S, N and Fe geological record. Yet, the reliability of stable isotopes as biological and environmental proxies has been recently questioned. Short-chain hydrocarbons synthesized via Fischer?Tropsch-type reactions in hydrothermal environments are depleted in 13C in a way typically ascribed to metabolic processes such as photosynthesis and methanogenesis (small delta13CPDB = [(13C/12C)sample/(13C/12C)std -1 x 1000] =-30 to -60 permil). This suggests that carbon isotopic composition might not be an effective discriminant between biologic and non-biologic sources. Sulfur isotopes, and particularly the 33S/34S ratios show variations in the geological record usually interpreted as reflecting changes in the redox state of the atmosphere and in the biologically related sulfur cycle. Yet, thermochemical reactions might produce similar isotopic fractionations. Nitrogen has been longtime ignored as biosignature because being extremely fragile compared to the more stable graphitic forms of C. Indeed, it can be easily fractionated by metamorphic or hydrothermal-driven reactions. However, N has an advantage over other isotopic systems such as those of C and S. The dominant source of N at the surface of the Earth, that is, the atmospheric triple-bonded N2, is so stable that only a very limited number of metabolic processes can bridge the abiotic and biotic world. Finally Fe (small delta56Fe = (56Fe /54Fe)sample/(56Fe /54Fe)std -1 x 1000) has very little isotopic fractionation (+-1permil) and numerous studies shown that the biological-induced fractionation is not completely understood or yet measured. Here we present new data on N isotopes and their behavior in cherts and banded iron formations of South Africa (3.45 Ga Hooggenoeg Fm., Barberton Greenstone Belt) and India (2.9-2.7 Ga Bababudan Group, Dharwar Craton). Combination of two or more isotope markers (N, C and Fe) with largely different geochemical natures may help us to discriminate between possible fractionation pathways, biotic or abiotic, and/or rule out part of the anticipated post-depositional fractionation events. This is the case of the India Banded Iron Formations, where N isotopes have been coupled with Fe and C isotopes. Observed Fe, C and N isotopic co-variations in cherty and iron-rich layers have been related to the appearance of denitrification and dissimilatory iron reduction in the water column at the onset of the Great Oxygenation Event. Organic nitrogen was trapped as ammonium (NH4+) in hydromuscovite and feldspars preserved in cherty formations of the Hooggenoeg Fm. at the Komati River, South Africa. Here nitrogen isotopes have been coupled with argon isotopes (40Ar/36Ar). Indeed, an indirect relation relates NH4+ which replace K+ ions in the structure of K-bearing silicates and radiogenic 40Ar*, which is produced by electron capture of K+. These formations show small delta15N values of +7.1+-0.5 to +12.6+-0.4permil, higher than those usually found in Early Archean ammonium (-5 to +2permil). K-Ar dating of mica and feldspars give younger Proterozoic ages of 2137+- 15 Ma and 1191+- 27 Ma, respectively. This suggests that the mineral phase preserving ammonium is not a closed system and post-depositional metamorphic events likely reset the K-Ar clock. The same phenomenon possibly caused 1) partial devolatilization of the pristine organic N with preferential loss of 14N and increase of the small delta15N values; or 2) isotopic exchange with metasomatic fluids which usually contain 15N-enriched nitrogen.

キーワード: life, Archean, stable isotope
Keywords: life, Archean, stable isotope

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Geochemical constraints on the partial pressure of carbon dioxide in the Archaean atmosphere from Banded Iron Formations

Geochemical constraints on the partial pressure of carbon dioxide in the Archaean atmosphere from Banded Iron Formations

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There is geological evidence from the widespread preservation of waterlain sediments that Earth's climate resembled the present during the Archean, despite a much lower solar luminosity. This was cast as a paradox by Sagan and Mullen in 1972. Kasting (1993) suggested a solution to the paradox by increased mixing ratios of greenhouse gasses, notably CO2 in the early atmosphere. However geochemical evidence for high partial pressures of CO2 are absent in marine sediments as well as in paleosols. We have used banded iron formation (BIF) to characterize the composition of the atmosphere. BIFs originated as chemical sediments precipitated from the Archaean ocean and sedimented as particles to the seafloor. Magnetite is ubiquitous in Archaean BIFs which indicates that it was thermodynamically stable during exposure of the primary sediment to ocean water and during subsequent diagenesis and compaction of the sediment. The involvement of biologic processes in the original precipitation of iron-rich minerals and/or sediment diagenesis does not alter the constraint of magnetite saturation. The stability relations of magnetite preclude CO2 mixing ratios much higher than the present atmospheric level (~3-5 times PAL). At higher partial pressures of CO2 siderite would replace magnetite as the stable iron bearing phase. The CO2 pressure of the atmosphere is expressed in the CO2 concentration of seawater through the water column and well into the sediment because CO2 is highly soluble in water. In the absence of substantial compensation for the lower solar irradiance by greenhouse gasses in the atmosphere, we have examined the factors that controlled Earth's albedo. These are primarily the surface albedo of Earth and the abundance and properties of clouds. We have applied a model that takes into account the apparent growth of Earth continents (Collerson and Kamber 1999) and the absence of land vegetation during the Precambrian for the evolution of the surface albedo, and a model for the abundance and properties of clouds that takes into account the lower abundance of biogenic cloud condensation nuclei in a less productive prokaryotic world. The higher transparency of the atmosphere for short wave incoming solar radiation and the lower surface albedo on an early Earth dominated by oceans, provided significant compensation for the lower solar irradiance which allow the presence of liquid oceans, even at greenhouse gas concentrations broadly similar to the present day values.

We therefore suggest that the thermostasis during Earth geologic record, is not paradoxical, but is the combined effect of many factors, which are to a large part biologically controlled.

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キーワード: carbon dioxide, Archaean, Faint early sun, BIF
Keywords: carbon dioxide, Archaean, Faint early sun, BIF

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「たんぽぽ」計画における国際宇宙ステーション上での微生物曝露実験
Microbe space exposure experiments at International Space Station (ISS) in the mission ”Tanpopo”

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To explain how organisms on the Earth were originated at the quite early stage of the history of Earth, Panspermia hypothesis was proposed [1, 2]. Recent findings of the Martian meteorite suggested possible existence of extraterrestrial life, and interplanetary migration of life as well. On the other hand, microbes have been collected from high altitude using balloons, aircraft and meteorological rockets since 1936, though it is not clear how could those microbes be ejected up to such high altitude [3]. Indeed, we have also collected microorganisms at high altitude by using airplanes and balloons. Spore forming fungi and Bacilli, and Deinococci have been isolated in these experiments. We also collected two novel species of the genus *Deinococcus*, one from top of troposphere (*D. aerius*) and the other from bottom of stratosphere (*D. aetherius*) [4-6]. In addition, we collected various spore-forming bacilli and their related species. Spores and Deinococci are known by their extremely high resistance against UV, gamma ray, and other radiation [4]. *D. aerius* and *D. aetherius* showed high resistance comparable with *D. radiodurans* R1 to the UV and radiation such as gamma ray. If microbes could be found present even at the higher altitude of low earth orbit (400km), the fact would endorse the possible interplanetary migration of terrestrial life.

We proposed the ”Tanpopo” mission to examine possible interplanetary migration of microbes, and organic compounds on Japan Experimental Module (JEM) of the International Space Station (ISS) [7]. Tanpopo consists of six subthemes. Two of them are on the possible interplanetary migration of microbes ? capture experiment of microbes at the ISS orbit and space exposure experiment of microbes. In this paper, we focus on the space exposure experiment of microbes.

Microbes in space are assumed be exposed to the space environment with a kind of clay materials that might protect microbes from vacuum UV and cosmic rays, or exposed as the aggregates of which outer cells might protect inner cells from vacuum UV and cosmic rays. Dried vegetative cells of *D. radiodurans* and our novel deinococcal species isolated from high altitude are candidates for the exposure experiment. In addition, we are planning to perform another space exposure experiments of microbes. In this paper, we discuss current status of exposure experiment of microorganisms defined for the Tanpopo mission and others.

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細胞の重層により真空紫外線照射下での微生物の生存率が高まる
Prolonged survival of multilayer bacteria under UV radiation and vacuum

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In early 20th century, Arrhenius proposed the possible migration of life through space. The Hypothesis is called Panspermia Hypothesis (1908). In the hypothesis, the interplanetary transfer of single spores is propelled by radiation pressure. However, the solar UV has been proven to be lethal for unshielded microorganisms (Nicholson et al., 2000; Horneck et al., 2010), which invalidated his Hypothesis.

Another possible form of the interplanetary transfer of life, micro-aggregate or micro-clump, has just emerged from recent studies. Space environment exposure experiments evidenced that microorganisms in thick layers can survive larger UV doses than single cells. Some bacterial spores in multilayer-spore samples survived intense solar UV radiation, while all the spores in monolayer were killed (Horneck et al., 1994, 1995; Mancinelli and Klovstad, 2000). Terrestrial microorganisms may be transported into the upper atmosphere and space by human activities (e.g., spacecraft launch) and natural mechanisms (e.g., electric field, meteorite impact). Based on the microbiological studies in the upper atmosphere, we have roughly estimated the altitude-dependent distribution of microorganisms, suggesting the extended distribution of microorganisms into space (Yang et al., 2009). Bacterial cell clumps have been found in the upper atmosphere (about 40-km altitude) (Wainwright et al., 2003). The cells of the *Deinococcus* strains (ST0316 and TR0125) we isolated from the upper atmosphere (about 10-km altitude) multiply and grow in aggregated form (Yang et al., 2009).

However, there has no study to quantitatively examine the relationships between microbial survival, size of micro-aggregate and UV doses. It is unknown what size of micro-aggregate may protect some cells inside it from long-term space UV radiation. Our current study investigates quantitatively the survival of bacteria against extraterrestrial UV radiation in dependence of sizes of cell aggregates, assessing the possibility of viable transfer of microorganisms in aggregated form.

We have obtained preliminary data on the survival of *D. radiodurans* against UV_{172nm} radiation under vacuum in dependence of the cell aggregate thickness. At the same UV_{172nm} dose, larger cell aggregate exhibited higher survival rate. The preliminary results suggest that upper layers of cells protected cells underneath from the UV_{172nm} inactivation, and that 20 micrometer of thickness was enough for protecting a high percent of cells at lower layers alive under UV_{172nm} and vacuum conditions.

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火星表面におけるメタン酸化菌探査
Japan Astrobiology Mars Project (JAMP)

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生命には水が必須である。もう一つ生命の維持に重要な因子としてギブス自由エネルギーがある。動物は食物と酸素無しには生存できないが、それは両者が自由エネルギーの獲得に必要だからである。火星で生命が誕生して現在もまだ生存し続けているとするならば、現在まで自由エネルギーが入手可能な場所でなければならない。

生物による自由エネルギー獲得方法としては、呼吸（動物）、光合成（植物）、化学合成（化学合成微生物）の三つが知られている。火星におけるメタンの発見と、地球におけるメタン酸化鉄還元細菌の発見（Beal ら 2009）から、我々は火星表面において現在もまだメタン酸化鉄還元細菌（化学合成微生物の一種）が生存しうるのではないかと推定するに至った。

もし、火星に於いて生命が誕生し現在も生存しているとすれば、そこは生存にとって困難な条件をさける環境で無ければならない。火星の様々な環境の内で温度、気圧、重力等は地球の生命を考えた場合には十分に生存可能な環境である。放射線も生死に影響を与えるほどの強度は持っていない。唯一、紫外線が重要な致死要因となる。しかし、紫外線は様々な物質によって吸収されるので、薄い火星土壌に覆われるだけで、十分生育可能な環境となる。細胞内の液体の水は地球型生命にとって必須であるが、細胞外の液体の水は生存にとっては必須ではない。従って、メタンと酸化鉄のような酸化型物質の両者がある場所であれば、数センチメートル程度の深さでも微生物は生存している可能性があると推定している。

微生物探査の方法としては、蛍光色素をもちいた蛍光顕微鏡観察を自動的に行う。これまで多くの蛍光色素が開発されている。その中から、生命の定義に対応した色素を組み合わせて用いる。細胞の内外を区別する膜（境界）の存在を識別する色素、細胞の複製にひつような遺伝物質を識別する色素、細胞の代謝を司る酵素の存在を識別する色素を組み合わせて用いる。これらの色素の組み合わせから、「細胞」の特徴を抽出することができる。

さらに、その後「細胞」らしき粒子のアミノ酸分析を行う。地球の生物はすべて 20 種類の L 型アミノ酸からなるタンパク質を持っている。火星の「細胞」らしき粒子が地球と同じアミノ酸かどうかを調べる事により、「細胞」の由来を知ることができる。その他、現在検討中の探査方法について報告する。

キーワード: 火星, 生命探査, 微生物, メタン酸化菌, 蛍光顕微鏡
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