

初期太陽系形成過程におけるL型アミノ酸過剰生成機構の理論的研究 Theoretical Investigation of a Mechanism of Chirality Induction for Amino Acids in the Early Solar System

佐藤 皓允^{1*}, 庄司 光男¹, 神谷 克政¹, 梅村 雅之¹, 矢花 一浩¹, 白石 賢二¹

SATO, Akimasa^{1*}, Mitsuo Shoji¹, Katsumasa Kamiya¹, Masayuki Umemura¹, Kazuhiro Yabana¹, Kenji Shiraiishi¹

¹ 筑波大学

¹ University of Tsukuba

現在の地球上の生命は、生体高分子であるアミノ酸で形成されている。アミノ酸は鏡像異性体であり、L型とD型が存在する。化学合成ではL型とD型は等量生成されるが、生命のタンパク質合成ではL型アミノ酸のみが生成される。この不斉アミノ酸生成の原因は、未だ解明されておらず、分子進化や生命の起源に関わる謎の一つである。この原因を説明するシナリオとして、初期太陽系形成時、円偏光照射により宇宙空間中のラセミ化アミノ酸が特異的に破壊されることでL型アミノ酸過剰が引き起こされて、現在のL型世界を形成したとする説がある。

近年、上記のシナリオを裏付ける実験結果や観測事実が報告されている。基本的なアミノ酸であるアラニン、バリン、イソバリンやその他のアミノ酸前駆体が隕石中に発見され、それら高分子の存在比も同様にL型に偏っていることが判明した。また一方で、円偏光が広範囲に分布している領域がオリオン座の大質量星形成領域(OMC-1)で観測された。さらに実験室中で、アミノ酸に円偏光を照射することで一方のアミノ酸鏡像異性体により特異的に破壊されることも報告されている。加えて実験で、少量の鏡像異性体過剰が増大し、最終的に支配的になることも分かっている。これらの発見は、生命の起源が地球外由来であること、生命におけるこの偏りと、隕石中で観測された偏りの原因が同じであることを示唆している。この異性体過剰の起源を解明することは、初期太陽系形成時の様子と生命の起源を理解する上で必要不可欠である。しかしながらまた、解明されていない課題も多く残されている。星間空間におけるアミノ酸の化学合成機構や、円偏光照射によるL型アミノ酸過剰の生成機構などは未だ分かっていない。

これらの解明には、アミノ酸の光吸収性と光励起による崩壊・改変反応の過程を解析することが重要である。異性体の偏りは、鏡像異性体に対する特異的な光分解、すなわちラセミ化アミノ酸への円偏光照射による異性化反応が原因であると考えられる。このようなアミノ酸の崩壊過程や構造変化の機構を知るためには、励起状態と励起による解離反応過程を追跡することが必須である。特に異性化反応においては、反応に関わる原子である不斉炭素と主鎖-側鎖をつなげる炭素との結合解離反応について検討する事が最も重要であると考えられる。

本研究では特に、L型アミノ酸の光吸収性とその励起状態を解析した。「円偏光のアミノ酸への照射 電子励起 構造変化」の一連の過程を電子レベルで解明し、円偏光によるアミノ酸過剰の発生を理論的に解明する。そのため、アミノ酸鏡像異性体の円偏光照射下における光物性を、量子論に基づく第一原理計算法(密度汎関数法: DFT)により解析する。アミノ酸の基底状態と円偏光光励起によって生じる励起状態のポテンシャルエネルギー曲線を詳細に明らかにし、断熱過程及び非断熱過程におけるアミノ酸の光構造物性を解明する。得られるポテンシャルエネルギー曲線から、アミノ酸構造破壊につながるエネルギー励起とその円偏光依存性を明らかにする。特に、鏡像異性体を持っている最も基本的なアミノ酸であるアラニンやバリン、イソバリンは他のアミノ酸の異性化に対してもカギとなると考えられるため、これら3つのアミノ酸について解析を行う。

アミノ酸の光物性を調べるため、まず星間空間におけるアミノ酸の安定構造を決定した。さらにその構造における光吸収強度と円偏光二色性を計算し、星間空間においてアミノ酸がどのような光により励起されやすいかを検証した。その後、上述のアミノ酸におけるC-C結合の解離反応を仮定し、反応過程でのポテンシャルエネルギー曲面を計算した。得られたポテンシャルエネルギーから、アミノ酸の構造崩壊・改変を引き起こすような反応経路を定性的に推定した。

計算の結果、これらのアミノ酸では、励起エネルギーが8-12 eV(励起波長100-150nm)の領域に円偏光二色性のピークがあることが分かった。特に我々は、この領域内から計4本の結合解離反応経路を推定した。アラニンではエネルギー9.81 eVの励起が結合解離を引き起こしやすく、かつ光吸収強度・円偏光二色性共にピークを持つ。バリンでは10.00 eV, 10.91 eVの励起状態が同様の条件を持つ。またイソバリンでは9.32 eVの励起が結合解離反応を誘発している。これら4本の非断熱ポテンシャルカーブは、基底構造において光吸収強度・円偏光二色性共に高い値を持ち、エネルギー的に結合解離を引き起こしやすい。従って、このような反応経路に対する励起がアミノ酸異性体過剰を引き起こす原因となると考えられる。

これらの解析結果は、励起波長110-135nmの領域、従って真空紫外線波長領域の円偏光照射がアミノ酸の異性体過剰を誘発する事を示唆している。

キーワード: 鏡像異性体, アミノ酸, 偏光, 原始太陽系星雲

Keywords: enantiomer, amino acid, polarized light, proto-solar nebula

火星における CO₂, CH₄ ハイドレートの放射線分解による有機物生成の可能性 Possibility of organic matter formations in irradiated CO₂ and CH₄ hydrates on Mars

大島 基^{1*}, 谷 篤史¹, 北野勝久², 菅原武³, 大垣一成³

OSHIMA, Motoi^{1*}, TANI, Atsushi¹, Katsuhisa Kitano², Takeshi Sugahara³, Kazunari Ohgaki³

¹ 大阪大学大学院理学研究科, ² 大阪大学大学院工学研究科, ³ 大阪大学大学院基礎工学研究科

¹Science, Osaka Univ., ²Engineering, Osaka Univ., ³Engineering Science, Osaka Univ.

To look for evidence of life on Mars, explorations of organic matter is important. There are some possibilities of the formations of organic matter on Mars; for example, by biological activity and by radiolysis and photolysis of mixtures of icy materials. If organic matter exist on Mars, to identify the detected organics as the matter by biological activity, it is necessary to investigate reaction products and their amount by radiolysis and photolysis of the ice mixtures, and to distinguish organics by biological activity from ones by radiolysis and photolysis. As the icy materials on Mars, it is suggested that gas hydrates would exist on Mars, based on the discussion of temperature and pressure conditions. Gas hydrates are crystalline inclusion-compounds, which are composed of hydrogen bonded water molecules encaging gas molecules (e.g. CO₂, CH₄). Most of them are stable at high pressures and/or low temperatures. Average temperature of Martian surface is about 210 K, the Martian atmosphere consists of about 95% CO₂ and the average atmospheric pressure is about 0.56 kPa (Kieffer et al., 1993). From the observations of the Mars Express spacecraft, methane with 10-40 ppmv concentrations has been detected in the Martian atmosphere and on surface of the ground (Formisano et al., 2004; Mumma et al., 2009). In Martian conditions, it is suggested that CO₂ and CH₄ hydrates are formed in about 10 m below the ground and on the polar caps in winter (e.g. Max and Clifford 2001; Prieto-Ballesteros et al., 2006). Since water ice exists on Martian surface, the environment on the Martian surface should be enough to form CO₂ and CH₄ hydrates. In this case, Martian gas hydrates should be irradiated by natural radiation from radioisotopes in sediments as well as cosmic rays, which may cause radical formation in CO₂ and CH₄ hydrates.

Radiation-induced radicals in CH₄ and CO₂ hydrates have been investigated by electron spin resonance (ESR) measurements. Methyl radical is mainly formed by gamma-ray irradiation at 77 K in CH₄ hydrate (Takeya et al., 2004), and not stable above 180 K at 0.1 MPa (Tani et al., 2006). Carboxyl radical, hydrogen atom and hydroxyl radical are formed by gamma-ray irradiation at 77 K in CO₂ hydrate, hydrogen atom and the hydroxyl radical are not stable above 120 K at 0.1 MPa and the carboxyl radical quickly disappears at 180 K (Oshima et al., submitted). In thermal conditions on Mars, these radicals in the hydrates are unstable, and some products may form through the radical reactions. In this study, to investigate the organic products from radicals induced in CO₂ and CH₄ hydrates on Martian conditions, we analyzed the aqueous solution after dissociation of the hydrates irradiated at 195 K by ion chromatography and gas chromatography-mass spectrometry (GC-MS).

Formic acid and oxalic acid are observed in aqueous solution after dissociation of irradiated CO₂ hydrate. Methanol and formaldehyde are observed in irradiated CH₄ hydrate. If CO₂ and CH₄ hydrates exist on Mars, these organics will be formed in the hydrates and accumulated on the polar caps and below subsurface.

キーワード: ガスハイドレート, 有機物, ラジカル, イオンクロマトグラフ, ガスクロマトグラフ質量分析, 火星

Keywords: Gas hydrates, Organic matter, Radicals, Ion chromatography, Gas chromatography-mass spectrometry (GC-MS), Mars

たんぽぽ：たんぽぽ計画:有機物・微生物の宇宙曝露と宇宙塵・微生物の捕集 Tanpopo: Astrobiology exposure and micrometeoroid capture experiments

山岸 明彦¹, 横堀 伸一^{1*}, 橋本 博文², 今井 栄一³, 河合 秀幸⁴, 小林 憲正⁹, 三田 肇⁵, 中川 和道⁶, 奥平 恭子⁷, 田端 誠², 太刀川 純孝², 藪田 ひかる⁸, 山下 雅道², 矢野 創², たんぽぽ WG²
YAMAGISHI, Akihiko¹, YOKOBORI, Shin-ichi^{1*}, HASHIMOTO, Hirofumi², IMAI, Eiichi³, Hideyuki Kawai⁴, KOBAYASHI, Kensei⁹, MITA, Hajime⁵, NAKAGAWA, Kazumichi⁶, OKUDAIRA, Kyoko⁷, Makoto Tabata², Sumitaka Tachikawa², YABUTA, Hikaru⁸, Masamichi Yamashita², YANO, Hajime², Tanpopo WG²

¹ 東京薬大・生命科学, ²JAXA/ISAS, ³ 長岡技大・生物, ⁴ 千葉大・理, ⁵ 福岡工大・工, ⁶ 神戸大・院人間発達環境学, ⁷ 会津大, ⁸ 大阪大・院理, ⁹ 横浜国大・院工

¹Sch. Life Sci., Tokyo Univ. Pharm. Life Sci., ²JAXA/ISAS, ³Dept. Bioeng., Nagaoka Univ. Tech., ⁴Fac. Sci., Chiba Univ., ⁵Fac. Eng., Fukuoka Inst. Tech., ⁶Grad. Sch. Human Develop. Environ., Kobe Univ., ⁷Univ. Aizu, ⁸Grad. Sch. Sci., Osaka Univ., ⁹Grad. Sch. Eng., Yokohama Natl. Univ.

For the origin of life on Earth emerged within a short period after the end of heavy bombardment, Panspermia hypothesis was proposed (e.g. Arrhenius 1908; Crick 1981). Recent findings of the Martian meteorite suggested possible existence of extraterrestrial life, and interplanetary migration of life as well.

Microbes have been collected from high altitude using balloons, aircraft and meteorological rockets since 1936, even it is not clear how could those microbes be ejected up to such high altitude. Spore forming fungi, spore forming Bacilli, and Micrococci (probably Deinococci) have been isolated in these experiments. We have also isolated novel deinococcal species high altitude (Yang et al. 2010, 2011). These spores and Deinococci are known by their extremely high resistance against UV, gamma ray, and other radiation. If microbes could be found present even at the higher altitude of low earth orbit (400km), the fact would endorse the possibility of interplanetary migration of terrestrial life.

On the other hand, from the viewpoints of chemical evolution for study of origin of terrestrial life, where is the home of organic compounds which might have become precursors of materials such as protein and nucleic acids. Recent studies suggest that the some of such organic compounds were created in space. Then, they reached the surface of Earth via meteorites, cosmic dusts, and so on. One of problems to study such materials of extraterrestrial origin is contamination of materials of terrestrial origin. Avoiding contamination of terrestrial materials from the extraterrestrial materials is quite important issues for this kind of study. Capturing such extraterrestrial materials before falling down on the surface of Earth might be one of possible solutions.

TANPOPO, Japanese name of dandelion, is a plant species, whose seeds with floss are spread by wind. We propose this mission to examine possible interplanetary migration of microbes, and organic compounds on Japan Experimental Module (JEM) of the International Space Station (ISS) (Yamagishi et al. 2008). Ultra low-density aerogel will capture micrometeoroid and space debris. Particles captured by aerogel will be analyzed after the initial curation of the aerogel and tracks in it. Careful curation of the tracks in the aerogel will provide information on the size and velocity of meteorites captured. The particles will be characterized in terms of mineralogical, organic and microbiological properties. The aerogel with low density and layered structure is ready for production in Japan.

In addition to particle-capture on ISS, we also proposed direct exposure experiments of microorganisms and organic compounds with/without model-clay materials that might protect microorganisms and organic compounds from UV and cosmic ray. Spore of *Bacillus* sp., *Deionococcus radiodurans*, and novel Deionococcal species isolated from specimen collected from high altitude by us are candidate subjects for exposure. Amino acids and complex organic compounds that can be formed in space are planned to be exposed.

All the analytical techniques are ready to conduct the TANPOPO mission. Our proposal was accepted as a candidate experiments on Exposed Facility of ISS-JEM. In this paper, we discuss current status of exposure/capture experiments of microorganisms defined for the TANPOPO mission.

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生化学機能の進化から考える生命の起源

Origins of life from the point of view of evolution of biochemical functions

小林 憲正^{1*}

KOBAYASHI, Kensei^{1*}

¹ 横浜国立大学

¹Yokohama National University

生命の起源は、通常、タンパク質や核酸といった物質レベルでの化学進化の面からのみ考察されてきた。しかし、無生物的に生成する有機物は、一般に高分子態の複雑有機物となることが多い。このような「がらくた分子」が機能を持ち、その機能の進化の末に生命が誕生した可能性を、種々の模擬実験の成果をもとに検証する。

キーワード: 生命の起源, ホモキラリティ, 触媒活性, 有機凝集体, がらくたワールド, 複雑有機物

Keywords: origins of life, homochirality, catalytic activities, organic aggregates, Garakuta World, complex organic compounds

地球生命の起源と誕生した場所 Origin and birth place of life on the Earth

丸山 茂徳^{1*}
MARUYAMA, Shigenori^{1*}

¹ 東京工業大学
¹Tokyo Institute of Technology

Birth of life

In spite of those new trends, and against reluctant astronomers, I point out the idea against it. First of all, the life cannot be formed only by water and CO₂. Phosphorous is a key critical element to run metabolism in life as an example. The related major and trace elements are all derived from the rock, not from ocean and atmosphere. The water-rock interaction driven by steady-state supply of heat by magma at mid-oceanic ridge was the birth place of life on the Earth, and another survival place of life is the surface of the Earth where continent (source of nutrients) interacts with ocean-atmosphere, resultant constant supply of nutrients to the ocean. Engine to drive the system is Sun, whereas the deep-sea hydrothermal system is plate tectonic supply of MORB magma. Phosphorous is nearly absent at MOR and absent in underlying mantle which are critically important if we discuss the origin of life in the Hadean time.

To form life, we it is critical to supply phosphorous and related other nutrients continuously to the birth place through the water-rock interaction which has never been considered seriously. Moreover, the chemical composition of primordial ocean could be pH=1-2 and enriched heavy metals in oxidized material of water.

Primordial continent, anorthosite with KREEP on the Hadean Earth

To overcome such hard conditions to bear life, hydrogen-producing environment under peridotite-water hydrothermal system with P-bearing ore as well as nutrients could be only available on the deep-lake on primordial continents with KREEP basalts. The latter could be erupted basalts, gabbro (dike or sill) and lower mafic crust. If primary ocean was thin, the primordial continents (20km upper crust of anorthosite + 20-25km lower mafic crust) could be above sea-level, to transport nutrients into lakes which were clean to bear life by evaporation through ocean.

How to synthesize life on the Hadean Earth: A new model

First life was synthesized by the successive FT reactions from inorganic compounds under the excess amounts of P-bearing and other nutrients (ore body) in the deeply fractured lake with constant magma supply underneath. The birth place was under anoxic conditions (H₂) local in an oxidized material of water. The most difficult process is the process from RNA world to DNA world, which may have taken over several hundreds of million years.

After the birth of life in such a localized area, the mother primordial continents have all gone into deep mantle remaining life on the deep-sea hydrothermal system. Plate tectonics has operated to clean-up ocean chemistry by the formation of ores at mid-oceanic ridges to transport them into mantle. Salinity was 3-5 times more in the Precambrian time, and plate tectonics was not effective to omit halogens from ocean into mantle. Continent-collision orogeny was critical to dilute salinity after the drop-down of sea-level at 800-600Ma.

イヌア地域における 3.8 億年前の非生物的炭素 Abiogenic graphite in the 3.8 Ga Isua Supracrustal Belt

掛川 武^{1*}

KAKEGAWA, Takeshi^{1*}

¹ 東北大学院理

¹ Graduate School of Science, Tohoku Univ

Graphite is known to occur in the >3.7 billion years old Isua Supracrustal Belt (ISB) of western Greenland. The unequivocal documentation of biogenicity for graphite is complicated by the possibility of secondary graphite precipitation from metamorphic or igneous fluids and the difficulties in distinguishing biogenic from secondary graphite. Here I report the discovery of siderite-rich veins enriched in reduced carbon in the western ISB. In the studied area, metamorphosed basaltic rocks are dominant. Three layers of banded iron formations, enriched in magnetite, quartz, grunerite, and Fe-rich garnet, are found in the studied area. It is found that the carbonate-rich vein occurs in some banded iron formations, and such veining extends approximately 100 m from north to south. The carbonate carbon concentrations of this vein range from 2.5 to 4.5 wt %C. The concentrations of graphite range from 0.1 to 5.0 wt %C. The mineralogy associated with abundant graphite is quite similar to the secondary carbonate veins found in eastern ISB (van Zuilen et al., 2002).

Results of the present geological survey constrain that the carbonate vein was formed by interaction between pre-existing BIFs and carbonic fluids during metamorphism. Siderite was formed during the early stage of metasomatism and became a subject for further metamorphism, producing magnetite and graphite. Because BIFs do not contain recognizable amounts of graphite, graphite in the carbonate veins were certainly formed during the vein formation, thus the product by metamorphism. This finding is a second report of abiogenic graphite in the ISB. Such abiogenic graphite most likely widespread in ISB, because carbonation of BIFs are commonly found throughout the belt.

On the other hand, ¹³C-depleted graphite from sedimentary rocks are present in ISB, in particular 2 km north from the surveyed area of this study. Graphite in those sedimentary rocks are interpreted as biogenic in origin. Detailed geological, mineralogical and isotope analyses allow us to distinguish graphite generated during sedimentation from that produced during metamorphism.

Keywords: abiogenic, Isua, Archean

Was the Archean atmosphere reducing? Was the Archean atmosphere reducing?

大本 洋^{1*}

OHMOTO, Hiroshi^{1*}

¹NASA Astrobiology Institute and Department of Geosciences, Penn State University

¹NASA Astrobiology Institute and Department of Geosciences, Penn State University

The current paradigm postulates the following scenarios for the evolution of the atmosphere and oceans: Oxygenic photoautotrophs evolved at ~2.7 Ga, but the atmosphere and oceans remained reducing (i.e., $p\text{H}_2 > 10^{-6}\text{atm} > p\text{O}_2$) until the 'Great Oxidation Event (G.O.E.)' at ~2.45 Ga when the atmospheric $p\text{O}_2$ dramatically rose to ~10% PAL and the ocean surface layer became oxygenated, while the deep oceans remained anoxic. Previous researchers have presented the following observations in some (but not all) Archean-aged rocks to support this paradigm: (a) loss of Fe from paleosols; (b) abundance of banded iron formations (BIFs); (c) presence of 'detrital' grains of uraninite and pyrite; (d) lack of U- and Mo enrichments in black shales; (e) presence of anomalous isotopic fractionations (AIF or MIF) of sulfur in shales and barite beds; (f) presence of unusual isotopic compositions of N and Fe in sedimentary rocks. However, none of these observations are unequivocal evidence for a reducing Archean atmosphere, since all these characteristics have also been found in younger rocks. We have also demonstrated experimentally that the AIF-S signatures, which were previously linked to the UV photolysis of volcanic SO_2 in an O_2 - and O_3 -free atmosphere, can occur during thermochemical sulfate reduction by solid organic matter. We can better explain the above characteristics (c)-(f) by diagenetic, hydrothermal, and metamorphic processes, rather than by atmospheric processes.

In an anaerobic world under a reducing atmosphere, organic synthesis would have occurred through anoxygenic photoautotrophy (e.g., $\text{CO}_2 + 2\text{H}_2 \Rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$), and the decomposition of the organic matter by fermentation (e.g., $\text{CH}_2\text{O} \Rightarrow \text{CO} + \text{H}_2$ and $3\text{CH}_2\text{O} \Rightarrow 2\text{CO} + \text{CH}_4 + \text{H}_2\text{O}$). As the atmospheric CO_2 was converted to reduced C compounds (CO , CH_4 , and C) and not completely recycled back to CO_2 , the atmospheric CO_2 would have continuously decreased, even with continuous supplies of CO_2 by volcanic gas and weathering of carbonates; CO_2 would have disappeared in <~100 million years since the emergence of anoxygenic photoautotrophs and created an icy, dead planet. But this did not happen. The maintenance of a CO_2 -rich atmosphere and the life on Earth through geologic history would have required the recycling of organic matter by aerobic organisms.

A small, but growing, number of researchers postulate that the emergence of oxygenic photoautotrophs and the development of a fully-oxygenated atmosphere-ocean system took place before ~3.5 Ga. They cite the following similarities between Archean and Phanerozoic rocks to support their model: (i) the ranges of organic-C and pyrite-S contents in shales; (ii) the common $\delta^{13}\text{C}$ values of carbonates and shales; (iii) the abundance of sulfate-rich rocks; (iv) the wide $\delta^{34}\text{S}$ ranges for pyrite and sulfates in sedimentary rocks and ore deposits; (v) the common $\delta^{15}\text{N}$ values of shales and cherts; (vi) the Fe, Mo and Cr isotope values of sedimentary rocks; and (vii) the behaviors of various redox sensitive elements (e.g., Fe, Mn, U, Mo, W, As, Ce) in paleosols, BIFs, and hydrothermally-altered submarine basalts.

Keywords: Archean, atmosphere, MIF, GOE

Does bimodal distribution of carbon isotopes of 3.0 Ga kerogen mean oxygenic photosynthesis?

Does bimodal distribution of carbon isotopes of 3.0 Ga kerogen mean oxygenic photosynthesis?

掛川 武^{1*}, 横田和也¹

KAKEGAWA, Takeshi^{1*}, Kazuya Yokota¹

¹ 東北大学大学院理

¹ Graduate School of Science, Tohoku University

In order to constrain the mid-Archean anaerobic and aerobic ecosystem, geological and geochemical studies were performed on ca. 3.0 Ga sedimentary rocks at the northern section of Lundy Lake Greenstone Belt, Ontario, Canada [1][2]. The metamorphic grade reached to greenschist to amphibolite facies in the studied area. Mafic pillow lavas and gabbro are dominant rocks in the studied area. Banded iron formations and black shales, intercalated with mafic volcanics, are found at four different horizons. Each unit of sedimentary rocks has 1 to 15 m thickness. Black shales at all localities contain significant amounts of organic carbon, ranging from 0.3 to 9.2 wt %C. Such high concentrations suggest the microbial productivities were very high during sedimentation.

Pyrite is abundant in one a specific black shale horizon. Pyrite occurs as fine-grained or nodular shape. The fine-grained type occurs concordantly with sedimentary structure and this type is interpreted as direct precipitates from the contemporary submarine hydrothermal plume. Detailed petrography suggests that nodular type was formed during diagenesis by submarine hydrothermal fluids, which introduced peripherally in stratified sediments. Pyrrhotite-pyrite assemblage and sphalerite compositions in nodular samples suggest that associated fluids were very reducing and most likely containing hydrothermal hydrogen.

Bimodal distribution of carbon isotope compositions was found among examined kerogen samples. One mode appears between -47 to -41 per mil (PDB; mode 1), suggesting activities of methanogens during sedimentation. Geological survey indicates that activity of methanogens was strongly concealed with contemporary submarine hydrothermal activities and sulfide mineralization. On the other hand, carbon isotope compositions of kerogen from other horizons show -29 to -21 per mil (PDB; mode 2). Those samples are not accompanied with submarine sulfide mineralization and did not show carbon isotope signatures of methanogens. Widespread nature of such mode-2-type kerogen suggests that photosynthesizing bacteria were active in the water column.

Black shales of mode 2 type are often intercalated with magnetite-rich banded iron formations. Some samples show high mole ratios of C(org)/Fe, suggesting that anoxygenic photosynthesis, such as Fe-oxidizing bacteria, is not likely for the origin of mode-2-type kerogen [3]. In other words, the high C(org)/Fe ratios may imply the activity of cyanobacteria in the 3.0 Ga Lundy Lake ocean.

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Keywords: Archean, photosynthesis, Lundy Lake

複合イオウ同位体比の特徴と堆積環境との関連

Linking multiple sulfur isotopic characteristics of Archean sedimentary rocks to their depositional environments

渡邊 由美子^{1*}, 濱崎 浩¹, CHORNEY Andrew¹, 大本 洋¹

WATANABE, Yumiko^{1*}, HAMASAKI, Hiroshi¹, CHORNEY, Andrew¹, OHMOTO, Hiroshi¹

¹ ペンシルヴァニア州立大学

¹Penn State University

Many researchers have linked the anomalously fractionated (or commonly called mass independently fractionated) isotopes of sulfur (AIF-S or MIF-S) in sedimentary rocks to UV photolysis of volcanic SO₂ and to an O₂-poor atmosphere. However, serious discrepancies exist between the AIF-S signatures in natural samples and those of the products (S₀ and SO₄²⁻) of SO₂ photolysis using a broad-band UV lamp which simulates the sun light. The produced S₀ and residual SO₂ possess only very small AIF-S signatures (i.e., $\delta^{33}\text{S}/\delta^{34}\text{S} = 0.58 \pm 0.04$). Based on theoretical and experimental investigations, we have proposed that the AIF-S signatures in some (if not all) Archean sedimentary rocks were produced by chemisorption-redox reactions involving solid phases (e.g., organic matter, iron oxides, carbonates, clays and aqueous S-bearing species (SO₄²⁻ and H₂S)) during the diagenesis of sediments in hydrothermal environments. According to our model, the characteristics of AIF-S signatures may vary depending conditions of the chemisorption-redox reactions (e.g., type and surface area of the solid phase, concentration of the aqueous species, temperature, reaction time, open or closed-system). To evaluate the validity of our model, we have examined the relationships among the AIF-S characteristics ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values) of sulfides and sulfates, their modes of occurrence (e.g., disseminated, nodules, layers, veins), and the lithology of their host rocks.

We have recognized that sulfides (and sulfates) that formed in similar depositional environments generally exhibit similar AIF-S characteristics. For example, sediments accumulated in closed euxinic basins under the influence of submarine hydrothermal activity (e.g., pyritic black shales and siderite-rich sediments in the 2.5 Ga McRae and 2.7 Ga Jeerinah Formations) generally possess $+\delta^{34}\text{S}$ and $+\Delta^{33}\text{S}$ values or $-\delta^{34}\text{S}$ and $-\Delta^{33}\text{S}$ values. Barite- and sulfide-bearing sediments accumulated in shallow, evaporitic basins (e.g., the 3.5 Ga Dresser and 2.7 Ga Tambiana Formations) often possess $-\delta^{34}\text{S}$ and $+\Delta^{33}\text{S}$ values for the sulfides and $+\delta^{34}\text{S}$ and $-\Delta^{33}\text{S}$ values for the barite.

The observed relationships between AIF-S signatures and depositional environments, and the frequent occurrence of sediments with no AIF-S signatures in Archean sedimentary rocks (e.g., 2.7 Ga Hardy lacustrine Formation), are difficult to explain by the current popular model that links AIF-S to atmospheric UV reactions. Rather, the data can be best explained by our model that links AIF-S to chemisorption-redox reactions (e.g., thermochemical sulfate reduction (TSR), replacement of iron oxides by pyrite) under large-scale hydrothermal conditions. Therefore, the AIF-S record of sedimentary rocks may be linked to the thermal and biological evolution of the Earth, rather than to the atmospheric evolution.

Keywords: sulfur isotope, Archean

全生物共通祖先の遺伝子を再現する

Molecular resurrection of the genes of common ancestor of all the living organisms

山岸 明彦^{1*}

YAMAGISHI, Akihiko^{1*}

¹ 東京薬科大学生命科学部

¹Depart. Mol. Biol., Tokyo Univ. Pharm. Life Scie.

地球上の全生物は1種類の生物を祖先として進化してきた。その共通祖先の性質を進化系統樹をもとに解析することができる。現存する生物の遺伝子を解析することから分子進化系統樹を作製することができるが、同じ手法をもちいて共通祖先の遺伝子の配列を推定する事もできる。推定した遺伝子を大腸菌内で発現し、精製することにより、過去の生物がもっていたタンパク質の性質を調べる事ができる。こうした方法によって、全生物の共通祖先、古細菌の共通祖先、細菌の共通祖先の性質を調べた結果を報告する。

キーワード: 全生物の共通祖先, コモノート, LUCA, タンパク質, 耐熱性

Keywords: Common ancestor, Commonote, LUCA, Protein, thermostability

模擬惑星間環境におけるアミノ酸関連物質の軟X線・極端紫外光に対する安定性・変成評価

Stability and alteration of amino acid-related compounds against soft X-rays and extreme UV in interplanetary space

川本 幸徳^{1*}, 江藤 碧¹, 岡部 拓人¹, 大林 由美子¹, 金子 竹男¹, 高橋 淳一², 三田 肇³, 神田 一浩⁴, 小林 憲正¹
KAWAMOTO, Yukinori^{1*}, Midori Eto¹, OKABE, Takuto¹, OBAYASHI, Yumiko¹, Takeo Kaneko¹, TAKAHASHI, Jun-ichi²,
MITA, Hajime³, Kazuhiro Kanda⁴, KOBAYASHI, Kensei¹

¹ 横浜国立大学, ²NTT, ³ 福岡工業大学, ⁴ 兵庫県立大学

¹Yokohama National University, ²NTT, ³Fukuoka Institute of Technology, ⁴University of Hyogo

模擬惑星間環境におけるアミノ酸関連物質の軟X線・極端紫外光に対する安定性・変成評価を行った。

キーワード: アミノ酸, アミノ酸前駆体, 放射光, 軟X線, 惑星間空間, 生命の起源

Keywords: amino acids, amino acid precursors, synchrotron radiation, soft X-rays, interplanetary space, origins of life

軟X線および重粒子線照射による惑星間における核酸塩基の安定性の評価 Studies on stability of nucleic acid bases by irradiation with soft X-rays and heavy ions

岡部 拓人^{1*}, 川本 幸徳¹, 江藤 碧¹, 大林 由美子¹, 金子 竹男¹, 高橋 淳一², 神田 一浩³, 吉田 聡⁴, 小林 憲正¹
OKABE, Takuto^{1*}, KAWAMOTO, Yukinori¹, Midori Eto¹, OBAYASHI, Yumiko¹, Takeo Kaneko¹, TAKAHASHI, Jun-ichi²,
Kazuhiro Kanda³, KUWANO-YOSHIDA, Akira⁴, KOBAYASHI, Kensei¹

¹ 横浜国立大学, ²NTT, ³ 兵庫県立大学, ⁴ 放射線医学総合研究所

¹Yokohama National University, ²NTT, ³University of Hyogo, ⁴National Institute of Radiological Sciences

アミノ酸や核酸塩基類等の生体関連物質は、隕石中で発見されており、宇宙環境下で合成され隕石等によって地球上にもたらされ、生命の起源となった可能性がある。星間塵や隕石中に含まれる核酸塩基は、宇宙環境で宇宙線等により変性を受ける可能性が考えられる。本研究では、加速器を用い軟X線及び重粒子線に対する核酸塩基の安定性及びその変性を評価した。

キーワード: 核酸塩基, 軟X線, 重粒子線, 生命の起源, 惑星間塵, 隕石

Keywords: nucleic acid bases, soft X-rays, heavy ions, origins of life, interplanetary dust particles, meteorites

海底熱水系におけるアミノ酸生成の可能性の検証 Possible amino acid formation pathways in submarine hydrothermal systems

近藤 裕一^{1*}, 栗原 広成¹, 桑原 秀治², 大林 由美子¹, 金子 竹男¹, 小林 憲正¹

KONDO, Yuichi^{1*}, Kurihara Hironari¹, KUWAHARA, Hideharu², OBAYASHI, Yumiko¹, Takeo Kaneko¹, KOBAYASHI, Kensei¹

¹ 横浜国立大学大学院工学府, ² 東京大学大学院新領域

¹Graduate School of Engineering, Yokohama National University, ²Graduate School of Frontier Sciences, University of Tokyo

生命の誕生に必要なアミノ酸の生成の場としては、星間、原始大気、海底熱水系などが考えられる。原始大気が二酸化炭素・窒素などを主とする非還元型の場合、原始大気中でのアミノ酸などの生体関連有機物の生成は限定的となるが、カルボン酸類の生成は期待できる。このようなカルボン酸類、特にケト酸類が海底熱水系にとりこまれ、そこでアンモニアと反応することによりアミノ酸の生成が期待できる。本研究では、海底熱水系をモデルに作成したフローリアクターを用いて、ケト酸とアンモニアを反応させたところ、アミノ酸の生成が確認できた。

キーワード: 海底熱水系, アミノ酸, 原始大気, 火花放電, フローリアクター, 生命の起源

Keywords: submarine hydrothermal systems, amino acids, primitive atmosphere, spark discharge, flow reactor, origins of life

高温高圧における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 Effects of glycine and its decomposition products on polymerization of methionine under high temperature and pressure

黄 叡^{1*}, 古川 善博¹, 掛川 武¹

HUANG, Rui^{1*}, FURUKAWA, Yoshihiro¹, KAKEGAWA, Takeshi¹

¹ 東北大学大学院理学研究科

¹ Graduate School of Science, Tohoku University

Polymerization of amino acids is an essential process for the origin of life. Several geological settings have been proposed as the place for the polymerization: sub-marine hydrothermal vent (Imai *et al.*, 1999), tidal flats (Lahav *et al.*, 1978), and marine sediments (Nakazawa *et al.*, 1993). Previous studies suggest the importance of the marine sediments to produce longer peptides (Ohara *et al.*, 2007; Otake *et al.*, 2011). These previous studies suggest that the reactivity of each amino acid is widely different. This may lead to skepticism about the formation of peptides composed of plural amino acids. However, there has been no experiment that investigated the oligomerization of plural amino acids. In this study, we investigated polymerization of methionine under the conditions of high temperature and high pressure (at 175°C, 150 MPa, 0-96 hours).

Starting materials were solid methionine and solid methionine with solid glycine, water, aqueous ammonia, or ammonium hydrogen carbonate. The additives in the starting materials other than glycine (water, aqueous ammonia, and ammonium hydrogen carbonate) are simulating 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 additives 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. 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).

Methionine was polymerized to di-methionine, tri-methionine and methionine diketopiperazine in experiments adding water, ammonia, ammonium hydrogen carbonate, and glycine. On the other hand, peptides other than di-methionine were not formed in experiments using methionine alone. Methionyl-glycine and glycyl-methionine were produced in experiments containing each additive. In all experiments, methionine decomposed with reaction time. In experiments with additives, reaction rates of methionine decomposition and methionine-peptide formation were increased. These rates were especially increased in samples containing aqueous ammonia, and ammonium hydrogen carbonate, suggesting that ammonia and carbon dioxide promote the production rates of peptides and decomposition reactions of methionine. Compared with previous study (Ohara *et al.*, 2007), these results indicate that the reaction rate of methionine peptide formation was far lower than that of glycine. However, this rate was increased with addition of glycine. The present results also suggest that decomposition products of glycine especially ammonia and carbon dioxide increased the reaction rate of methionine.

When these results are applied to diagenesis in Hadean marine sediments, these results suggest that amino acids of low reactivity may be activated by amino acids of high reactivity and produced peptides composed of both amino acids.

初期地球における有機物生成に対する塩の影響 Effects of salt on organic molecule formations by oceanic impacts on early Earth

鈴木 千月香^{1*}, 古川 善博¹, 小林 敬道², 掛川 武¹

SUZUKI, Chizuka^{1*}, FURUKAWA, Yoshihiro¹, Takamichi Kobayashi², KAKEGAWA, Takeshi¹

¹ 東北大学理学研究科, ² 物質・材料研究機構 超高压グループ

¹ Graduate School of Science, Tohoku University, ² High Pressure Group, National Institute for Materials Science

When the surface of Hadean Earth solidified, it is thought that the atmosphere of the Earth was composed mostly carbon dioxide and nitrogen (Kasting and Howard, 1993). It has been suggested that one of the process to supply organic molecule on early Earth was the oceanic impact. It was suggested that amines, carboxylic acids, and glycine were formed by the shock-recovery experiments simulating oceanic impact on early Earth (Furukawa et al., 2009). The previous study used starting materials comprising mixture of iron, nickel, carbon (¹³C), and gaseous nitrogen or ammonia. However, no previous study has examined effects of brine composition on the formation of organic molecules by oceanic impact. In this study, shock-recovery experiments were performed with a single-stage propellant gun to investigate the effects of ionic strength on the formation of organic compounds by oceanic impact on early Earth. We used starting materials comprising mixture of iron, nickel, carbon (¹³C), gaseous nitrogen, and sodium chloride solution or water. After the impact experiments, soluble organic compounds were extracted into water and analyzed amines, amino acids, and ammonia by liquid chromatography-mass spectrometer (LC/MS). Solid materials were analyzed using X-ray powder diffractometry (XRD) after drying. Glycine, methylamine, ethylamine, and propylamine whose carbons are composed of ¹³C were identified in the sample free from sodium chloride. While, only ¹³C-methylamine and ¹³C-ethylamine were identified in the sample containing sodium chloride. Iron was more oxidized in the sample containing sodium chloride. This suggests that more ammonia was formed in the sample containing sodium chloride. On the other hand, yields of amines in the sample free from sodium chloride were higher than those containing sodium chloride. This suggests that sodium chloride restricted the reaction to form alkyl chain or reactions between ammonia and hydrocarbons. The present results suggest that sodium chloride restricts the reactions forming organic molecules by oceanic impact on early Earth.

グリコールアルデヒドとグリセルアルデヒド間の反応に対するほう酸の影響 Effects of borate on the reaction between glyceraldehyde and glycolaldehyde

堀内 真愛^{1*}, 古川善博¹, 掛川武¹

HORIUCHI, Mana^{1*}, Yoshihiro Furukawa¹, Takeshi Kakegawa¹

¹ 東北大学大学院理学研究科地学専攻

¹Department of EARTH SCIENCE, Graduate School of Science, Tohoku University

Ribose is an essential component of RNA, and its formation in the prebiotic Earth is important to promote chemical evolution for origin of life. For the abiotic ribose formation, the formose reaction has been investigated by previous researchers [e.g., 1]. The formose reaction produces carbohydrates by series of polymerization of formaldehyde with catalytic base [2]. The carbohydrates produced in this reaction contain pentoses (ribose, arabinose, xylose, and lyxose). One of the problems is that these carbohydrates are highly reactive in alkaline solutions. Therefore, pentoses are rapidly decomposed. Recently, researchers proposed that ribose is stabilized by the complexation with borate and silicate [3, 4]. Ricard et al., (2004) offered the experimental data indicating the increased stability of the total amount of pentoses by the complexation with borate. However, there has been no clear evidence as to which pentoses are stabilized by effects of borate. Because the formose reaction produces variety of carbohydrates, it is difficult to perform quantitative analysis of each product. In particular, quantitative analysis of ribose needs chromatographic separation accompanied with mass spectrometry analysis. However, a previous analytical method for each pentose needed derivatization. In the present study, we report the qualitative analytical method for ribose in the mixture of pentoses without derivatization. Then, we analyzed ribose in the products of a simplified formose reaction in the presence of borate.

New analytical method for pentoses and pentose-borate complex was developed using a liquid chromatograph (2695 separation module; Waters Co.) connected to a tandem mass spectrometer (Quatromicro API; Waters Co.). Several ligand exchange columns and eluents were tested in order to identify the suitable combination to separate pentoses and pentose-borate complexes. As a result, pentoses were separated using the ligand exchange columns with a function of zinc coordination. The ligand exchange columns with a function of sodium coordination retained pentose-borate complexes. Using these analytical methods, we performed experiments to examine borate effects to stabilize individual pentose (experiment 1) and products by the simplified formose reaction under borate presence (experiment 2). In the experiment 1, decomposition rates of individual pentose were investigated in an alkaline solution. Experiments were performed either with or without sodium borate. The results indicate that the presence of borate affected differently on the stability of individual pentose. The decomposition rates of ribose and arabinose were decreased significantly in borate solution, although decomposition rates of xylose and lyxose were not affected by borate.

In the experiments 2, glyceraldehyde and glycolaldehyde was reacted in base with or without sodium borate. Formation of pentoses including ribose was confirmed and the yields of all pentoses became maximum within 5 minutes. After 5 min, the yields of pentoses decreased, although the yields of some pentoses experiments with borate became higher than those without borate. This result indicates that effects of borate differ depending on individual pentoses. In both experiments, the yields of ribose increased by the addition of borate. Pre-biotic ribose was most likely formed and stabilized under borate-rich Hadean oceans, which was also supported by finding of borate minerals in the early Archean sedimentary rocks.

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水溶液中のペプチド生成・分解速度に及ぼす金属イオン (Ca^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+}) および pH の影響

Effects of metal ions (Ca^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+}) and pH on the formation and decomposition rates of di- and tripeptides

坂田 霞^{1*}, 藪田 ひかる¹

SAKATA, Kasumi^{1*}, YABUTA, Hikaru¹

¹ 大阪大学大学院理学研究科宇宙地球科学専攻

¹Osaka University, Department of Earth and Space Science

【序論】

近年、カンラン岩の蛇紋岩化で発生する塩基性の流体が噴出する大西洋中央海嶺のロストシティー熱水地域や南チャモロ海山の低温湧水系が発見され (Kelley et al. 2005; Hulme et al. 2010), 海底の塩基性流体環境が初期地球での生命の誕生及び進化の場の1つとして注目されている (Russell, 2003). Sakata et al (2010) は, 150 の塩基性水溶液 (pH 9.8) 中でグリシン (Gly) の重合速度が極大になることを明らかにし, 初期地球での塩基性海底熱水系はジペプチドの非生物的合成に有利である可能性を示した. しかし, 塩基性水溶液中の Gly の重合反応に及ぼす金属イオンの影響については, ほとんど研究されていない. そこで, 本研究では, 様々な pH 条件下, Ca^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+} をそれぞれ含む Gly 水溶液の加熱実験を行い, グリシルグリシン (GlyGly), グリシルグリシルグリシン (GlyGlyGly) およびジケトピペラジン (DKP) の生成・分解速度定数 (k_n) を決定した.

【実験】

100 mM Gly 水溶液, 金属イオン濃度が 5 mM になるよう CaCl_2 , MgCl_2 , ZnCl_2 , CuCl_2 をそれぞれ加えた 100 mM Gly 水溶液, CaCl_2 の濃度を 200, 400mM に調製した 100 mM Gly 水溶液を作成した. 各水溶液の pH を酸性 (pH = 2.2 - 2.3), 中性 (pH = 4.5 - 6.0), 塩基性 (pH = 9.8 - 9.9) にそれぞれ調製した (CuCl_2 を加えたものは pH = 3.4, 9.8 の 2 種). 各試料を 0.5ml ずつピレックス試験管に入れ, アルゴン置換, 脱気封管し, 140 °C で 1~74 日間加熱した. 加熱後の水溶液を 10 倍に希釈後, 100 μ l を高速液体クロマトグラフィー (HPLC) で分析した. 本研究では, $2\text{Gly} \rightarrow \text{GlyGly}$ (k_1), $\text{GlyGly} \rightarrow \text{DKP}$ (k_2), $\text{GlyGly} + 2\text{Gly} \rightarrow \text{GlyGlyGly}$ (k_{-1}), $\text{DKP} + \text{GlyGly} \rightarrow \text{GlyGlyGly}$ (k_{-2}), $\text{Gly} + \text{GlyGly} \rightarrow \text{GlyGlyGly}$ (k_3), $\text{GlyGlyGly} \rightarrow \text{Gly} + \text{GlyGly}$ (k_{-3}) の反応速度式を用いた. 各実験から得られた Gly, GlyGly, DKP, GlyGlyGly の濃度の経時変化に, 上記 6 つを組み合わせた反応速度式で最小自乗フィッティングを行い, 各反応速度定数を求めた.

【結果と考察】

Ca^{2+} , Mg^{2+} , Zn^{2+} を含む水溶液における GlyGly の生成濃度は, 全ての pH 条件で, 金属イオンを含まない水溶液の場合に比べて低かった. Ca^{2+} の濃度が高くなるほど GlyGly 濃度は減少した. 一方, Cu^{2+} を含む塩基性水溶液における GlyGly の生成濃度は, 金属イオンを含まないものに比べて, 酸性の場合では低く, 塩基性の場合では高かった. また, Cu^{2+} を含む水溶液でのみ GlyGlyGly が生成し, 塩基性で最も高い濃度を示した. DKP 生成濃度は, いかなる金属イオンを含む塩基性水溶液でも減少した. Ca^{2+} , Mg^{2+} , Zn^{2+} を含む水溶液 (5 mM) では, 全ての pH 条件で, 金属イオンを含まないものよりも低い k_1 , k_{-1} , k_2 , k_{-2} を示した. このことから, これらの金属イオンは GlyGly や DKP の生成を抑制することが考えられる. Cu^{2+} を含む場合は, 金属イオンを含まないものよりも k_1 , k_{-1} が高く, k_2 , k_{-2} が低かった. これは, Cu^{2+} が Gly, GlyGly 間の反応を活性化し, GlyGly の環化反応を抑制することを示唆する. また, k_3 , k_{-3} は塩基性での値の方が酸性よりも高かった. 以上の結果から, Cu^{2+} は Gly の重合反応を促進し, その促進効果は塩基性でより顕著であることが明らかになった. このような, 金属イオンの種類によるペプチド生成・分解速度の違いは, 金属イオンと Gly の錯形成時の立体構造の違いに依存するためと考えられる.

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Keywords: glycine, metal ions, pH, polymerization reaction, hydrolysis reaction, reaction rate

無水および含水条件下における鉱物表面でのグリシンの挙動について Decomposition and peptide formation of glycine on oxide and mineral surface under dry and wet conditions

淵田 茂司^{1*}, 益田 晴恵¹

FUCHIDA, Shigeshi^{1*}, MASUDA, Harue¹

¹ 大阪市立大学大学院理学研究科生物地球系専攻

¹Department of Geosciences, Faculty of Science, Osaka City University

Peptide formation is an important process of the chemical evolution of precursor life on the primitive earth. It has been believed that sediments were good environment to proceed the chemical evolution, since mineral surface promoted oligomerization of amino acids and other biomolecules. In this study, the thermal behavior of amino acid adsorbed on minerals surface dry and wet condition was observed to evaluate the role of minerals for oligomerization.

Glycine (Gly) was adsorbed on alumina, amorphous silica and montmorillonite in 0.1 M solution. After drying, those were heated at 150 degree C for 3-288 hrs under wet and dry condition in glass ampoules. Gly and peptides were desorbed from mineral surface by 0.1 M CaCl₂ and the amounts of Gly remained and synthesized peptides were determined using HPLC.

The amount of Gly remaining on minerals exponentially decreased with heating time; 20 to 48 % Gly remained on mineral surface under dry condition after 288 hrs, and 59 to 73% under wet condition. 70% and 98% of Gly remained after heating without minerals under the dry and wet conditions, respectively. Minerals would not be protectors of amino acid but good catalysts to promote Gly reaction. Kinetic calculation indicates that the reaction rate of amino acids on mineral surface is 1.5-6 times faster under dry condition than wet condition. Since the decomposition of amino acids under wet condition was more slowly than under dry condition, dehydration would be the most dominant reaction under dry condition. Water inhabits Gly reaction under high temperature condition. The three types of peptide: diketopiperazine (DKP), diglycine (Gly₂) and triglycine (Gly₃) were detected in the system including montmorillonite heated under dry condition and reference solution. Peptides were not formed when amino acid adsorbed on alumina and silica was heated both in dry and wet conditions, probably because the concentration of peptide on alumina and silica surface was too low. The 15.57% of Gly monomer became peptides on montmorillonite under dry condition, and the most abundant product was DKP (10.03%). On the other hand, only 0.5% of Gly became DKP and Gly₂ were yielded in the solution without minerals. Thus, the peptides are accumulated more under the dry condition than hydrothermal condition, and the montmorillonite is a good catalyst.

Water was added to montmorillonite system after heating at dry and 150 degree C condition (dry/wet condition) for 168 hrs to check the change of stability of peptide synthesized and Gly monomer before and after the hydrolysis. 11.17% of DKP remained after heating in dry condition, while only 1.54 % of DKP remained in dry/wet condition. Decomposition rates of Gly₂ and Gly₃ were lower than that of DKP in those systems. The water added in the system promoted hydrolysis of DKP and Gly monomer, and destabilized those on the montmorillonite surface. The DKP on the montmorillonite would decomposed by hydroxyl ion, which was generated on mineral surface by the reaction with water. The existence of excessive water and hydroxyl ion is obstacle to condense DKP and elongate to form longer peptide. The maintaining of thermal dry condition is important to form and condense DKP on clay mineral surface. The condensation of DKP would be important as the first step of chemical evolution of life. If so, dry condition and existence of clay minerals would be essential factors to proceed the chemical evolution of precursor life on the primitive earth.

キーワード: ペプチド生成, 無水堆積物, グリシン, 粘土鉱物, 化学進化, ジケトピペラジン

Keywords: peptide formation, dry sediment, glycine, clay mineral, chemical evolution, diketopiperazine

「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"

河口 優子^{1*}, Yang Yinjie¹, 川尻 成俊¹, 白石 啓祐¹, 杉野 朋弘¹, 高橋 勇太¹, 谷川 能章², 鳴海 一成³, 佐藤 勝也³, 橋本 博文⁴, 吉田 聡⁵, 小林 憲正⁶, 中川 和道², 横堀 伸一¹, 山岸 明彦¹

KAWAGUCHI, Yuko^{1*}, YANG, Yinjie¹, Narutoshi Kawashiri¹, Keisuke Shiraishi¹, SUGINO, Tomohiro¹, Yuta Takahashi¹, Yoshiaki Tanigawa², NARUMI, Issay³, Katsuya Satoh³, HASHIMOTO, Hirofumi⁴, Satoshi Yoshida⁵, KOBAYASHI, Kensei⁶, NAKAGAWA, Kazumichi², YOKOBORI, Shin-ichi¹, YAMAGISHI, Akihiko¹

¹ 東京薬大・生命科学, ² 神戸大・院人間発達環境学, ³ 原子力機構・量子ビーム, ⁴ JAXA/ISAS, ⁵ 放医研・放射線防御セ, ⁶ 横浜国大・院工

¹Sch. Life Sci., Tokyo Univ. Pharm. Life Sci., ²Grad. Sch. Human Develop. Environ., Kobe Univ., ³Quantum Beam, JAEA, ⁴JAXA/ISAS, ⁵Res. Cent. Radiation Protect. NIRS, ⁶Grad. Sch. Eng., Yokohama Natl. Univ.

Origin of life on the Earth is one of most important issues for the biological studies. 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]. 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. Our two high-altitude isolates of Deinococci were then suggested to be novel species by molecular phylogenetic analyses and other microbiological characterizations (*D. aereus* from top of troposphere and *D. aetherius* from bottom of stratosphere) [4-6]. Spores and Deinococci are known by their extremely high resistance against UV, gamma ray, and other radiations [4]. *D. aereus* and *D. aetherius* showed high resistance comparable with *D. radiodurans* R1 to the UV and ionizing radiation such as gamma rays. If microbes could be found present even at the higher altitude of low earth orbit (400 km), 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 different depth of layered cells. This simulates different sizes of cell aggregates. Surface cells may protect inner cells against UV, although the former might die. Dried vegetative cells of *D. radiodurans* and our novel deinococcal species isolated from high altitude are candidates for the exposure experiment. We are now testing survivals of deinococcal species and strains under the harsh environmental conditions simulating ISS environmental conditions (UV, radiation, temperature, etc). The species we testing are *D. radiodurans* (R1, and some mutant strains for DNA repair systems which might affect survivability of cells under these conditions), *D. geothermalis*, *D. aereus*, and *D. aetherius*. In this paper, we discuss current status of exposure experiment of microorganisms defined for the Tanpopo mission and others.

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Keywords: International Space Station, *Deinococcus radiodurans*, *Deinococcus aereus*, *Deinococcus aetherius*, Space exposure

多重循環系水惑星における生命活動体形成の特徴と問題点：生命体がなぜできないか？

A characteristic and problems of active life materials formed at the multiple cyclic systems in water planet

三浦 保範^{1*}

MIURA, Yasunori^{1*}

¹ 非常勤 (大学)

¹ Visiting (Univ.)

最近地球内外で生命体形成に関する研究が盛んになっているが、その特徴と問題点から、古期生命体の考えを中心にまとめてみる。

1) 生命体は複雑な炭素等の軽元素主体の分子からなる活動物体で、数種の液体・固体の物質状態と混合した複合共生循環系を形成し、活動水惑星のミニタイプの活動体である。

2) 生命体活動には、長周期地球惑星活動体 (約五十億年単位) において、生命活動で短期 (年から百万年単位) に分解循環する場での複合反応により、エネルギー源とその地域環境に応じた生命体形成が行われる。そのため「生命体の分解と生成」が可能になる「活動的な水惑星での破壊と合体形成」の大きな支えが必要である。活動体の生命体や水惑星では停止と破壊は容易であるが、引き続き新しい物体・環境の形成は、長期単期の多重の循環系が確立していない場である「古期の地球・生命体」等で、かなり時間を要する過程である。

3) この考えを、地球惑星以外に適用すると、広い水惑星反応場が存在しないと複雑な化学反応で循環系を形成しないので、多量の水のない天体 (月・無水惑星) には生命体が現存できない。たとえ、局所的な流体層形成 (衝撃波過程) が表面衝突や地下溶融で形成されても、循環系のない一過性のものであればその場生命活動体は形成継続できない。小惑星では、衝撃波生成モノマーの無機・有機物間以外は水大気の状態間の循環性がなく、生命前駆体となる巨大分子の安定的な形成自体が困難となる。

4) 閉鎖系の生命活動体は、炭素循環系で動的消滅の繰り返しである。それでも循環系のない地球外天体で生命体が残存できるとすれば、むしろ生命活動体が形成できる水惑星の惑星間衝突により内部に循環を停止した生命体化石が形成しやすいと考えられる。その意味で、惑星間衝突の破片集合体でその天体の一部が混在残留していると、炭素循環系の痕跡を残す生命体化石の発見が可能であると思われる。そのため、月・惑星等の地球外天体の探査は重要である。

5) 閉鎖系の生命活動体 (人類生命体を含む) は、地球の循環場から地球外に短期間旅行に出かけることは可能で、太陽系内の大循環に入ると考えられるが、しかし現在共生している大きな水惑星 (地球型) 循環系から顕著に逸脱できない循環場にあると思われる。

キーワード: 循環系, 生命活動体, 水惑星, 惑星間衝突, 生命体化石, 月

Keywords: Cyclic system, Active life materials, Water planet, Planetary impact, Life fossil, The moon