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BAO01-P01 会場:コンベンションホール 時間:5 月 24 日 15:30-17:00

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

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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

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BAO01-P02 会場:コンベンションホール 時間:5 月 24 日 15:30-17:00

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 stabillity of nucleic acid bases by irradiation with soft X-rays and heavy ions

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OKABE, Takuto[1*], KAWAMOTO, Yukinori[1], Midori Eto[1], OBAYASHI, Yumiko[1], Takeo Kaneko[1], TAKAHASHI, Jun-ichi[2], Kazuhiro Kanda[3], KUWANO-YOSHIDA, Akira[4], KOBAYASHI, Kensei[1]

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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

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BAO01-P03 会場:コンベンションホール 時間:5 月 24 日 15:30-17:00

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

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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

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BAO01-P04 会場:コンベンションホール 時間:5 月 24 日 15:30-17:00

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

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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^{o}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^{o}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.

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BAO01-P05 会場:コンベンションホール 時間:5 月 24 日 15:30-17:00

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

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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.

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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 glycoraldehyde

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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（Ca2+, Mg2+, Zn2+,Cu2+）および pH の影響

Effects of metal ions (Ca2+, Mg2+, Zn2+, Cu2+) and pH on the formation and decomposition rates of di- and tripeptides

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【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 m M 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 ずつパイレックス試験管に入れ，アルゴン置換，脱気封管し，140 ℃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, 2Gly → GlyGly（k_1），GlyGly → DKP（k_2），GlyGly → 2Gly（k_{-1}），DKP → GlyGly（k_{-2}）, Gly + GlyGly → GlyGlyGly（k_3），GlyGlyGly → Gly + 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+} を含む場合では、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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キーワード: グリシン, 金属イオン, pH, 重合反応, 加水分解反応, 反応速度
Keywords: glycine, metal ions, pH, polymerization reaction, hydrolysis reaction, reaction rate

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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

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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 $CaCl_2$ 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 (Gly_2) and triglycine (Gly_3) 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 aluminia 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 Gly_2 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 Gly_2 and Gly_3were 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

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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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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. aerius* 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. aerius* 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. aerius*, 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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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

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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的活動体である。

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は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的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
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