

## 彗星および氷に富む天体における初期水質変成作用による無機物-有機物共進化

Evolution of inorganic and organic matters during the early stages of aqueous activity in a cometary body recorded in Antarctic micrometeorites

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Introduction: The interactive evolution of inorganic and organic materials is one of the hot issues of planetary science with a special interest to the search of possibility of life in planetary systems. Micrometeorites (MMs) recovered from surface snow of the Antarctica are extremely primitive, which contains ultracarbonaceous and chondritic porous MMs (CP MMs), and we have made a systematic investigation of MMs by using SEM, TEM, XANES, and SIMS to get through understanding of the evolution and interaction of inorganic and organic materials in planetary environments.

Samples and methods: We collected ~400 MMs preserved in ~300 kg snow, and selected seven porous MMs, which were embedded in annealed Au sheet with a hydraulic press in the clean room and coated by Pt, from which ~100 nm-thick FIB sections were prepared without using organic epoxy resin. The FIB sections were processed with a low voltage argon ion milling machine to minimize the damage during FIB sample preparation. Carbon-, N-, and O-XANES spectra of the FIB sections were acquired using STXM, and then, TEM observation was performed. Isotope imaging was performed for the remainder of D10IB009 CP MM pressed into a Au sheet for isotopographs of  $^1\text{H}^-$ ,  $^2\text{H}^-$ ,  $^{12}\text{C}^{14}\text{N}^-$ ,  $^{12}\text{C}^{15}\text{N}^-$ .

Results and discussion: The MMs show evidence for very early stages of aqueous activities for both inorganic and organic components, and we recognize three stages based on mineralogy and chemistry of organic and inorganic materials. Stage I is characterized by alteration only in organic materials, but inorganic materials do not show evidence for aqueous alteration. The inorganic materials are totally anhydrous including GEMS and enstatite whiskers/platelets, which are almost identical to those in anhydrous IDPs. Organic materials in two MMs at this stage have abundant high carboxyl functionality, and one of them contains nitrile and/or nitrogen heterocyclic groups with D and  $^{15}\text{N}$  enrichments, which are thus highly pristine. However, other two CP MMs are poorer in organic materials and show high aromaticity, which are indistinguishable from those of hydrated carbonaceous chondrites. Stage II is characterized by alteration of inorganic matter. GEMS was changed into GEMS-like amorphous silicate by hydration and oxidation, and the GEMS-like amorphous silicate in Stage II has relatively homogenous compositions than GEMS in Stage I. Nano-phase Fe metal that was abundant in the stage I was depleted, and instead, Fe-rich phyllosilicate was found

coexisting with GEMS-like amorphous silicate. Stage III is defined by the appearance of Mg-rich phyllosilicate and Mg-Fe carbonate, which indicates reactions among Fe-rich phyllosilicate in Stage II, Mg-rich olivine and pyroxene, and organic materials and/or C-bearing ice.

The MMs are porous and “freeze-dry” processes took place during and after aqueous alteration, where liquid water was sublimated. The temperature of the reaction would be kept at near zero degree C. Possible parent bodies would be comets or icy asteroids. If further aqueous alteration took place, magnetite would be formed, which is often observed as framboidal aggregates and plaquettes in IDPs. The aqueous alteration in comets and porous icy bodies differ from that in chondrite parent bodies in that it took place locally and heterogeneously. On the other hand, aqueous alteration in chondrite parent bodies took place more homogeneously due to pervasive liquid water distribution in more compact bodies.

キーワード：彗星、水質変成、無機物-有機物

Keywords: comet, aqueous alteration, inorganic-organic matter

## カンラン石存在下におけるアルデヒド・アンモニアからのアミノ酸合成

## Amino acid synthesis from aldehydes and ammonia in the presence of olivine

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## 【序論】

太陽系において始原的な化学組成をもつ炭素質コンドライトには多種の地球外起源のアミノ酸が含まれている。地球生命の構成物質が地球外物質中から発見されたことから、アミノ酸は隕石有機物の中でも最も研究がなされてきた1つである。特に、炭素質隕石の水質変成度がアミノ酸の分布（例えば、 $\alpha$ -アミノイソ酪酸や $\beta$ -アラニン）や不斉炭素をもつイソバリンのL体鏡像異性体過剰率（Lee）と相関があることが注目されている。それらは水質変成がアミノ酸生成に影響を与えることを示唆しているが、その詳細な生成機構は解明されていない。本研究では隕石母天体環境を模したアミノ酸合成実験を行い、その分布やLeeを分析して隕石アミノ酸の生成機構を解明することを目的とした。

## 【実験】

アンモニア/ホルムアルデヒド/アセトアルデヒドまたはケトン（100/10/1 モル比）を含む水溶液（300  $\mu$  L）をカンラン石粉末に加えて、 $N_2$ 置換したガラスアンプル中で60℃、6~28日間加熱した（カンラン石を加えない系も実施）。反応物質の熱水抽出液を分割して、一方を6M 塩酸で加水分解した。加水分解と未加水分解画分それぞれを陽イオン交換樹脂で精製後、トリフルオロアセチル/イソプロピルエステル誘導体化を行い、ガスクロマトグラフ質量分析計で分析した。標準試料の保持時間とマスペクトルを用いてアミノ酸を同定・定量した。

## 【結果と考察】

炭素数5までの計16種類のアミノ酸が同定され、それらの中では炭素数2のグリシンが最も多く存在した（出発物質の炭素量に対して最大約3500 ppm）。その他には主にセリン、イソセリン、アラニン、 $\beta$ -アラニン、 $\beta$ -(アミノメチル)コハク酸、 $\beta$ -アミノ酪酸、ホモセリン、アスパラギン酸、グルタミン酸が存在した（それぞれ最大約600, 250, 240, 240, 160, 110, 60, 60, 50 ppm）。カンラン石の存在しない加水分解画分では比較的少量のグリシン、セリン、イソセリン、アラニン、 $\beta$ -アラニン、 $\beta$ -アミノ酪酸（それぞれ最大約840, 30, 110, 80, 90, 90 ppm）が検出されたのに対して、カンラン石存在下の加水分解画分においては、これらほとんどのアミノ酸濃度が著しく増加した（それぞれ最大約3500, 600, 250, 240, 240, 110 ppm）。加水分解後にアミノ酸濃度が増加する特徴は隕石アミノ酸と一致している。

検出されたアミノ酸分布（ $\alpha$ -アミノイソ酪酸やイソバリンの未検出など）からは隕石アミノ酸生成で提案されているストレッカー反応とは異なる反応経路が示唆される。その生成機構として、ホルミルアニオンがアルデヒドとアンモニアから生成されるイミニウムカチオンに対して求核攻撃し、その後酸化を経ることで $\alpha$ -アミノ酸を生成する経路が考えられる。より炭素数の多いアミノ酸（ $> C_3$ ）はアルドール反応によって生成するアルデヒドを出発物質と考えると、検出された $\alpha$ -、 $\beta$ -アミノ酸生成を網羅的に説明することができる。

カンラン石存在下におけるアルデヒド・アンモニアからのアミノ酸生成の生成機構をより詳細に解明するためには更なる研究が必要である。

キーワード：アミノ酸、炭素質コンドライト、水質変成過程、カンラン石、アルドール反応

Keywords: amino acids, carbonaceous chondrite, aqueous alteration process, olivine, aldol reaction

## 降着衝撃波による氷ダスト表面吸着分子の昇華：脱離エネルギーが分布を持つ場合

Thermal desorption of molecules from grain surface by accretion shocks: the effect of distribution of desorption energy

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Gravitational collapse of a molecular cloud is a transient process to form protostars and protoplanetary disks. The in-falling envelope onto the Keplerian disk often induces accretion shocks at their boundary. Recent ALMA observations suggested sublimation of various molecules, such as SO, from the icy grain surfaces (host grains) at the shocked region [1,2]. The sublimation would considerably affect the chemical environment of the nebula. The shock conditions for the sublimation were calculated numerically in a few papers [3-5]. However, these results were negative for the sublimation of molecules because the shock condition speculated from the ALMA observations is insufficient to sublime SO molecules from the host grains [4,5].

The numerical models assumed that the desorption energy of a certain molecular species is a single (average) value. However, temperature-programmed desorption (TPD) experiments indicated that the desorption energy is not well represented by a single value because of the heterogeneity of the host grain surfaces [e.g., 6]. If the desorption energy has a deviation from its average value, the sublimation from adsorption sites having smaller desorption energies may occur even by weaker shock heating. In this study, we revisit the desorption fraction when the distribution of the desorption energy is taken into consideration.

Let  $f(E_d)$  be the distribution of the desorption energy,  $E_d$ , of a certain species. The fraction of molecules that have the desorption energies in a range from  $E_d$  to  $E_d + dE_d$  is given by  $f(E_d)dE_d$ . The desorption fraction  $\langle P_d \rangle$  is calculated by integrating a product of  $P_d(E_d)$  and  $f(E_d)$  over  $E_d$ , where  $P_d(E_d)$  is the desorption probability of molecules as a function of  $E_d$ . In order to obtain  $P_d(E_d)$ , we numerically calculate the thermal history of host grains based on the one-dimensional plane-parallel shock-wave heating model [e.g., 7]. In addition, we assume that  $f(E_d)$  is the normal (Gaussian) distribution with the mean  $E_{d0}$  and the standard deviation  $\Delta E_d$ . We investigate the dependence of  $\langle P_d \rangle$  on  $\Delta E_d$  for various shock conditions.

Let us introduce the numerical results of when molecules adsorbed on 0.1 micron-sized host grains with  $E_{d0} = 2000$  K meet the accretion shock with the pre-shock gas number density of  $10^8 \text{ cm}^{-3}$  and the shock velocity of 1 km/s. When the desorption energy has no deviation ( $\Delta E_d = 0$  K), we obtain  $\langle P_d \rangle = 1.7 \times 10^{-9}$ .  $\langle P_d \rangle$  increases with the increase of  $\Delta E_d$ :  $1.7 \times 10^{-8}$ ,  $1.7 \times 10^{-5}$ , and  $1.5 \times 10^{-2}$  for  $\Delta E_d = 100$ , 200, and 400 K, respectively. The deviation of the desorption energy increases the desorption fraction of molecules by orders of magnitudes. This result suggests that molecules adsorbed on the host grains in molecular clouds can desorb more easily than that expected before.

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キーワード：降着衝撃波、氷ダスト、衝撃波加熱、吸着分子、昇華

Keywords: Accretion shock, Icy grain, Shock heating, Adsorbed molecules, Sublimation

## アルマによるTW Hya周りの原始惑星系円盤中のCOガス観測

## ALMA observations of CO gas depletion in the protoplanetary disk around TW Hya

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近年の赤外線・電波観測技術の向上により、原始惑星系円盤の観測的研究が急激に進展している。特に大型ミリ波サブミリ波望遠鏡アルマによる高空間分解能・高感度観測は、円盤内の惑星形成領域の物理・化学構造を明らかにすると期待される。

本講演では、アルマによるTW Hyaまわりの原始惑星系円盤中の<sup>13</sup>C0とC<sup>18</sup>O分子輝線観測の結果を報告する。<sup>13</sup>C0よりガス温度を求め、C<sup>18</sup>Oよりガスの柱密度分布を求めた結果、C0ガスがC0スノーラインの内側でも非常に少ないことが明らかになった。H<sub>2</sub>ガスとC0ガスの比が星間雲と同程度と仮定すると、ガス・ダスト比は1~0.1程度になり、星間雲の典型的なガス・ダスト比100に比べると2-3桁もガスが減少していることになる。解釈としては、実際にH<sub>2</sub>ガスがダストに比べて減少しているか、あるいはC0ガスのみ減少しているかの2通りが考えられるが、ハーシェル宇宙望遠鏡によるTW Hyaまわりの円盤からのHD分子輝線観測の結果によると、H<sub>2</sub>ガスは十分に存在すると思われる。従って、H<sub>2</sub>ガスが減少しているわけではなく、C0ガスが減少していると考えられる。C0スノーラインの内側でもC0ガスが減少している原因としては、C0がダスト表面反応により、有機分子など、より大きく蒸発しにくい分子になり、ダスト表面に留まっている可能性がある。

キーワード：原始惑星系円盤、C0分子輝線、有機分子生成

Keywords: protoplanetary disks, CO line emission, formation of organic molecules

原始惑星系円盤の化学反応計算と、赤外線分光観測によるスノーライン・C/O比分布の検出可能性  
How to measure snowlines and C/O ratio distributions in protoplanetary disks using  
infrared spectroscopic observations

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原始惑星系円盤(以下、"円盤")は、比較的単純な分子種(e.g.,  $\text{H}_2\text{O}$ , CO,  $\text{CO}_2$ , HCN)から複雑な有機物(COMs)まで様々な分子種を含む。最近ではSpitzer宇宙望遠鏡や、地上の大型望遠鏡(e.g., VLT, Keck)による赤外線分光観測などで、比較的単純な分子種の様々な輝線が検出され始めている (e.g., Pontoppidan et al. 2010a&b, Mandell et al. 2012)。

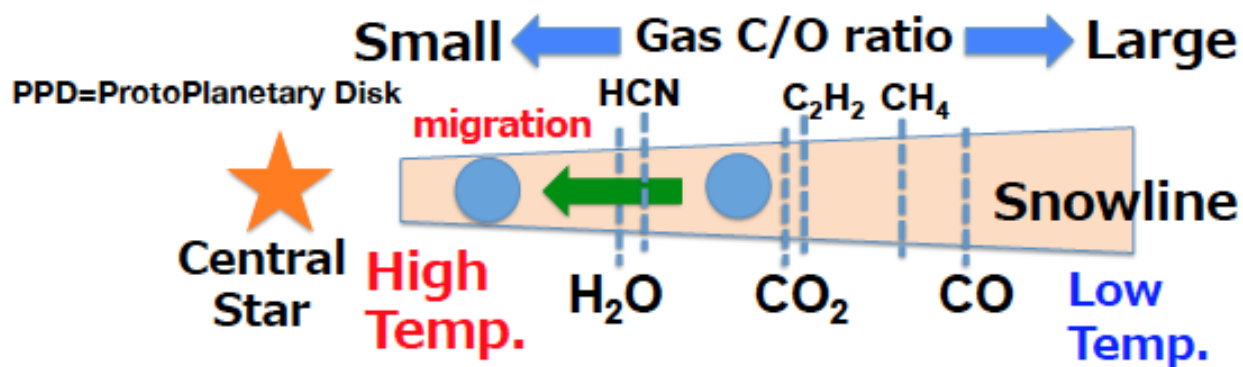
円盤はほぼケプラー速度で回転しているため、円盤から放射される輝線はドップラーシフトを受け広がっている。この輝線のプロファイル形状の解析から、輝線放射領域の中心星からの距離の情報が得られる。これまで我々は、円盤の化学反応ネットワーク計算と放射輸送計算の手法を用いて、 $\text{H}_2\text{O}$ 輝線プロファイルの観測から円盤内の $\text{H}_2\text{O}$ 分布、特に $\text{H}_2\text{O}$ スノーラインを同定する可能性を調べてきた。その結果、アインシュタインA係数が小さく、励起温度が高い $\text{H}_2\text{O}$ 輝線を用いた高分散分光観測を実施する事で、 $\text{H}_2\text{O}$ スノーラインの位置を同定できる可能性が示されている(Notsu et al. 2016a, ApJ submitted & 2016b in prep.)。

ここで円盤内では凝結温度の違いにより、分子種ごとにスノーラインの位置は異なると考えられる。その為、円盤ガス・ダスト中のC/O比は、中心星からの距離に応じて変化すると考えられる。例えば $\text{H}_2\text{O}$ スノーラインの外側では、多くの酸素が $\text{H}_2\text{O}$ の形でダスト表面に凍結する一方、炭素の多くはCOなどの形で円盤ガス中に留まるので、ガス中でC/O比が大きくなる。また、近年系外惑星大気のC/O比が測定され始めているが(e.g., Madhusudhan et al. 2014)、円盤と惑星大気のC/O比を比較する事で、惑星形成理論に制限を加えられる事が示唆されている(e.g., Oberg et al. 2011)。

そこで我々は、これまでの化学反応計算を発展させ、円盤ガス・ダスト中のC/O比や、比較的単純かつ主要な分子種(e.g.,  $\text{H}_2\text{O}$ , CO,  $\text{CO}_2$ , HCN) の組成分布を調べている。同時に放射輸送計算も進め、C/O比などを同定するのに適した輝線の調査を進めている。その結果、同じ分子種のアインシュタインA係数(放射係数)や励起温度が異なる輝線を使う事で、円盤内の異なる領域のC/O比に制限を加えられる事が分かってきた。例えばHCNの場合、3 $\mu\text{m}$ 帯の輝線では円盤外側、14 $\mu\text{m}$ 帯の輝線では円盤内側の構造に迫る事が可能である。これは14 $\mu\text{m}$ 帯の輝線の方が3 $\mu\text{m}$ 帯の輝線と比べ、ダストの吸収係数が小さく励起温度が低いため、円盤内側のHCNガスが豊富な領域を追う事が出来るからである。本発表ではまずT-Tauri円盤の場合の解析結果を中心に報告し、将来の近-中間赤外線の分光観測 (e.g., TMT/MICHI, SPICA) との関係についても議論する。また時間の許す範囲で、Herbig Ae星の場合の解析結果の報告と議論も行う。

キーワード：スノーライン、原始惑星系円盤、化学反応計算、C/O比、赤外線分光観測、惑星形成

Keywords: snowline, protoplanetary disk, chemical reactions, C/O ratio, infrared spectroscopic observation, planet formation



**There are radial dependences of Gas & Dust C/O ratio in Protoplanetary disks.**

e.g., Pontoppidan et al. 2014

## 鉄基板上でのFT型触媒反応実験における反応効率の温度依存性

Temperature dependence of reaction efficiency in the Fischer-Tropsch-type catalytic reaction on an iron substrate

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Fischer-Tropsch type catalytic reaction has been believed to be one of simplest and most fundamental formation processes of organic molecules, which dominantly occurred on the surface of cosmic dust particles, such as iron, magnetite, amorphous iron silicate and graphite, in the period from the late stage of molecular cloud to the solar nebula. Experimental approaches to find the environment, where catalytic reaction was progressed efficiently, have been attempted in laboratories [1-5]. In the experimental studies, organic molecules ranging from methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), benzene ( $\text{C}_6\text{H}_6$ ) and toluene ( $\text{C}_7\text{H}_8$ ), to more complex species such as acetone ( $\text{C}_3\text{H}_6\text{O}$ ), methyl amine ( $\text{CH}_3\text{NH}_2$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ) and N-methyl methylene imine ( $\text{H}_3\text{CNCH}_2$ ) have been produced at temperature above 573 K and relatively high pressure ( $10^5$  Pa). In case of actual environment in the early nebula environment, the temperature and pressure should be below 500 K and under  $10^2$  Pa, respectively. It is not obvious that the results of the reaction experiments are able to extrapolate to the actual early nebula environment. Therefore, we newly developed an experimental system to test the catalytic chemical reactions in the lower temperature (100-800 K) and pressure ( $10^{-3}$ - $10^0$  Pa) using an iron substrate. Our experimental system has a temperature-controlled substrate, a Fourier transform infrared spectrometer (FT-IR), and two quadrupole mass spectrometers (Q-MSs). Although FT-IR is able to measure the vibration modes of adsorbed and produced molecules on the surface, we have not been used it during the first experiment at higher temperature. We found a strong signal of mass 20 in the Q-MSs spectra in a continuous gas flow of a mixture gas of  $\text{D}_2$  and CO. The intensity of the signal decreases as temperature decrease from 800 to 400 K and becomes weaker than the detection limit below 300 K. The mass 20 corresponds to  $\text{D}_2\text{O}$  and  $\text{CD}_4$ , which are first products in the Fischer-Tropsch type reaction. In our presentation, the detail results using iron substrate will be presented as a function of temperature.

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キーワード：触媒反応、有機分子、実験

Keywords: catalytic reaction, organic molecule, experiment

宇宙電波観測による低質量星形成領域L1527における炭素鎖分子HC<sub>3</sub>Nの<sup>13</sup>C同位体比の精密決定

The precise determination of the <sup>13</sup>C isotopic ratios for carbon chain molecule HC<sub>3</sub>N in the low-mass star forming region L1527 by radio observations

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直線炭素鎖分子は、これまで暗黒星雲で観測されてきた。近年では、class 0の進化段階にある低質量星形成領域L1527でも観測されている[1]。我々は、直線炭素鎖分子の生成機構を調査するため、基本的な直線炭素鎖分子であるHC<sub>3</sub>Nの<sup>13</sup>C同位体の観測を、グリーンバンク100 m望遠鏡と野辺山45 m望遠鏡を用いて行った。

44-109 GHz帯の回転遷移を用い、同位体比を[H<sup>13</sup>CCCN] : [HC<sup>13</sup>CCN] : [HCC<sup>13</sup>CN] : [HCCCN] = 1.00 : 1.01 ± 0.03 : 1.35 ± 0.04 : 86.4 ± 2.2 (括弧内1σ誤差)と精密に決定できた。また、窒素の同位体<sup>15</sup>Nについては、同位体比 [HCC<sup>13</sup>CN]/[HCCC<sup>15</sup>N] = 5.26 ± 0.24 と [HCCCN]/[HCCC<sup>15</sup>N] = 338 ± 15を得ることができた。H<sup>13</sup>CCCNとHC<sup>13</sup>CCNの存在量が等しいことから、L1527では、HC<sub>3</sub>Nは二つの等価な炭素を持つC<sub>2</sub>H<sub>2</sub>とC<sub>2</sub>H<sub>2</sub><sup>+</sup>から生成することがわかった。この結果は、これまで同位体比が観測された暗黒星雲TMC-1と同じであった

[2]。よって、HC<sub>3</sub>Nのこの生成機構は分子雲進化における暗黒星雲からclass 0の段階まで普遍的に成り立つことが明らかになった。

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キーワード：電波、炭素鎖分子、同位体

Keywords: radio, carbon chain molecule, isotopic ratio

## 低温光化学反応による分子雲での有機物形成・進化

Formation and evolution of molecular cloud organic matter: Thermal and photo-irradiation effects

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Simulation experiments on UV-photochemistry of molecular cloud ice have shown that complex organic matter remains as a residue after warming up to room temperatures [e.g. Greenberg, 2002]. These compounds could be the precursors of a part of the organic matter found in comets and meteorites, but it is not clear how the organic-bearing ice formed in the ISM may have evolved through temperature increase and irradiations by UV-photons and cosmic rays until their incorporation into Solar System bodies.

We developed an experimental apparatus called PICACHU, an acronym for Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University [Piani et al., 2014] in order to simulate the formation and evolution of ice and organic residues through UV irradiation and heating. Typical ISM gases (a mixture of H<sub>2</sub>O, CO, NH<sub>3</sub>, and CH<sub>3</sub>OH) were deposited onto the substrate cooled down to ~12 K and simultaneously irradiated by UV photons under high vacuum. Gases, desorbed from the ice during heating and post-irradiation, were monitored by a quadrupole mass spectrometer (QMS). In-situ observation of the deposited ice during warm-up and/or irradiation was also made with an optical microscope. A part of the organic residues formed by warming-up was re-irradiated with UV photons at room temperature. The residual organic materials were examined with a laser microscope, an atomic force microscope, a field-emission secondary electron microscope and transmission electron microscopes. Viscoelastic measurements were performed with a nano-indentation technique.

During the warming-up of the UV-photoprocessed ice (H<sub>2</sub>O:NH<sub>3</sub>:CH<sub>3</sub>OH = 2:1:1, 5:1:1, 10:1:1 and, 2:1:0), we observed the deformation of ice film and the formation of bubbles at ~ 65 -140 K, which was not observed for non-irradiated ice. The formation of bubbles was associated with outbursts of gases mostly composed of hydrogen. The formation of bubbles indicates that the ice at low temperature behaves like a supercooled liquid.

The organic residue irradiated by UV-photon (~ 10<sup>14</sup> photons cm<sup>-2</sup> s<sup>-1</sup>) at room temperature for 3-10 days, which corresponds to ≤10<sup>4</sup>-year irradiation in diffuse clouds, showed a significant morphological change from the residues with no room-temperature UV irradiation. The porosity and roughness of the residue increased and discrete and round nanoparticles were observed that may be similar to some nanoglobules found in meteorites. Viscoelastic properties were also changed by the room-temperature UV-irradiation, indicating that organic-coating on inorganic dust could play as efficient glue on dust aggregation but, at the same time, could also enhance the aggregate brittleness.

キーワード：分子雲、有機物、光化学反応

Keywords: molecular cloud, organic matter, photochemical reaction

## 星間空間における宇宙風化を模擬した水素イオン照射実験

## Space weathering in the interstellar medium by hydrogen ion irradiation

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宇宙空間にはダストと呼ばれる固体微粒子が普遍的に存在する。ダストは主に進化末期星の大気外層や、超新星爆発で放出されたガスから生成されると考えられている。また、結晶質ケイ酸塩ダストは星周に存在するが、星間空間にはほとんど存在しないことが観測から分かっている。星間空間に結晶質ケイ酸塩が存在しない理由の一つに、結晶質ケイ酸塩の構造破壊による非晶質化が考えられる[1]。構造破壊の原因としては、1. 粒子同士の衝突、2. 宇宙線の照射、3. 超新星爆発の衝撃波によって加速された星間イオンの照射、4. 初期太陽系での太陽風照射、が考えられる。本研究では、星間空間におけるこのような破壊現象を広義の宇宙風化と呼ぶ。

星間空間での宇宙風化を模擬して、これまでにolivine、enstatite、diopsideなどへの照射実験が行われているが、実験の容易さから最も豊富なガス種である水素ではなくヘリウムイオンを使っているものが多い[1-4]。しかし、結晶内部の構造変化やプリスターとよばれる水ぶくれ構造の特徴は照射ガス種によって異なる可能性がある[5]。そこで本研究では、主にH<sup>+</sup>イオンの照射による構造変化の条件を定めることを目的とし、ダスト模擬物質へのイオン照射実験を行った。

星間ケイ酸塩ダストを模擬した物質として、olivine (San Carlos産)、enstatite(タンザニア産)、合成単結晶forsterite、serpentine((Mg<sub>2.8</sub> Fe<sub>0.2</sub>)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>)、MgSiO<sub>3</sub>組成の急冷ガラスを用いた。また、IDP、始原隕石中に豊富に含まれるとされるFeSを模擬したpyrrhotite(Fe<sub>0.9</sub>S)と、鉄隕石も用いた。試料は大きさ3x5x0.5 mmに加工し、表面は1 μm以下まで研磨後、表面を化学研磨処理した。

実験は若狭湾エネルギー研究センターで行った。加速エネルギー40keVのH<sub>2</sub><sup>+</sup>、10keVのH<sub>2</sub><sup>+</sup>イオンを用い、それぞれ照射量10<sup>16</sup>~10<sup>18</sup> ions/cm<sup>2</sup>および10<sup>17</sup> ions/cm<sup>2</sup>を照射した。照射時間が60分以上になる試料に関しては温度上昇を防ぐため水冷ステージを利用した。照射後の試料は走査型電子顕微鏡(SEM)により表面構造の変化を観察した。

olivine、enstatite、forsterite、serpentine、pyrrhotite表面にプリスターの生成が認められた。40keV H<sub>2</sub><sup>+</sup>イオンを照射した場合、プリスターが生成する照射量は、olivine、enstatite、serpentine、pyrrhotiteに関しては10<sup>18</sup> ions/cm<sup>2</sup>以上で、forsteriteは10<sup>17</sup> ions/cm<sup>2</sup>以上であった。鉄隕石とMgSiO<sub>3</sub>ガラスには表面変化は観察されなかった。10keV H<sub>2</sub><sup>+</sup>イオンを照射した場合、すべての試料から表面変化は観察されなかった。olivine、forsterite、serpentine、pyrrhotiteのプリスターは楕円形状であった。同一試料上のプリスターサイズはほぼ均一であったが、forsterite上のプリスターが最も小さく100 nmほどの大きさで、olivineとpyrrhotiteのプリスターは約3 μm、serpentineはやや大きく4-5 μmほどであった。enstatiteには波状の形状をしたプリスターが数μmの間隔で並んでいるような構造がみられた。

Matsumoto (2014)は鉄含有量の多いolivine試料に対して10 keV H<sub>2</sub><sup>+</sup>イオンを10<sup>17</sup> ions/cm<sup>2</sup>照射し、プリスター生成を示した[4]が、本研究では同様条件でプリスターを確認できなかった。これは試料の鉄含有量の違いに起因すると考えられ、鉄を多く含むolivineの方が構造が破壊されやすいことを示唆する。enstatiteに関しては、40keV H<sub>2</sub><sup>+</sup>イオンの照射でプリスター形成に必要な照射量は、先行研究で調べられた50keVのHe<sup>+</sup>イオンによる非晶質化照射料より一桁多い[2]。Pyrrhotiteに関しては、過去の1MeV Kr<sup>+</sup>イオン照射実験において結晶完全な非晶質化は認められなかったが[6]、本実験において40keV、H<sub>2</sub><sup>+</sup>、10<sup>18</sup>ions/cm<sup>2</sup>でプリスターが生成することがわかった。これらの違いはイオン質量と大きさの違いによるものであると考えられる。

今後、照射試料の内部構造を集束イオンビーム加工および透過電子顕微鏡観察により行う予定であり、SEM観察の結果と合わせて報告する。

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キーワード：宇宙風化、ダスト、照射実験、星間空間

Keywords: Space weathering, Dust, Irradiation experiment, ISM

エンスタタイト凝縮実験に向けた装置改良とSiO<sub>2</sub>-MgO蒸発実験

Development of experimental setups for condensation experiments of enstatite and evaporation experiments of SiO<sub>2</sub>-MgO

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Enstatite whiskers elongated to the [001] axis were identified in chondritic porous interplanetary dust particles (CP-IDPs), Antarctica Micrometeorite (AMM), and samples from a comet Wild 2, while those elongated to the [001] axis are common in minerals occurred in the Earth and meteorites [1-4]. The condensation conditions of enstatite whiskers, however, have not been shown quantitatively. Moreover, the difference in the morphology of enstatite whiskers may reflect their different condensation conditions in the early solar system. In order to constrain on the formation conditions of enstatite whiskers with different crystal habits, we aim to construct the experimental setup that can control the condensation temperature, supersaturation ratio, and partial pressure of a hydrogen gas. In this presentation, we report the current status of our experimental setups and preliminary results of SiO<sub>2</sub>-MgO evaporation experiments.

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キーワード：実験、凝縮、蒸発、エンスタタイト

Keywords: experiment, condensation, evaporation, enstatite

## あかり衛星による小惑星起源ダストの観測

## AKARI observations of asteroidal dust

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The zodiacal emission is the thermal emission from the interplanetary dust and the dominant diffuse radiation in the mid- to far-infrared wavelength region. From the results of the Infrared Astronomical Satellite (IRAS) observations, it was found that there are many small-scale structures in the zodiacal emission distribution, such as dust band pairs at the ecliptic latitudes of  $\pm 1.4$  and  $\pm 2.1$  degrees (the inner band) and  $\pm 9.3$  degree (the outer band). It is suggested that recent disruption events among multikilometer bodies in the main asteroid belt within the last several million years are major supply sources of the dust particles in the dust bands, and they produce a edge-brightened toroidal distributions of dust. We conducted observations of the asteroidal dust bands with the Japanese infrared satellite AKARI in mid- and far-infrared wavelengths region. AKARI clearly detects the zodiacal dust-band structures. We derived the heliocentric distances of dust bands from the AKARI observations: 1.9 AU and 2.2 AU from the Sun for the inner and the outer bands, respectively. Based on the AKARI spectroscopic observations in mid-infrared, the dust particles in the outer band show a slight different spectral shape of the silicate feature from those of other regions which are thought to be cometary origins. It is highly probable that we obtain the mid-infrared spectra of micron-sized asteroidal dust grains for the outer band regions. We will discuss the size distribution and silicate composition for the dust grains in outer bands.

キーワード：黄道光、ケイ酸塩、小惑星

Keywords: zodiacal light, silicate, asteroids

## 赤外分光法によるアモルファス氷の表面構造の解析

## Analyses of surface structure of amorphous ice using infrared spectroscopy

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In interstellar molecular clouds, water molecules deposit on dust grains, and forms amorphous ice. The amorphous ice includes various molecules such as CO, CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>CO, and so on. These molecules undergo chemical evolutions to organic molecules through various processes. Because the deposited amorphous ice has a large surface area due to its uneven structure, the surface of amorphous ice has an important role for chemical evolutions of included molecules in molecular clouds [1].

Structure of amorphous ice depends on formation condition [2], and has been mainly classified by density into two types: low-density amorphous (LDA) and high-density amorphous (HDA) ice. The densities of the LDA and HDA ice are  $0.94 \pm 0.03$  and  $1.1 \pm 0.1 \text{ g cm}^{-3}$ , respectively. Although there are various studies for structures and properties of amorphous ice in bulk states, only a few studies have been reported for surface. In the present study, the surface structure of amorphous ice was analyzed by measurements of infrared (IR) spectra for thin film of vapor-deposited amorphous ice.

Amorphous ice was prepared with vapor deposition of distilled and degassed water on a substrate of oxygen-free copper at 43 K. The deposition rate was controlled to be a value in range of 0.02-0.61 nm/min. The inner pressure of the vacuum chamber during the deposition was about  $5.0 \times 10^{-5}$  Pa. The IR spectra were measured using Shimadzu IRPrestage-21.

The spectral features change with deposition. According to the assignments of IR spectra for amorphous ice [3], the O-H stretching vibration band observed in  $2800\text{--}4000 \text{ cm}^{-1}$  was decomposed into three vibration modes (i.e., in-phase and out-of-phase modes of symmetric stretching, and asymmetric stretching mode). From the variations of the wave number of the out-of-phase mode, the variations in water structure of amorphous ice were analyzed.

The result shows that the wave number of the out-of-phase mode increases as the thickness of the amorphous ice increases, and gradually approaches a constant value of  $3480 \text{ cm}^{-1}$ . From the observed variations, the thickness of the surface layer is estimated to be around 20 nm. Furthermore, the wave numbers of the surface layer and bulk state are estimated to be  $3420$  and  $3480 \text{ cm}^{-1}$ , respectively. Because these values are close to those for HDA and LDA ice [4], the internal part of the sample is confirmed to be HDA ice. For the surface layer, the density is smaller than that of the internal part. Therefore, it is supposed that the structure is a close representation of LDA ice. Furthermore, it was found that the surface structure of the amorphous ice depends on deposition rate. From the results, we discuss the structure and dynamics of amorphous ice surface. References:

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## アモルファス氷表面構造の密度依存性

## Effects of Density on Surface Structure of Amorphous Ice

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In interstellar molecular clouds, various molecules (for instance, H<sub>2</sub>O, NH<sub>3</sub>, CO, CO<sub>2</sub>, and so on) are formed from elements such as H, C, O, and N by deposition on dust grains [1]. Most of H<sub>2</sub>O exists as a thin shell of amorphous ice around dust grain. The deposited molecules undergo chemical evolutions to organic molecule through various processes [2]. The structure of amorphous ice surface is an important factor to understand the molecular evolution in molecular clouds. Amorphous ice is formed by vapor deposition of H<sub>2</sub>O gases [3] or compression of crystalline ice [4]. The structure of amorphous ice depends on formation processes and is classified into two types: high-density amorphous (HDA) and low-density amorphous (LDA) ices [4]. To investigate the effects of internal structure on surface structure, the molecular dynamics (MD) calculations of amorphous ice were performed.

The KAWAMURA potential model [5] was used for the MD calculations. The amorphous ice was prepared by quenching a liquid phase consisting of 2760 water molecules from 280 to 235 K with 2.5 K/fs in cooling rate. After annealing at 235 K, the system was cooled to 10 K. The density of amorphous was controlled with the time period of the annealing at 235 K. An infinite surface was simulated by replicating the cell in the directions parallel to the surface using periodic boundary conditions. The pressure was kept at 0.1 MPa. The layer with 5 Å in thickness from the outmost atom was analyzed as the surface layer.

The calculations show that the density of amorphous ice at 10 K depends on the temperature history before the cooling to 10 K. In the case that the time period of annealing at 235 K was 1400 ps, for instance, the formed amorphous has the minimum density of 0.962 g/cm<sup>3</sup> at 10 K. For the case that the system was directly quenched from 300 to 10K without annealing at 235 K, the density reaches its maximum value of 1.095 g/cm<sup>3</sup>. Because a significant change of density was observed at 235 K, we controlled the density of internal part of amorphous ice with time period of the annealing at 235 K.

The result shows that the density of the surface layer is smaller than that of the internal part, and increases as the density of the internal part increases. The decrease in molecular density observed in the surface layer is attributed to the uneven structure and large amplitude of the thermal vibrations of water molecules. To investigate the contribution of the uneven structure, the radial distribution function (RDF) was calculated. The position of the second peak, which is observed at around 4.1 Å, of surface layer is about 0.3 Å large than that of internal part. This suggests that the surface layer has a lower density even if there is no unevenness. The amplitude of the thermal vibration is measured by the atomic displacement parameter (ADP). The calculation indicates that ADP of surface layer is larger than that of internal part, and depends on internal density. This result is consistent with the calculation of RDF. In the RDF result the broadening of peaks was observed for surface layer. It is concluded that the structure of surface layer is affected by density of internal part. This effect of internal structure on surface structure of amorphous ice might have important implications for molecular evolution in molecular clouds.

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## 低温真空下におけるヘルプガス含有二酸化炭素ハイドレートの形成メカニズム

## Formation of Carbon-Dioxide Clathrate Hydrates including Help Gases under Vacuum Conditions

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In interstellar molecular clouds, water molecules condense on dust grains. The condensed water exists as amorphous ice in the cold clouds and is transformed into various structures depending on thermal conditions and compositions of including molecules. Blake et al. [1] proposed the presence of clathrate hydrates in cometary ice. From the results using transmission electron microscopy and Fourier transformed infrared spectroscopy, they showed the phase transition of vapor deposited amorphous ice including CH<sub>3</sub>OH and CO<sub>2</sub> into type-II hydrate at around 120 K.

Clathrate hydrates are inclusion compounds consisting of water molecules and a variety of guest molecules. Most hydrates form one of two distinct crystallographic structures, type-I and -II, depending on the sizes and shapes of the guest molecules. The structure of CO<sub>2</sub> hydrate formed under a high-pressure condition is type-I [2]. For the hydrate from the vapor deposited amorphous ice by Blake et al. [1], the structure was type-II due to the help-gases effect of CH<sub>3</sub>OH. For the CO<sub>2</sub> hydrate grown epitaxially on a hydrate under vacuum condition, the structure depends on the structure of the hydrate as the substrate [3]. In order to investigate the formation mechanisms of CO<sub>2</sub> hydrate including help-gases under vacuum conditions, we analyzed infrared spectra of vapor deposited amorphous ice including CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>O during warming.

The CO<sub>2</sub>/H<sub>2</sub>O ratios of the prepared gas mixtures were 0.13–16.8. The gas mixtures were deposited onto a substrate of oxygen-free copper at 43 K. After the deposition, the substrate was warmed from 43 to 160 K. Infrared spectra were measured at approximately 1 min intervals during deposition at 43 K and at 2 K intervals during warming. Furthermore, CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>O mixed hydrates were prepared from gas mixtures of H<sub>2</sub>O, CO<sub>2</sub>, and C<sub>3</sub>H<sub>6</sub>O with various compositions, and were measured spectra with the same procedures.

From the variation in spectral features of H<sub>2</sub>O–CO<sub>2</sub> ice with warming, remarkable changes were found at 82 K. The wave numbers of the O–H stretching modes of H<sub>2</sub>O and the C–O asymmetric stretching modes of CO<sub>2</sub> change significantly at this temperature. Furthermore, significant gas release and exothermic temperature rise were observed. These results suggest that the crystallization of amorphous ice begins at 82 K. From the wave numbers of C–O asymmetric stretching modes, the formed crystal is determined to be type-I hydrate. From the formation conditions of CO<sub>2</sub> hydrate, we propose the phase diagram of the H<sub>2</sub>O–CO<sub>2</sub> system under vacuum conditions. In addition, the formation processes of mixed hydrate including CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>O were analyzed. The result shows that the transition temperature of the mixed hydrate depends on the guest composition. From the results, we discuss the formation mechanisms of clathrate hydrates under vacuum conditions.

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## アンモニアのモンモリロナイト及びサポナイトへの吸着・脱着に伴う窒素同位体分別

## Nitrogen isotopic fractionation of ammonia accompanied with adsorption-desorption process on montmorillonite and saponite

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Solar system objects show wide variation in the nitrogen isotopic composition. The  $\delta^{15}\text{N}$  value (‰, normalized as vs. Air) ranges from -400‰ in the solar wind [1] and Jovian atmosphere [2] to around +1500‰ of comets, chondrites, and interplanetary dust particles (IDPs)[3, 4]. These pristine solar system materials also show occasional extreme  $^{15}\text{N}$ -enrichment up to +5000‰ [5, 6]. This  $\delta^{15}\text{N}$  variation in the solar system objects is considered to have been inherited from the cold interstellar environments [7]. However, only a few models can explain the interstellar chemistry to enhance  $^{15}\text{N}$ -enrichments, such as photodissociation of nitrogen molecules and subsequent formation of ammonia [8], and conceivable isotopic fractionation processes have not well understood.

In the study, we conducted simple adsorption-desorption experiments using ammonia gas and two clay minerals (montmorillonite and saponite). From the results, we propose the adsorption-desorption process of ammonia on grain surface of interstellar dusts as a potential mechanism for  $^{15}\text{N}$ -enrichment in interstellar environments. Ammonia is a simple nitrogen-containing molecule and one of major nitrogen carriers in the molecular clouds. It is a highly reactive chemical and regarded as a precursor for other complex nitrogen-containing molecules. Thus, adsorption of ammonia could be a first step for grain surface chemistry to form more complex organic molecules. The adsorption-desorption experiments were performed to examine the possibility of nitrogen isotopic fractionation of ammonia by adsorption and desorption on the clay minerals. Each clay mineral sample, with controlled amount of water (0, 5, 10, 20 wt.% vs. dry clay minerals), was sealed into the glass serum bottles with ammonia gas (+27‰, SI Science). The glass vial was rested for a week under room temperature (25°C) to reach a stable state before analysis. After the initial analysis was completed, the glass vial was vacuumed for 1 to 8 hours to examine the results under vacuumed environment. The nitrogen isotopic composition of the adsorbed ammonia at each step of the experiments was determined by nanoEA/IRMS technique [9].

The results showed that adsorbed ammonia generally had larger  $\delta^{15}\text{N}$  value than the initial ammonia gas. The degree of isotopic fractionation from the initial ammonia were +2.4~+40.3‰ for montmorillonite and -1.6~44.4‰ for saponite as  $\Delta^{15}\text{N}$  value. There was also a negative correlation observed between the adsorbed ratio (wt. %) and the  $\delta^{15}\text{N}$  value. When the glass vial was vacuumed for only 1 hour, the  $\delta^{15}\text{N}$  of the remaining ammonia increased (+64.1‰ for montmorillonite and +60.1‰ for saponite as  $\Delta^{15}\text{N}$  value). However, when the glass vial was vacuumed more than 1 hour, selective removal of  $^{15}\text{NH}_3$  was observed. The water content of the sample was not an influential factor throughout the experiments. The results suggest that adsorption and desorption of ammonia on clay minerals causes significant nitrogen isotopic fractionation ( $\Delta^{15}\text{N}=-1.6\sim+64.1\%$ ) and could be a potential mechanism for  $^{15}\text{N}$ -enrichment in interstellar environments.

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Keywords: nitrogen isotopic fractionation, adsorption, ammonia, molecular clouds, grain surface chemistry

## 星間氷を模擬した光化学反応実験生成物のアミノ酸分析

## Amino acid analysis of photochemically processed interstellar ice analogues

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Amino acids are one of major constituent of living organisms on the Earth, so they are essential molecules for the origins of life. Many scenarios for the endogenous production of amino acids on the early Earth have been proposed [e.g., 1, 2]. On the one hand, the extraterrestrial delivery of them is also considered as a likely candidate [e.g., 3, 4]. Carbonaceous chondrites are known to contain abundant amino acids up to 250 ppm [5] and more than 80 species were identified [6]. In addition, the simplest amino acid: glycine was also detected in the cometary grains returned by stardust mission [7]. The extraterrestrial amino acids are considered to have been formed by aqueous alteration on the meteoritic parent bodies or in the presolar interstellar environments. Although, the formation process, as well as the place to be taken, is still on a debate, the existence of amino acid in comets as well as the isotopic signatures of them suggest that at least some amino acids and the precursors of them are interstellar origin [8].

In the study, we conducted laboratory experiments to synthesize interstellar ice analogues from typical interstellar gases and analyzed their amino acid composition. For the experiments that simulate the condition in the interstellar medium (ISM), we utilized an apparatus called PICACHU: Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University. In this PICACHU apparatus, the typical ISM gases ( $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3 = 2:1:1$ ) were introduced into the chamber and deposited onto the surface of a sappier glass there, which were refrigerated at  $\sim 12$  K. During the deposition of the ice, UV photons were continuously irradiated under highly vacuumed condition for 71 hours, because photochemical reactions in the ice, which were processed by stellar ultraviolet (UV) photons and cosmic rays, are important for the formation of complex organic molecules in ISM. In addition, we made two ice samples and one of them was further irradiated by UV for 232.5 hours after heated to room temperature in order to simulate subsequent decomposition in warmer environments. Then, the organic residues of the two ice samples were extracted by methanol and analyzed by GC-MS and GC/NPD after the derivatization for GC analysis.

The results showed that 11 species of amino acids were formed in the interstellar ice analogues, which were irradiated only at  $\sim 12$  K. The most abundant amino acid was glycine and the second most abundant one were  $\beta$ -alanine and alanine. Their abundances are about fourth of that of glycine. The abundance of each amino acid generally decreased with the increase of the carbon number of the amino acids. This trend was consistent with the previous study [9]. Then, the further irradiated sample showed the general decrease in the abundances of amino acids, but some of them were still remained. The survived ratio differed among amino acids and glycine was the most resistant to the irradiation ( $\sim 80\%$  remained.). These results indicate that amino acids can be formed by the UV irradiation to the interstellar ice and can survive subsequent irradiation in the warmer environments.

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