Methane and HDO/H2O in the Martian atmosphere studied by ultra-high spectral resolution

*Hiromu Nakagawa[1], Shohei Aoki[3], Hideo Sagawa[4], Kosuke Takami[1], Yasumasa Kasaba[1], Isao Murata[1], Guido Sonnabend[6], Manuela Sornig[7], Takeshi Sakanoi[2], Masato Kagitani[2], Kuhn Jeffrey[8], Ritter Joseph[8], Shoichi Okano[2], Makoto Taguchi[5]

1.Planetary Atmosphere Physics Laboratory, Department of Geophysics, Graduate School of Science, Tohoku University, 2.Planetary Plasma and Atmospheric Center, Graduate School of Science, Tohoku University, 3.Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di AstroFisica, 4.Faculty of Science, Kyoto Sangyo University, 5.Rikkyo University, 6.Radiometer Physics GmbH, 7.German Aerospace Center, 8.Institute for Astronomy, University of Hawaii, Advanced Technology Research Center

The Mid-Infrared LAser Heterodyne Instrument (MILAHI), which operates onboard the dedicated Tohoku 60cm telescope (T60) at the summit of Mt. Haleakala, has been designed for investigating the trace gases (Methane, HDO/H2O, etc) in the terrestrial atmospheres, such as Mars and Venus. The limitation to detect such trace gases from the ground-based is mainly due to the difficulty of correcting the atmospheric absorptions in the Earth atmosphere. High spectral resolution of MILAHI (>10E6) enables to retrieve them without any ambiguity due to the reproduction of atmospheric spectra on Earth.
In this study, we focus on the detection of methane and HDO/H2O in the Martian atmosphere. As a local oscillator (LO), newly installed quantum cascade laser (QCL) nicely covers 7.7 micron wavelength for these molecules. It is the only IR heterodyne instrument that gives access to new spectral range as compared with previous instruments of this kind.
Because the facility/instrument is just becoming to be operational in these years, the first Mars campaign will be performed on Feb.-Mar. 2016, with large Doppler shift (~15 km/s) between Mars and Earth. Prediction of the radiative transfer model indicates that the determination with two- VSMOW precision could be obtained by 15-minute integration. Upper limit 100ppb of methane will also be determined by 32-hours integration.
Further continuous observations will help to constrain (i) the possibility of biological/geological activities in the current Martian atmosphere, and (ii) water cycle and its evolution on Mars.

Keywords: Methane, HDO/H2O, Heterodyne

Primordial Anorthositic Continent on Mars and Planetary Habitability

*James Dohm[1], Shigenori Maruyama[2]

1.University Museum, University of Tokyo, 2.Earth-Life Science Institute, Tokyo Institute of Technology

The Moon has primordial continental crustal materials consisting of anorthosite. Anorthosite has been recently discovered on the Martian surface as well, with occurrence possibly extensive similar to the lunar-like global anorthosite crust [1]. A felsic primordial Martian crustal basement, in addition to anorthosite, may include andesite [2] and granite [3]. A key example of this may be the conglomeratic alluvial-fan materials of Peach Vallis in Gale crater which are interpreted to be representative of the ancient felsic crust [4] of Terra Cimmeria exposed by the Gale impact [5]. Terra Cimmeria is one of the ancient geological provinces of Mars, dated to be > 4.0 Ga based on impact crater statistics, stratigraphy, and magnetic data, which records major contractional, transtensional, and extensional tectonism [6]. In the case of the Earth, the occurrence of anorthosite is observed to be limited in the geological record, however, lunar and Martian surface geology indicates that anorthosite was likely more universal on the Earth as primordial continent during the first 600 million years after its formation.Difference in the presence of an anorthositic continent is due to the size of planet. The reason why the primordial continent of the Earth disappeared is explained by the strength and duration of mantle convection. On Mars, due to its size and relatively rapid heat loss, a proposed early phase (~>3.93 Ga) of plate tectonism shut down [7] before the primordial crust could be destroyed.The presence of a primordial continent is the essential and most significant factor as it determines the fate of the planet to be habitable or not. The key is to have limited amount of an initial ocean to emerge a significant extent of primordial continent at the surface, as well as to operate plate tectonics on the planet [8].When this logic is applied to a super-Earth, it suggests that a primordial continent forms on the surface but that the continent is transported into the deep mantle due to strong mantle convection immediately following its formation. After the primordial continent disappears from the surface of the planet, the supply of nutrients necessary for life terminates. Even if a primordial ocean existed on the surface of a super-Earth, the ocean would disappear before life emerges. Therefore, there is very little chance for life to emerge on a super-Earth. Mars, on the other hand, may hold significant environmental information not only about extremely ancient Mars and the solar system, but also possible early life. References: [1] Carter, J., Poulet, F. (2013) Nature Geoscience 6, 1008-1012. [2] Bandfield, J.L. et al. (2000) Science 287, 1626–1630. [3] Wray, J.J. et al. (2013) Nature Geoscience 6, 1013-1017, doi:10.1038/ngeo1994. [4] Sautter, V. et al. (2015) Nature Geoscience, doi:10.1038/ngeo2474. [5] Anderson, R.C. et al. (2015) GSA Annual Meeting in Baltimore, Paper No. 203-11. [6] Dohm, J.M. et al., 2013. In "Mars Evolution, Geology, and Exploration", Nova Science Publishers, Inc., pgs. 1-34. [7] Baker, V.R. et al. (2007) In “Super-plumes: Beyond plate tectonics”, Springer, p. 507–523. [8] Maruyama, S. et al., 2013. Geoscience Frontiers 4, 141-165.

Keywords: Mars, anorthosite, Earth, Moon, habitable trinity

Analysis of amino acids synthesized in a gas plume by projectile-impact in nitrogen gas (Model experiment of asteroid's impacts)

*Tetsu Mieno[1], Hitomi Abe[2], Kazuki Okochi[5], Sunao Hasegawa[3], Hiromi Shibata[4], Yoko Kebukawa[1], Kensei Kobayashi[2]

1.Grad. School of Sci. & Technol., Shizuoka Univ., 2.Grad. School of Eng., Yokohama National Univ., 3.ISAS, JAXA, 4.Fac. Eng., Osaka Univ., 5.Grad. School of Sci., Shizuoka Univ.

When asteroids have impacted onto Titan with atmosphere, hot gas-plumes were formed, in which many kinds of organic molecules and clusters could have synthesized, and the products deposited on the surface. To make clear these hypothetical reactions, simulations experiment has been carried out using a JAXA 2-staged gas-gun. [1] A polycarbonate bullet (7.1 mm diam.) is accelerated to 7 km/s and impacted onto an iron target in a pressurized chamber, where nitrogen pressure is 1 atm (On the iron target, ice or ice+ hexane layer is set). Immediately after the impact, a hot and bright gas plume appears and grows to the size of 10 cm for about 25 us. Then, it is cooled and disappears. In the gas plume, many kinds of organic molecules and nano-particles are synthesized and deposit on the inner surface of the chamber as black soot. This soot is carefully collected and analyzed. Collected soot is refluxed and the extracted liquid is dubsyllized (labeled) and measured by HPLC. As a result, amount of amino amino acids (glycine and alanine) are detected. [2] Especially, in case of the hexane + ice + iron target, the amount of amino acids increased. In 1 mg of the soot, about 2 nmol of glycine is included. By several contamination tests, it can be concluded that these amino acids are synthesized by the impact reaction. Then, 6 M of HCl is added in the produced soot and hydrolysis at 110 C for 24 hrs is carried out. After deionization, the cation-ion HPLC analysis is carried out. [3] As a result, glycine, alanine, aspartic acid, γ-aminobutyrate, etc are detected. The amount is much larger by the hydrolysis. This mean that the amino acids are generated in the form of precursors. To prove the effect of contamination, D/L ratio of the amino acids will be measured. We will also do the impact experiment by changing the experimental conditions. On the other hand the sample is measured using FT-IR and LD-TOF-MS. And we could confirm that there are amount of amino acids in the soot samples. Titan has nitrogen atmosphere and has been impacted by huge number of asteroids. Now we demonstrated the synthesis of amino acids by the impact experiment. Therefore, we could consider that large amount of amino acids were produced and stored on Titan. References: [1] T. Mieno, S. Hasegawa, "Production of carbon clusters by impact reaction using light-gas-gun in experiment modeling asteroid collision", Appl. Phys. Express 1(2008) 067006-1-3.[2] K. Okochi, T. Mieno, K. Kondo, S. Hasegawa, K. Kurosawa, "Possiblity of Production of Amino Acids by Impact Reaction Using a Light-Gas Gun as a Simulation of Asteroid Impacts", Orig. Life Evol Biosph 45 (2015) 195-205.[3] T. Horiuchi, Y. Takano, K. Kobayashi, K. Marumo, J. Ishibashi, T. Urabe, "Amino acids in water samples from deep sea hydrothermal vents at Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean", Org. Geochem., 35 (2004)1121-1128.

Keywords: impact of asteroid, Titan, synthesis of amino acids, hog gas plume, gas gun experiment

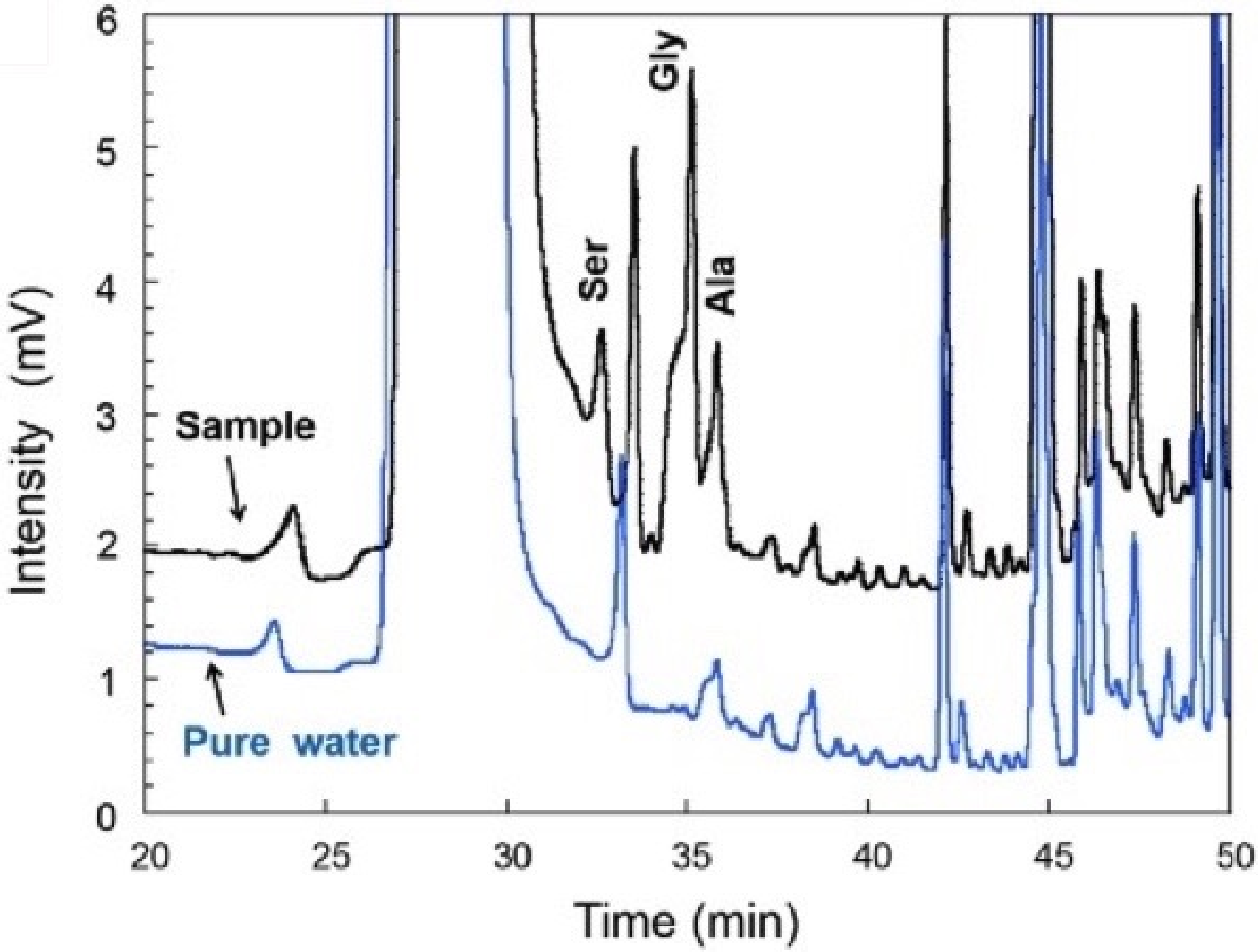

Fig. 1 HPLC chart of the sample refluxed by pure water and dabsylized, where the ice + hexane + iron target is used. The chart of dabsyliezed water is also shown. (quoted from ref. 2.)

Formation of Super-complex Amino Acid Precursors in Interstellar Ice Analogues by Particles Irradiation

*Kensei Kobayashi[1], Tomoyuki Matsuda[1], Shingo Enomoto[1], Midori Eto[1], Yoko Kebukawa[1], Hajime Mita[2], Satoshi Yoshida[3], Hitoshi Fukuda[4], Kotaro Kondo[4], Yoshiyuki Oguri[4]

1.Department of Chemistry, Yokohama National University, 2.Faculty of Engineering, Fukuoka Institute of Technology, 3.National Institute of Radiological Sciences, 4.Tokyo Institute of Technology

A large number of amino acids have been detected in extracts of carbonaceous chondrites, and their relevance to the origin of life on the Earth is discussed. There are several scenarios of the formation of such extraterrestrial amino acids or their precursors. One of them is the interstellar model proposed by Greenberg et al. (2002): Volatiles such as water, carbon monoxide, methanol and ammonia were frozen onto the surface of interstellar dust particles (ISDs) in dense clouds to form ice mantles. The ice mantles were irradiated with cosmic rays and UV induced by cosmic rays, and complex organic compounds were formed in the ice mantles. Such dusts with organics were aggregated into planetesimals or comets when the solar system was formed. Organic compounds were survived with some alteration during the formation of small bodies to be cometary / meteoritic organic compounds.
In order to examine possible formation of complex molecules in ISD ice mantles, a frozen mixture of water, methanol and ammonia was irradiated with high-energy carbon ions (290 MeV/u) from HIMAC, NIRS, Japan. For comparison, gaseous mixtures of water, ammonia, carbon monoxide, carbon dioxide, and/or methane were irradiated with protons (2.5 MeV) from a Tandem accelerator, Tokyo Tech, Japan. Amino acids were determined by cation exchange HPLC before and after acid hydrolysis. Products, both before and after acid hydrolysis, were analyzed FT-IR for characterization.
Heavy ion irradiation of the liquid mixtures also yielded amino acids after hydrolysis. When ratio of CH_3OH and NH_3 to H_2O were decreased, amino acid yield decreased, but even in the case of CH_3OH: NH_3: H_2O = 10: 1: 37 (close to those of some of the observed interstellar ices), amino acids were detected. In the HIMAC experiment, the energy of heavy ions were quite high and pass through the target mixtures with only small part of energy was deposited to the target, which is the same situation as what happens in dense clouds. The present results suggested that amino acid precursors can be formed in water-rich ice mantles of interstellar dust particles (ISDs) by the action of cosmic rays.
When gaseous mixtures of possible interstellar media were irradiated, it was shown that carbon monoxide gave much more glycine than methane as a carbon source. However, methane was an important starting material to give alanine and other amino acids with aliphatic side chains.
Actual interstellar ices are complex mixtures of carbon monoxide, methanol, methane, formaldehyde, ammonia and so on. We can expect that a wide variety of molecules including precursors of many kinds of amino acids and nucleic acid bases could be formed in interstellar ices by cosmic rays.

Keywords: Ice mantles of interstellar dust particles, Amino acids, Super-complex organic molecules, Cosmic rays, Heavy ions bombardment

Current status of Tanpopo: Astrobiology Exposure and Micrometeoroid Capture Experiments at the Exposure Facility of ISS-JEM

*Akihiko Yamagishi[1], Hirofumi Hashimoto[2], Hajime Yano[2], Shin-ichi Yokobori[1], Eiichi Imai[3], Makoto Tabata[4], Hideyuki Kawai[4], Kensei Kobayashi[5], Hajime Mita[6], Hikaru Yabuta[7], Masumi Higashide[8]

1.Tokyo University of Pharmacy and Life Science, Department of Molecular Biology, 2.ISAS/JAXA, 3.Nagaoka Univ. Tech, 4.Chiba Univ., 5.Yokohama Natl. Univ., 6.Fukuoka Inst. Tech., 7.Osaka Univ., 8.JAXA

Tanpopo, a dandelion in Japanese, is a plant species whose seeds with floss are spread by wind. We proposed this mission to examine possible interplanetary migration of microbes, and organic compounds at the Exposure Facility of Japan Experimental Module (JEM: KIBO) of the International Space Station (ISS). The Tanpopo mission consists of six subthemes: Capture of microbes in space (Subtheme 1), exposure of microbes in space (Subtheme 2), analysis of organic compounds in interplanetary dust (Subtheme 3), exposure of organic compounds in space (Subtheme 4), measurement of space debris at the ISS orbit (Subtheme 5), and evaluation of ultra low-density aerogel developed for the Tanpopo mission (Subtheme 6). Exposure Panels for exposure of microbes and organic materials and Capture Panels for aerogel were launched on April 2015. The Panels were placed on the Exposed Experiment Handrail Attachment Mechanism (ExHAM) in the ISS. The ExHAM with Panels were placed on the Exposure Facility of KIBO (JEM) with the Japanese robotic arms through the airlock of KIBO. The trays and panels will be exposed for more than one year and will be retrieved and returned to the ground for the analyses.

Keywords: Space experiment, International space station, Microbes, Organic compounds, Silica aerogel

THE FIRST YEAR OPERATION AND INITIAL SAMPLE ANALYSIS AND CURATION REHEARSALS OF THE TANPOPO ASTROBIOLOGY EXPERIMENTS

*Hajime Yano[1], Satoshi sasaki[2], Junya Imani[2], Yuichi Yaguchi[3], Eiichi Imai[7], Makoto Tabata[4], Kyoko Okudaira[3], Yoko Kebukawa[5], Yukihiro Ishibashi[6], Hajime Mita[8], Takashi Ozawa[9], Mayumi Higashide[9], Yuko Kawaguchi[11], Daiki Horikawa[10], Akihiko Yamagishi[11]

1.Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, 2.Tokyo Univeristy of Technology, 3.University of Aizu, 4.Chiba University, 5.Yokohama National University, 6.Kyushu University, 7.Nagaoka University of Technology, 8.Fukuoka Institute of Technology, 9.Research and Development Directorate, Japan Aerospace Exploration Agency, 10.Institute of Advanced Biosciences, Keio Univeristy , 11.Tokyo University of Pharmacy and Life Sciences

Launched in April, 2015, the “TANPOPO” mission has beocme the first astrobiology space experiment of Japan. It aims to test various aspects of the “quasi-panspermia” hypothesis for exogenesis origin of life precursors and their interplanetary transport [1]. In May and November 2015, the first year samples were installed on two sets of the“ExHAM” pallet on the handrail of the ISS-Japan Experiment Module (JEM) Exposed Facility (EF) in the duration of 1-4 years. The TANPOPO experiment consists of following six sub-themes: 1) capture of microbes in space, 2) exposure of microbes in space, 3) exposure of organic compounds in space, 4) capture of organic compounds in micrometeoroids in space, 5) evaluation of ultra low-density aerogel developed for the Tanpopo mission, and 6) capture of space debris at the ISS orbit.
In 2015-2019, the TANPOPO employs blocks of the the least dense aerogels among past space missions as 0.01 g/cc [2] on the Capture Panels (CP) that will be exposed and retrieved to capture impacting solid microparticles such as organic-bearing micrometeoroids and possible terrestrial particles in the low Earth orbit. By analyzing captured micrometeoroids in the CPs, one can learn what kinds of extra-terrestrial organic compounds inside micrometeoroids to be transported from parent bodies and how they may be altered in outer space. Also by evaluating retrieved samples of exposed terrestrial microbes and astronomical organic analogs on the exposure panels, one can investigate their survivals and alterations in the duration of interplanetary transport.
If microparticles of terrestrial origin are ever impacted into the CPs, one can prove that terrestrial microbes (e.g., aerosols embedding microbial colonies) may be present, even temporarily and in “freeze dry” form in the low earth orbit altitudes.
The TANPOPO-Initial Sample Analysis and Curation (ISAC) has been in its rehearsal since January 2016 and will be conducted by its Preliminary Examination Team (PET) as soon as the first samples will be returned to the Earth after summer of 2016.
The ISAC plan for CPs covers the receipt of retrieved samples, their initial inspection and documentation, processing and distribution of the samples for detailed analyses of each sub-theme, cataloging for data archiving and sample storage. For initial inspection and documentation, they will map and measure aerogel penetration tracks and captured particles (e.g., incoming angle, track depth and track volume) by the original keystone machine at ISAS clean room. Then they will process keystones containing microparticles to be inspected further and their penetration tracks for allocation to respective sub-theme researchers, in accordance with their requests for the subsequent detailed analyses within the first 100 days after the Earth sample return [3].
References: [1] Yamagishi A. et al. 2009. *Trans. JSASS Space Tech. Jpn.* 7: Tk 49-Tk 55. [2] Tabata M. et al. 2011. *Biol. Sci. Space*. 25: 7-12. [3] Yokobori S. et al. 2009. *Life Evol. Biosph*. 39: 377-378.

Keywords: astrobiology, space experiment, micrometeoroids, panspermia, microbes

STXM-XANES analyses of Murchison meteorite powders captured by aerogel after hypervelocity impacts: A potential implication of organic matter degradation for micrometeoroid collection experiments

*Yoko Kebukawa[1], Kyoko Okudaira[2], Hikaru Yabuta[3], Aiko Nakato[4], David Kilcoyne[5], Sunao Hasegawa[4], Makoto Tabata[6], Kensei Kobayashi[1], Shin-ichi Yokobori[7], Ei-ichi Imai[8], Yuko Kawaguchi[7], Hajime Yano[4], Akihiko Yamagishi[7]

1.Yokohama National University, 2.University of Aizu, 3.Osaka University, 4.Japan Aerospace Exploration Agency, 5.Lawrence Berkeley National Laboratory, 6.Chiba University, 7.Tokyo University of Pharmacy and Life Sciences, 8.Nagaoka University of Technology

The ultralow-density silica aerogel (0.01 g/cm^3) has been developed at Chiba University [1], and is used as a dust capture medium in the Tanpopo mission that is an ongoing Japanese astrobiology space experiment at the Japanese Experiment Module (JEM) ‘Kibo’ on the International Space Station (ISS) [2]. One of the purposes of this mission is capturing micrometeoroids around the ISS orbit. The low-density aerogel is expected to reduce shock-degradation of materials by hypervelocity impacts (several kilometers per second), as previously used to capture the cometary dust particles from the Comet 81P/Wild 2 in the STARDUST mission [e.g. 3]. In order to evaluate potential degradation of the micrometeoroids by hypervelocity impact to the aerogel, we conducted the simulation experiments using a two-stage light-gas gun and Murchison meteorite as a micrometeoroid analog material. We conducted X-ray absorption near edge structure (XANES) analyses for the particles recovered from the impacts, using a scanning transmission X-ray microscopy (STXM).

Two-stage light-gas gun experiments were conducted at the Space Plasma Laboratory, ISAS/JAXA. We fired Murchison powder (micron-sized grains) into silica aerogels (0.01 g/cm^3) by shotgun method. In shot #399, 30-100 micron sized powder was fired at 4.4 km/s at a vacuum degree of 7.5 Pa, while in shot #1473, 37-60 micron sized powder was fired at 5.9 km/s at a vacuum degree of 9.5 Pa. Several grains of the Murchison meteorite manually extracted from the aerogel were embedded in sulfur separately, and sliced into 100 nm-thick sections with an ultramicrotome equipped with a diamond knife. Before analysis, the sections on the SiO-coated Cu TEM grids were mildly heated (<100°C, <15 min) until the sulfur sublimated off the grids. C-, N- and O-XANES analyses were performed for two grains from each shot (4 in total) using the STXM at beam line 5.3.2.2 in the Advanced Light Source, Lawrence Berkeley National Laboratory.

STXM images and elemental maps for C, N and O showed no clear evidences for surface degradation, nor differences between surface and interior of the sections of the Murchison grains after the experiments, although there were some heterogeneity of the elemental distributions and textures. Note that the heterogeneity of the elemental maps partially attribute to heterogeneity of the sample thickness that is mostly due to large porosity of this meteorite. The sizes of the analyzed ultramicrotomed sections that roughly represent the recovered grain sizes were in the range of 10 to 25 μm for shot #399, and in the range of 10 to 40 μm for #1473. The C-XANES were obtained at least a few micrometer inside of the grains. The C-XANES spectra of the Murchison after the 4.4 km/s shot have organic features at 285.0 eV assigned to aromatic/alkene C=C, absorption at 286.7 eV is assigned to ketone C=O, absorption at 287.5 eV is assigned to aliphatic C–C, absorption at 288.7 eV is assigned to carboxyl O–C=O, but in the case of the 5.9 km/s shot, most of these features disappeared. All sections show abundant oxygen mainly from silicates with some contributions from organics, but show low nitrogen contents. The results indicate that the Murchison grains recovered after 4.4 km/s impact into the 0.01 g/cm^3 aerogel seem generally intact, but the grains recovered after 5.9 km/s impact show drastic changes in organic structure. Although further discussion is required on the size effects, the threshold impact velocity for organic survivability might be between 4.4 and 5.9 km/s. At least, organic matter in micrometeoroids with entry velocity of ~4.4 km/s or less can survive from the impact to the 0.01 g/cm^3 silica aerogel.

References:
[1] Tabata M. et al. (2015) OLEB, 45, 225-229.
[2] Yamagishi A. et al. (2009) Trans. JSASS Space Tech. Japan, 7, Tk_49-Tk_55.
[3] Brownlee D. et al. (2006) Science, 314, 1711-1716.

Keywords: Micrometeoroids , Tanpopo mission, STXM-XANES, Carbonaceous chondrites

Pressure-induced formation of alanine oligopeptides at 25 °C

*Chikako Fujimoto[1], Ayako Shinozaki[2], Koichi Mimura[2], Tamihito Nishida[2], Hirotada Gotou[3], Kazuki Komatsu[1], Hiroyuki Kagi[1]

1.Geochemical Laboratory, Graduate School of Science, University of Tokyo, 2.Graduate School of Environmental Studies, Nagoya University, 3.Institute for Solid State Physics, University of Tokyo

Introduction

Oligomerization of amino acids can provide a clue to the origin of life because it is a fundamental step of protein synthesis. Under high pressure, increases of intermolecular interactions result in chemical reaction which cannot proceed under ambient condition. Oligomerization of amino acids was reported from experiments under high pressure and high temperature conditions simulating impact of comets, hydrothermal vents, diagenesis in sub-seafloor sedimentary environments (e.g., Sugahara and Mimura, 2015; Imai and Honda, 2010; Otake et al., 2011). In these experiments, both high pressure and high temperature are the important factors for amino acids oligomerization. However, it is unknown which factor is more efficient for forming oligomers. In this study, we focus on exclusive effect of high pressure on oligomerization reaction. We tested oligomerization of L-alanine under a room temperature and high-pressure condition. Fujimoto et al. (2015) reported pressure-induced oligomerization of L-alanine up to the trimer using GC-MS analysis (Fig 1). In the present study, we used LC-MSMS to detect higher oligomers.

Experimental procedures

All high-pressure experiments were carried out at 25 °C. Starting material was loaded in a high-pressure cell with three different conditions: wet, dry and solution (wet: L-Alanine powder with its saturated aqueous solution. dry: L-alanine powder. solution: saturated L-alanine aqueous solution.). Sample was compressed using a large-volume opposed-anvil apparatus or a “Kawai-type” multi-anvil apparatus. Experimental runs were conducted at pressures of approximately 5 GPa, 7 GPa, 9 GPa, 11 GPa, and 16 GPa using an opposed-anvil apparatus and 18 GPa and 23 GPa using a multi-anvil apparatus. After decompression to ambient pressure, run products were dissolved in pure water and analyzed using LC-MSMS.

Results and discussion

Alanine dimer was detected from all the run products. With increasing pressure, the yields of alanylalanine increased for each experimental condition (wet, dry, and solution). At pressures higher than 9 GPa, formation of alanine trimer was detected and the yield increased with pressure. These results are consistent with the results of Fujimoto et al. (2015). It is noteworthy that oligomerization of alanine occurred under water-coexisting conditions. In the pressure and temperature conditions applied in this study, water in the samples existed as ice VII, the oligomerization observed here was a solid-phase reaction. Higher oligomers were detected from the samples recovered from high pressure. Under the wet condition, the formed oligomers decreased with increasing the oligomer size and the largest oligomer detected was 8-mer.

This study revealed that oligomerization of amino acids occurs under high pressure at room temperature with existence of water as ice VII which is known to exist in the interiors of icy planets. This study proposes an interior of an icy planet as a new abiotic condition for oligomerization of amino acids.

Keywords: amino acids, high pressure, oligomerization

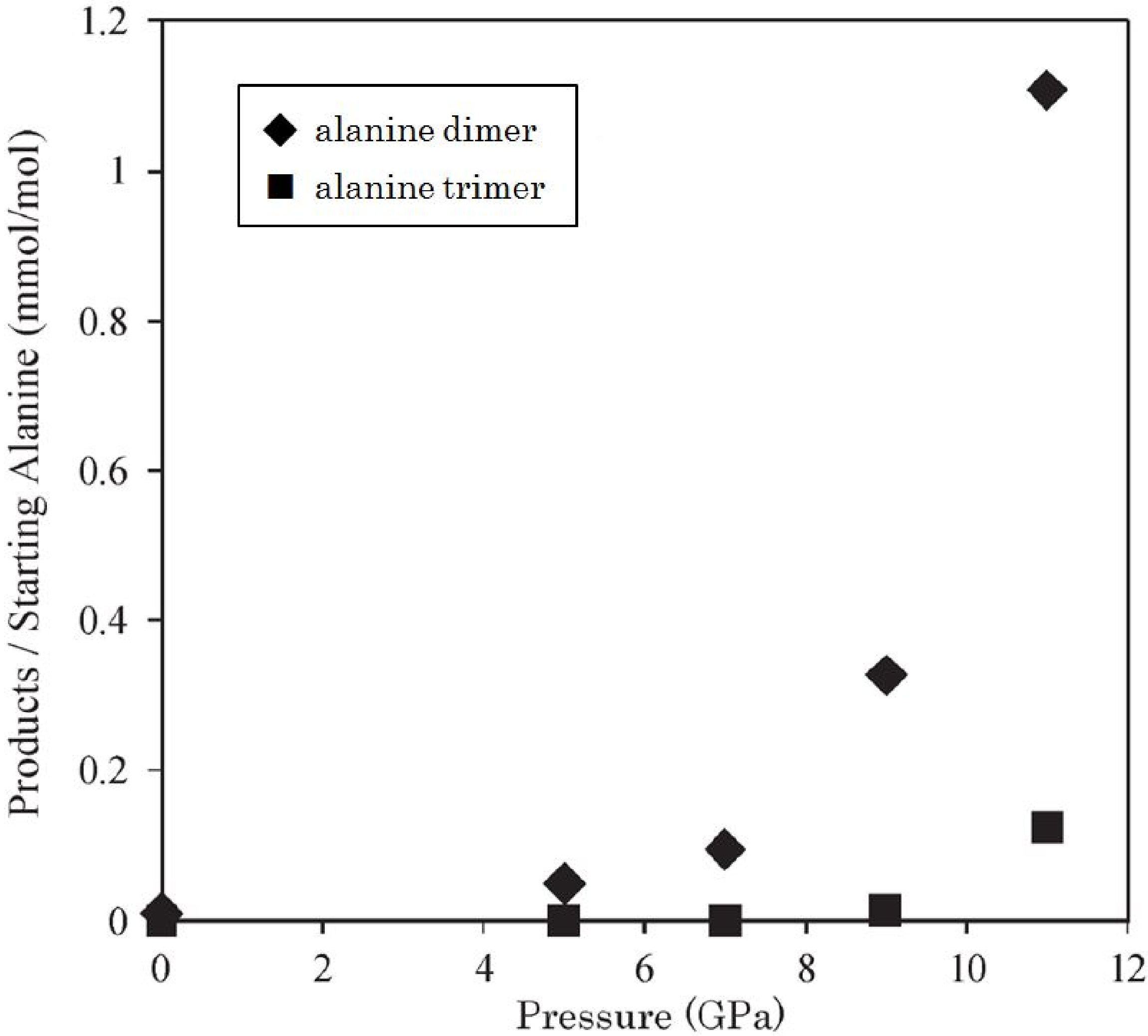

Fig. 1 Molar ratios of alanine dimer and trimer to starting alanine vs. pressure. (Fujimoto et al., 2015)

Epimerization of oligopeptides induced by radiation rays

*Toratane Munegumi[1]

1.Department of Science Education, Naruto University of Education

Proteins just after translation are composed of L-form homochiral amino acids. The formation process of homochiral polypeptides, which are fundamental for proteins, has not been elucidated. Although many hypotheses have been proposed, most of those relate to explaining the one-handed structure of amino acids. This research focuses the reactivity of oligopeptides to discuss epimerization of oligopeptides induced by irradiation using gamma rays and discharges, and the difference in epimerization rate between diastereomers.
Linear and cyclic alanine dipeptides were irradiated in solution or as solid state by gamma rays (1-24 kGy). The resulted reaction solutions were analyzed by means of HPLC equipped with achiral or chiral columns. Linear L-Ala-L-Ala epimerized faster (reaction rate constant: 0.017kGy^{-1}) than D-Ala-L-Ala (0.0033kGy^{-1}) in 1mM solutions. This suggests that such reaction conditions are not suited for accumulation of homochiral peptides. However, the results in the reactions using cyclic dipeptides showed heterochiral peptides epimerizes faster than homochiral peptides.

Keywords: epimerization, oligopeptides, gamma rays

Big Bang of life: unique composition of organic molecules at >3.95 Ga

*Kunio Kaiho[1], Ryosuke Saito[1], Tsuyoshi Komiya[2], Wladyslaw Altermann[3], Martin Van Kranendonk[4]

1.Graduate School of Science, Tohoku University, 2.University of Tokyo, 3.University of Pretoria, 4.University of New South Wales

The earliest life on Earth may have appeared at approximately 4.0 billion years ago (Ga) based on analyses of molecular clocks. However, there is no evidence of early life between 4.0 and 3.7 Ga. The type of the earliest life is also unknown. Here, we report that organic molecules derived from the earliest life have been detected from the oldest shallow-sea sedimentary rocks from Labrador, Canada, the age of which is >3.95 Ga. These molecules have two unique features: (1) branched alkanes (methyl- and ethyl-) and squalane exclusively dominate in these rocks; (2) *n*-alkanes and branched alkanes possess strong even-over-odd predominance in the number of carbons. These features have not been found in strata younger than 3.5 Ga. Among these molecules, it is difficult for squalane to be produced by non-biological processes. The dominance of squalane, which is derived from squalene, a constituent of archaeal lipid and precursor of both eukaryotic (sterol) and prokaryotic (hopanoid) lipids, suggests that this is a fundamental organic molecule of life common to all three domains, i.e., prokaryotes, archaea, and eukaryotes. This unique composition changed to a more normal composition between >3.95 Ga and 3.48 Ga. This change looks like dawn of the universe, i.e. Big Bang, because the unique type of life that occurred during this first short period of <0.5 billion years was followed by the current type of life that has persisted for >3.5 billion years. Giant impact of asteroids on Earth occurred between 4.03 and 3.85 Ga (Late Heavy Bombardment) evidenced by ages of impact craters of the moon. Those impacts could have eradicated the early life found in Labrador followed by emergence of the current type of life on Earth.

Keywords: early life, organic molecules, Late Heavy Bombardment, Archean

Significance of pyrobitumen in ca. 1.9 Ga Gunflint Formation: Unique feature of Paleoproterozoic Earth?

*Takeshi Kakegawa[1]

1.Graduate School of Science, Tohoku University

Occurrence of pyrobitumen has been known in Paleoproterozoic sedimentary rocks. However, their exact age, source rocks and extents have been constrained poorly. Here I report detailed description and new geochemical data of pyrobitumen in ca. 1.9 Ga Gunflint Formation. Pyrobitumen disseminated in oolitic carbonate, conglomerate and shale of Gunflint Formation. Some pyrobitumen occur as thin veins concordant with sedimentary bedding. These features suggest that large quantity of bitumen (or oil) introduced and disseminated in Gunflint sediments, when the sediments were still soft.

Carbon isotope compositions are much lighter than sedimentary organic matter, e.g., kerogen, in the same rocks. Kerogen in Gunflint Formation has a contrast compositions of pyrobitumen, suggesting that bitumen was generated elsewhere. Carbonaceous rocks are completely absent except Gunflint Formation in the studied area. This postulate bitumen (oil) generation and migration within Gunflint Formation.

Results of the present study suggest that (1) examined pyrobitumen is analogous to other Paleoproterozoic Shungite, (2) burial of organic matter were intensive even at 1.9 Ga, largely affecting C and N cycles of biosphere, (3) oil generation, migration, and solidification were most likely promoted by intensive Paleoproterozoic igneous activities. In particular, the combination of above (2) and (3) were unique to Paleoproterozoic Earth, largely contributing to remove atmospheric CO2.

Evidence of various microbial activities was reported from Gunflint Formation. There exist a possibility that a part of the past geochemical and electron microscopic evidence were records of microbial activities in migrating oil, rather than representing activities of Paleoproterozoic marine microorganisms.

Keywords: Paleoproterozoic, pyrobitumen, Gunflint

3 step model for the emergence of first life

*Shigenori Maruyama[1], Toshikazu Ebisuzaki[2], Taku Oshima[3]

1.Earth-Life Science Institute, Tokyo Institute of Technology, 2.RIKEN, 3.NAIST

The mystery of the origin of life cannot be solved only by biologist. This topic is solved only when multidisciplinary studies are conducted by all of scientists including astronomer, geochemist, chemist, and geologists. Our research group, mainly geologist, has revealed whole Earth history as cradle of life by the strategy of 4.6-billion-year Approach and Singularity Approach. Through these two approaches, we found out what necessary condition for the emergence of life was, and how the first life was, which provided 3 step model for the emergence of first life. This model explains that life was born through 3 steps, first primordial life, second primordial life, and third primordial life which is prokaryote. Details are as follows.
The first primordial life was born at natural nuclear geyser and living as extracellular symbiont. They should have survive by making symbiont as primitive ecosystem. Probably numerous numbers of small organelle (similar to present virus) existed. To enable them to survive, energy must have been supplied. Nuclear geyser played this important role. On Hadean Earth surface environment, Sun energy cannot be used and surface environment was too dangerous without geomagnetic field. Instead, nuclear geyser supply necessary energy continuously for proto-life.
Due to spout of geyser, first primordial life was tossed out of geyser to die, as solar energy at that time was too strong. They were left on the surface as tahr. After primordial atmosphere became thin enough to pass sun light, life can utilize sun energy on the surface of the Earth. Such life is second primordial life, which obtained new function to utilize solar energy by using principle of semi-conductor. Second primordial life was still extracellular symbiont.
Primordial ocean was too toxic with high acidity, high salinity, and heavy metals. Therefore, second primordial life experienced mass extinction due to influx of toxic ocean as a result of operation of plate tectonics. In spite of repeated mass extinction, some life could survive under strong outer force. Such life became the first life, in other words, first prokaryote on the Earth.

Keywords: origin of life, three step model, Hadean earth

