

## Theoretical Investigation of a Mechanism of Chirality Induction for Amino Acids in the Early Solar System

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Present terrestrial life is consisted of L-form amino acids, which are ones of enantiomers. Although L-form and D-form amino acids are generated equivalently by chemical synthesis in a laboratory, only L-form is produced in protein biosynthesis. The origin of chirality for amino acids is not revealed yet and remains as one of the big mysteries in the studies of molecular evolution and the origin of life. To explain it, it is thought that racemic amino acids in interstellar space were destructed asymmetrically by the irradiation of circularly polarized light (CPL) in the early solar system and enantiomeric excess was induced.

Recently, some observational and experimental results supporting this hypothesis have been reported. Amino acids and their precursors have been found in meteorites and their abundances are also biased to L-form. Besides, high circular polarization was observed in the Orion massive star-forming region (OMC-1). In a laboratory, the asymmetric decomposition of amino acid enantiomers by CPL irradiation has been reported. Moreover, it was experimentally proved that low enantiomeric excess could become higher and one enantiomer eventually became dominant. These results support that the origin of life was derived from outside the earth and the chirality of amino acids in life and the inclination found in meteorites should be same derivation. However, some problems to explain this hypothesis are remained, i.e. the mechanism of generation process of amino acids in space and the interaction between amino acid and CPL are not revealed.

To resolve them, the analysis of photo-properties of amino acids is now vital. Especially, the study for the UV light absorbability of amino acids and the destruction or decomposition process is imperative since enantiomeric excess should be mainly derived from the isomerization of racemic amino acids by CPL irradiation. In that sense, the analyses of the excited states for amino acids and their structural changes are important. In particular, it is necessary to study the mechanism of the bond dissociation of a chiral carbon and the carbon connecting to it since it plays a key role for the isomerization reaction.

In this study, we theoretically determined the excited states and potential energy surfaces (PES) for alanine, valine, and isovaline, which are ones of basic amino acids for life and found in meteorites. We first investigated the most stable structures in space at the density functional theory (DFT) level. Then we analyzed the isomerization processes. Especially, their energies, absorption intensities, and circular dichroism (CD) spectra were calculated to predict CPL-induced decompositions of amino acids. C-C bond dissociation pathways were examined in this study.

In the results, we found that the peaks of CD for the amino acids existed in the region of 8-12 eV (100-150 nm wavelength). Four plausible reaction pathways are extracted. For Alanine, the peaks of the absorbance and CD exist at the excitation energy of 9.81 eV. It may lead to the structural decomposition of D-form alanine. For valine, the peaks are found at the excitation energies of 10.00 eV and 10.91 eV. For isovaline, the excitation energy of 9.32 eV is applied to the conditions. These four curves are energetically likely to induce the bond dissociation of C-C and have the peaks of absorption intensity and CD at the ground state.

These results suggest the irradiation of vacuum-ultraviolet (VUV) CPL with the wavelength 110-135 nm for amino acids in space could induce enantiomeric excess. Furthermore, the pathways obtained in this study could be one of the clues to establish the hypothesis that enantiomeric excess based on isomerization was induced by the irradiation of VUV-CPL.

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

## Possibility of organic matter formations in irradiated CO<sub>2</sub> and CH<sub>4</sub> hydrates on Mars

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To look for evidence of life on Mars, explorations of organic matter is important. There are some possibilities of the formations of organic matter on Mars; for example, by biological activity and by radiolysis and photolysis of mixtures of icy materials. If organic matter exist on Mars, to identify the detected organics as the matter by biological activity, it is necessary to investigate reaction products and their amount by radiolysis and photolysis of the ice mixtures, and to distinguish organics by biological activity from ones by radiolysis and photolysis. As the icy materials on Mars, it is suggested that gas hydrates would exist on Mars, based on the discussion of temperature and pressure conditions. Gas hydrates are crystalline inclusion-compounds, which are composed of hydrogen bonded water molecules encaging gas molecules (e.g. CO<sub>2</sub>, CH<sub>4</sub>). Most of them are stable at high pressures and/or low temperatures. Average temperature of Martian surface is about 210 K, the Martian atmosphere consists of about 95% CO<sub>2</sub> and the average atmospheric pressure is about 0.56 kPa (Kieffer et al., 1993). From the observations of the Mars Express spacecraft, methane with 10-40 ppmv concentrations has been detected in the Martian atmosphere and on surface of the ground (Formisano et al., 2004; Mumma et al., 2009). In Martian conditions, it is suggested that CO<sub>2</sub> and CH<sub>4</sub> hydrates are formed in about 10 m below the ground and on the polar caps in winter (e.g. Max and Clifford 2001; Prieto-Ballesteros et al., 2006). Since water ice exists on Martian surface, the environment on the Martian surface should be enough to form CO<sub>2</sub> and CH<sub>4</sub> hydrates. In this case, Martian gas hydrates should be irradiated by natural radiation from radioisotopes in sediments as well as cosmic rays, which may cause radical formation in CO<sub>2</sub> and CH<sub>4</sub> hydrates.

Radiation-induced radicals in CH<sub>4</sub> and CO<sub>2</sub> hydrates have been investigated by electron spine resonance (ESR) measurements. Methyl radical is mainly formed by gamma-ray irradiation at 77 K in CH<sub>4</sub> hydrate (Takeya et al., 2004), and not stable above 180 K at 0.1 MPa (Tani et al., 2006). Carboxyl radical, hydrogen atom and hydroxyl radical are formed by gamma-ray irradiation at 77 K in CO<sub>2</sub> hydrate, hydrogen atom and the hydroxyl radical are not stable above 120 K at 0.1 MPa and the carboxyl radical quickly disappears at 180 K (Oshima et al., submitted). In thermal conditions on Mars, these radicals in the hydrates are unstable, and some products may form through the radical reactions. In this study, to investigate the organic products from radicals induced in CO<sub>2</sub> and CH<sub>4</sub> hydrates on Martian conditions, we analyzed the aqueous solution after dissociation of the hydrates irradiated at 195 K by ion chromatography and gas chromatography-mass spectrometry (GC-MS).

Formic acid and oxalic acid are observed in aqueous solution after dissociation of irradiated CO<sub>2</sub> hydrate. Methanol and formaldehyde are observed in irradiated CH<sub>4</sub> hydrate. If CO<sub>2</sub> and CH<sub>4</sub> hydrates exist on Mars, these organics will be formed in the hydrates and accumulated on the polar caps and below subsurface.

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

## Tanpopo: Astrobiology exposure and micrometeoroid capture experiments

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

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

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

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

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

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

### References

Arrhenius, S. (1908) *Worlds in the Making-the Evolution of the Universe* (translation to English by H. Borns) Harper and Brothers Publishers, New York.

Crick, F. (1981) *Life Itself*. Simon & Schuster, New York.

Yamagishi, A., et al. (2008) TANPOPO: astrobiology exposure and micrometeoroid capture experiments. International Symposium on Space Technology and Science (ISTS) Web Paper Archives. 2008-k-05

Keywords: International Space Station

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

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Origins of life have been discussed in the context of the evolution of proteins- and nucleic acids-related molecules. We have learned that complex organic compounds with high-molecular weights could be abiotically formed in simulated terrestrial and extraterrestrial environments. Such "Garakuta" molecules could have low biochemical functions, including catalytic activities. In this paper, possible evolution pathways via Garakuta molecules will be proposed in the context of the evolution of biochemical functions.

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

## Origin and birth place of life on the Earth

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### Birth of life

In spite of those new trends, and against reluctant astronomers, I point out the idea against it. First of all, the life cannot be formed only by water and CO<sub>2</sub>. Phosphorous is a key critical element to run metabolism in life as an example. The related major and trace elements are all derived from the rock, not from ocean and atmosphere. The water-rock interaction driven by steady-state supply of heat by magma at mid-oceanic ridge was the birth place of life on the Earth, and another survival place of life is the surface of the Earth where continent (source of nutrients) interacts with ocean-atmosphere, resultant constant supply of nutrients to the ocean. Engine to drive the system is Sun, whereas the deep-sea hydrothermal system is plate tectonic supply of MORB magma. Phosphorous is nearly absent at MOR and absent in underlying mantle which are critically important if we discuss the origin of life in the Hadean time.

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

### Primordial continent, anorthosite with KREEP on the Hadean Earth

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

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

First life was synthesized by the successive FT reactions from inorganic compounds under the excess amounts of P-bearing and other nutrients (ore body) in the deeply fractured lake with constant magma supply underneath. The birth place was under anoxic conditions (H<sub>2</sub>) local in an oxidized material of water. The most difficult process is the process from RNA world to DNA world, which may have taken over several hundreds of million years.

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

## Abiogenic graphite in the 3.8 Ga Isua Supracrustal Belt

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

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

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

Keywords: abiogenic, Isua, Archean

## Was the Archean atmosphere reducing?

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The current paradigm postulates the following scenarios for the evolution of the atmosphere and oceans: Oxygenic photoautotrophs evolved at ~2.7 Ga, but the atmosphere and oceans remained reducing (i.e.,  $p\text{H}_2 > 10^{-6}\text{atm} > p\text{O}_2$ ) until the 'Great Oxidation Event (G.O.E.)' at ~2.45 Ga when the atmospheric  $p\text{O}_2$  dramatically rose to ~10% PAL and the ocean surface layer became oxygenated, while the deep oceans remained anoxic. Previous researchers have presented the following observations in some (but not all) Archean-aged rocks to support this paradigm: (a) loss of Fe from paleosols; (b) abundance of banded iron formations (BIFs); (c) presence of 'detrital' grains of uraninite and pyrite; (d) lack of U- and Mo enrichments in black shales; (e) presence of anomalous isotopic fractionations (AIF or MIF) of sulfur in shales and barite beds; (f) presence of unusual isotopic compositions of N and Fe in sedimentary rocks. However, none of these observations are unequivocal evidence for a reducing Archean atmosphere, since all these characteristics have also been found in younger rocks. We have also demonstrated experimentally that the AIF-S signatures, which were previously linked to the UV photolysis of volcanic  $\text{SO}_2$  in an  $\text{O}_2$ - and  $\text{O}_3$ -free atmosphere, can occur during thermochemical sulfate reduction by solid organic matter. We can better explain the above characteristics (c)-(f) by diagenetic, hydrothermal, and metamorphic processes, rather than by atmospheric processes.

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

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

Keywords: Archean, atmosphere, MIF, GOE

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

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

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

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

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

[1]Davis and Jackson (1988) Geol. Soc. Amer. Bull. 100, 818-824. [2]Fralick and King (1996) West. Super. Trans. Ann. Workshop, pp. 29-35.[3]Kohnhauser et al.(2007) EPSL 258, pp.87-100.

Keywords: Archean, photosynthesis, Lamby Lake



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

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Many researchers have linked the anomalously fractionated (or commonly called mass independently fractionated) isotopes of sulfur (AIF-S or MIF-S) in sedimentary rocks to UV photolysis of volcanic SO<sub>2</sub> and to an O<sub>2</sub>-poor atmosphere. However, serious discrepancies exist between the AIF-S signatures in natural samples and those of the products (S<sub>0</sub> and SO<sub>4</sub><sup>2-</sup>) of SO<sub>2</sub> photolysis using a broad-band UV lamp which simulates the sun light. The produced S<sub>0</sub> and residual SO<sub>2</sub> possess only very small AIF-S signatures (i.e.,  $\delta^{33}\text{S}/\delta^{34}\text{S} = 0.58 \pm 0.04$ ). Based on theoretical and experimental investigations, we have proposed that the AIF-S signatures in some (if not all) Archean sedimentary rocks were produced by chemisorption-redox reactions involving solid phases (e.g., organic matter, iron oxides, carbonates, clays and aqueous S-bearing species (SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>S)) during the diagenesis of sediments in hydrothermal environments. According to our model, the characteristics of AIF-S signatures may vary depending conditions of the chemisorption-redox reactions (e.g., type and surface area of the solid phase, concentration of the aqueous species, temperature, reaction time, open or closed-system). To evaluate the validity of our model, we have examined the relationships among the AIF-S characteristics ( $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values) of sulfides and sulfates, their modes of occurrence (e.g., disseminated, nodules, layers, veins), and the lithology of their host rocks.

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

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

Keywords: sulfur isotope, Archean

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

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All the living organisms have been evolved from the common ancestor called LUCA, senancestor or Commonote. By analyzing the gene sequences or organisms it is possible to construct phylogenetic trees. By using the same technique it is possible to resurrect the gene sequence of the ancestors. The resurrected gene sequence can be constructed, expressed in *E. coli* and the product purified. I will report the results of the Commonote as well as the common ancestors of Bacteria and Archaea.

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

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

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Prebiotic organic matters such as amino acids have been found in extraterrestrial bodies. It was suggested that they were formed in cold space environment, and were delivered to the early Earth. Interplanetary dust particles (IDPs) were promising carriers since they could deliver organics safer than large meteorites or comets. On the other hand, IDPs are so small that they are directly exposed to the solar radiation, which may decompose or alter organic molecules in IDPs. In the present study, we evaluated the stability of amino acid-related compounds against soft X-rays and extreme ultraviolet light (EUV): Irradiation was performed at NewSUBARU BL-06 (Univ. Hyogo), and the irradiation products were analyzed by several methods including HPLC and XANES.

Five amino acid-related samples - Glycine (Gly), hydantoin (Hyd: precursor of glycine), isovaline (Ival), 5-Ethyl-5-methylhydantoin (EMHyd: precursor of isovaline) and complex organic compounds synthesized by proton irradiation of a mixture of CO, NH<sub>3</sub> and H<sub>2</sub>O (referred to as CAW) - were irradiated with continuous light from soft X-rays to IR (hereafter referred as to soft X-rays) at NewSUBARU BL-06 (University of Hyogo) under high vacuum condition. After collecting the irradiated sample with pure water, we measured the recovery ratio of each compound by using ion exchange or reversed-phase HPLC systems. In some cases, CaF<sub>2</sub> window was used to cut soft X-rays and EUV (referred as to VUV irradiation; cut-off wavelength is ca. 130 nm).

Amino acids or their precursors were gradually decomposed by soft X-rays irradiation, and water-insoluble organics were formed. The amino acid precursors (Hyd, EMHyd, CAW) were much more stable than the free amino acids (Gly, Ival) against soft X-rays. Thus, we could suggest that the precursor amino acids are likely to present more stable than free amino acids in space environment such as meteorite surface and in IDPs. Neither racemization nor formation of glycine was observed even after 99 % of the initial L-alanine was decomposed.

When CaF<sub>2</sub> window was used, little insoluble matters were formed. Thus, soft X-rays (including EUV) are responsible for the formation of insoluble organics. Soft X-rays fraction in the solar radiation is small in the present time, but it is supposed that the strong X-rays were emitted from the young Sun before the formation of planetesimals. It should be examined the possible formation of insoluble organic matter, that is now found in carbonaceous chondrites and comets, by the irradiation with high-energy photons from the young Sun.

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

## Studies on stability of nucleic acid bases by irradiation with soft X-rays and heavy ions

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Biological molecules such as amino acids and nucleic acid bases have been found in carbonaceous chondrites. It was supposed that they were synthesized from interstellar media, and brought in parent bodies of meteorites or comets in the early solar system. Organic compounds in extraterrestrial bodies are exposed to both cosmic and solar radiation. Organics in microscopic cosmic dusts are, especially, exposed to high-energy solar photons including soft X-rays and extreme UV light. In the present study, we irradiated nucleic acid bases with high-energy particles and photons from accelerator, and evaluate their stability in space.

Aqueous solution of nucleic acid bases (adenine, cytosine, uracil or guanine) was evaporated to dryness on a glass plate, and was irradiated with continuous light (infrared to the soft X-ray; hereafter referred to as soft X-rays) at BL-6 of NewSUBARU synchrotron facility (University of Hyogo) under high vacuum (ca.  $10^{-4}$  Pa). In the case of guanine, dried sample was covered with hexatriacontane to prevent sublimation during irradiation under vacuum. Irradiation through CaF<sub>2</sub> window was also performed in the case of adenine and uracil, where soft-X rays and UV below 130 nm were cut. Aqueous solution (1 mM each) of nucleic acid bases (adenine, uracil, cytosine) were irradiated with high energy carbon ions (290 MeV) at HIMAC (NIRS, Chiba, Japan). Nucleic acid bases after irradiation were determined by reversed-phase HPLC. Irradiated cytosine was also analyzed by MALDI-MS.

In the soft X-rays irradiation experiments, decomposition of nucleic acid bases was observed: purines (adenine, guanine) were more stable than pyrimidines (cytosine, uracil). By using a CaF<sub>2</sub> window, survival ratio of bases was increased. Soft X-rays were more effective for the decomposition of bases than VUV and UV. By reversed-phase HPLC analysis, no new compounds other than the original bases were detected, but water insoluble materials were observed on the glass plate. We are going to analyze the insoluble residues by MALDI-MS. Compared to the results of irradiation of amino acids and hydantoins (amino acid precursors) [1], nucleic acid bases were more stable than amino acids and hydantoins.

In the heavy ions irradiation, adenine was most stable among the bases examined. New peaks were observed in MALDI mass spectrum of cytosine after irradiation ( $m/z = 128, 222, 237, 333$ , etc.), which suggested the possible formation of multimers.

[1] Y. Kawamoto et al., Stability and alteration of amino acid-related compounds against soft X-rays and extreme UV in interplanetary space, JpGU 2012.

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

## Possible amino acid formation pathways in submarine hydrothermal systems

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In prior to the generation of terrestrial life, bioorganic compounds such as amino acids are essential. Possible sites for the formation of amino acids are (i) interstellar space, (ii) primitive atmosphere and (iii) submarine hydrothermal systems. If the primitive Earth atmosphere was neutral (i.e., chiefly composed of carbon dioxide and nitrogen), formation of amino acids was quite limited, but carboxylic acids could be formed by spark discharges and other energy sources. If the carboxylic acids, especially keto acids, formed in the atmosphere were introduced to submarine hydrothermal systems, we can expect the formation of amino acids from carboxylic acids and ammonia dissolved there. In the present work, we examined possible formation of keto acids from simulated primitive atmosphere, and possible formation of amino acids from keto acids and ammonia by using a flow reactor simulating submarine hydrothermal systems.

**Spark discharge experiments:** A mixture of carbon dioxide (300 Torr) and nitrogen (300 Torr) was introduced to a 400-mL Pyrex flask over 5 mL of water, and spark discharges were applied to the gas mixture for 12 hours. After discharges, the resulting products were recovered from the flask, and amino acids were analyzed after acid-hydrolysis of the product.

**Flow reactor experiments:** We constructed a specially designed flow reactor (supercritical water flow reactor [1]), which allowed aqueous samples heated up to 673 K for minutes without pre-heating and then quenched to 273 K. The pressure was maintained at 25 MPa during the heating. A mixed solution of 10 mM of pyruvic acid and 10 mM of ammonia was injected to the flow reactor, and heated at 473-673 K for 2 min. The resulting products recovered were acid-hydrolyzed, desalted with a Monospin SCX cation-exchange resin, and applied to an amino acid analyzer (Shimadzu LC-10A).

In the spark discharge products, we could not detect amino acids, but some carboxylic acids were detected by capillary electrophoresis. Thus it is difficult to obtain amino acids by spark discharges in neutral atmosphere. We are trying to detect keto acids in the discharge products.

Amino acids (glycine and serine) were detected after a mixture of pyruvic acid and ammonia was heated at 523 K in the flow reactor. It suggested that carboxylic acids and ammonia formed from neutral atmosphere could react to give amino acids in submarine hydrothermal systems.

[1] Islam, Md. N. et al., Bull. Chem. Soc. Jpn., 76, 1171-1179 (2003).

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

## 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°C, 150 MPa, 0-96 hours).

Starting materials were solid methionine and solid methionine with solid glycine, water, aqueous ammonia, or ammonium hydrogen carbonate. The additives in the starting materials other than glycine (water, aqueous ammonia, and ammonium hydrogen carbonate) are simulating decomposition products of glycine. Ammonium hydrogen carbonate decompose at about 60°C and yields ammonia, carbon dioxide, and water. For each starting material, 0.43 mmol of methionine were used. The amounts of additives were 0.43 mmol. Each starting material was sealed into a gold tube of 25 mm length and 5.5mm diameter. Then, high temperature and pressure conditions were applied using a test-tube-type autoclave system. Amino acids and their oligomers were extracted into aqueous solution from the experimental products and analyzed with a high performance liquid chromatograph connected to a mass spectrometer (LC/MS).

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

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

## 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 (<sup>13</sup>C), 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 (<sup>13</sup>C), 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 <sup>13</sup>C were identified in the sample free from sodium chloride. While, only <sup>13</sup>C-methylamine and <sup>13</sup>C-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.

## Effects of borate on the reaction between glyceraldehyde and glycolaldehyde

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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.

### References

[1] Butlerow, A., C. R. Acad. Sci. 53, 145-147 (1861). [2] Decker, P. et al., J. Chromatogra. 244, 281-291 (1982). [3] Ricardo, A. Carrigan, M. A.; Olcott, A. N., Benner, S. A., Science 303, 196 (2004). [4] Lambert, J. B., Gurusamy-Thangvelu, S. A., Ma, K., Science 327, 984-986 (2010).



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

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**Introduction:** Recent finding of the serpentinization-driven deep-sea vent systems producing basic fluids, such as the Lost City hydrothermal field (Kelley et al. 2005) and the south Chamorro seamount (Hulme et al. 2010), has improved our understanding that submarine basic seepages are plausible environments for the origin and evolution of life in the early Earth (Russell, 2003). In our previous study, it was revealed that the dimerization of glycine (Gly) in aqueous solution reached the maximum rate in basic solution at pH 9.8 and 150°C (Sakata et al., 2010), supporting Russell's hypothesis. However, the effects of metal ions on peptide formation under basic pH condition have not been well investigated. In this study, the heating experiments of Gly solution containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Cu}^{2+}$  were conducted under various pH conditions, in order to evaluate the effects of metal ions on the formation and decomposition rates ( $k_n$ ) of glycylglycine (GlyGly), glycylglycylglycine (GlyGlyGly) and diketopiperadine (DKP).

**Experimental:** Aqueous solutions of 100 mM Gly, 100 mM Gly containing with 5, 200 and 400 mM  $\text{CaCl}_2$ , 5 mM  $\text{MgCl}_2$ , 5 mM  $\text{ZnCl}_2$ , and 5 mM  $\text{CuCl}_2$ , respectively, were prepared. Each solution was adjusted to acidic (pH = 2.2 ~ 2.3), neutral (pH = 4.5 ~ 6.0) and basic (pH = 9.8 ~ 9.9). The solutions containing  $\text{CuCl}_2$  were adjusted to pH = 3.4 and 9.8. Half milliliter of each solution in a pyrex glass tube was replaced with Ar gas and sealed under vacuum. These samples were heated at 140°C for 1 to 74 days. After heating, the samples were 10 times diluted and 100 micro liters of each solution was analyzed by High Performance Liquid Chromatography (HPLC). In this experiment, the six reaction pathways were considered: 2 Gly to GlyGly ( $k_1$ ), GlyGly to 2 Gly ( $k_{-1}$ ), GlyGly to DKP ( $k_2$ ), DKP to GlyGly ( $k_{-2}$ ), Gly + GlyGly to GlyGlyGly ( $k_3$ ) and GlyGlyGly to Gly + GlyGly ( $k_{-3}$ ). The rate constants were determined by fitting the changes of the concentrations of Gly, GlyGly, GlyGlyGly and DKP with increasing heating time using the least-squares method.

**Results and discussion:** The concentrations of GlyGly in the aqueous solutions of Gly containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  under any pH condition, respectively, were lower than those without metal ions. The concentration of GlyGly decreased with increasing concentrations of  $\text{Ca}^{2+}$ . In the aqueous solutions of Gly containing  $\text{Cu}^{2+}$ , the concentration of GlyGly was higher at basic pH than those without metal ions, while it was lower at acidic pH. GlyGlyGly was yielded only in the solutions containing  $\text{Cu}^{2+}$ , and it was the most abundant at basic pH. Under the basic pH, the concentrations of DKP in the solutions containing any metal ion were lower than those in the solution of Gly only. All the rate constants ( $k_1$ ,  $k_{-1}$ ,  $k_2$  and  $k_{-2}$ ) for the aqueous solutions of Gly containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  (5 mM) at any pH were lower than those for the solution without metal ions. The result indicates that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  inhibit the formation of GlyGly and DKP. For the aqueous solution of Gly containing  $\text{Cu}^{2+}$ ,  $k_1$  and  $k_{-1}$  showed high values and  $k_2$  and  $k_{-2}$  showed low values compared to those without metal ions. Thus,  $\text{Cu}^{2+}$  promotes the reactions between Gly and GlyGly while it inhibits the reactions between GlyGly and DKP. In the solutions containing  $\text{Cu}^{2+}$ , the values of  $k_3$  and  $k_{-3}$  were higher at basic pH than those at acidic pH. Such differences in the formation and decomposition rates of di- and tripeptides due to the variety of metal ions can be caused by the steric effects of metal complexes of glycine.

### References:

Hulme et al. (2010) *Geochim. Geophys. Geosyst.* 11, 2009GC002674.

Kelley et al. (2005) *Science* 307, 1428-1434

Russell (2003) *Science* 302, 580-581

Sakata et al. (2010) *Geochim Cosmochim. Acta* 74, 6841-6851.

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

## 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<sub>2</sub> 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 inhibits Gly reaction under high temperature condition. The three types of peptide: diketopiperazine (DKP), diglycine (Gly<sub>2</sub>) and triglycine (Gly<sub>3</sub>) were detected in the system including montmorillonite heated under dry condition and reference solution. Peptides were not formed when amino acid adsorbed on alumina and silica was heated both in dry and wet conditions, probably because the concentration of peptide on alumina and silica surface was too low. The 15.57% of Gly monomer became peptides on montmorillonite under dry condition, and the most abundant product was DKP (10.03%). On the other hand, only 0.5% of Gly became DKP and Gly<sub>2</sub> 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<sub>2</sub> and Gly<sub>3</sub> were lower than that of DKP in those systems. The water added in the system promoted hydrolysis of DKP and Gly monomer, and destabilized those on the montmorillonite surface. The DKP on the montmorillonite would be 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.

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

## 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. aereus* from top of troposphere and *D. aetherius* from bottom of stratosphere) [4-6]. Spores and Deinococci are known by their extremely high resistance against UV, gamma ray, and other radiations [4]. *D. aereus* and *D. aetherius* showed high resistance comparable with *D. radiodurans* R1 to the UV and ionizing radiation such as gamma rays. If microbes could be found present even at the higher altitude of low earth orbit (400 km), the fact would endorse the possible interplanetary migration of terrestrial life.

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

Microbes in space are assumed to be exposed to the space environment with different depth of layered cells. This simulates different sizes of cell aggregates. Surface cells may protect inner cells against UV, although the former might die. Dried vegetative cells of *D. radiodurans* and our novel deinococcal species isolated from high altitude are candidates for the exposure experiment. We are now testing survivals of deinococcal species and strains under the harsh environmental conditions simulating ISS environmental conditions (UV, radiation, temperature, etc). The species we testing are *D. radiodurans* (R1, and some mutant strains for DNA repair systems which might affect survivability of cells under these conditions), *D. geothermalis*, *D. aereus*, and *D. aetherius*. In this paper, we discuss current status of exposure experiment of microorganisms defined for the Tanpopo mission and others.

### References

- [1] Arrhenius, S. (1908) Worlds in the Making-the Evolution of the Universe (translation to English by H. Borns) Harper and Brothers Publishers, New York
- [2] Crick, F. (1981) Life Itself. Simon & Schuster, New York
- [3] Yang Y. et al. (2009) *Biol. Sci. Space*, 23, 151-163
- [4] Yang, Y. et al. (2008) *Biol. Sci. Space*, 22, 18-25
- [5] Yang, Y. et al. (2009) *Int. J. Syst. Evol. Microbiol.*, 59, 1862-1866
- [6] Yang, Y. et al. (2010) *Int. J. Syst. Evol. Microbiol.*, 60, 776-779
- [7] Yamagishi, A. et al. (2008) *Int. Symp. Space Tech. & Sci. (ISTS) Web Paper Archives*. 2008-k-05.

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

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

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A study on formation of life materials becomes popular inside and outside the Earth, but tries to explain a fundamental concept of the old life materials from the recent characteristic and problems as follows:

1) Life materials are active substances consisting of complex carbon-rich light elements-based molecules, to form symbiosis circular system mixed with material states of liquids and solids, such as complicated mini-type of active water planet.

2) Active life materials are formed by various energy sources at environmental areas in multi-complex reaction processes of long active Earth planet (approximately 5 billion years unit) and short-term life activity (from a year to 1 million years unit). Therefore a strong support of destruction and formation on an active water planet is required to the decomposition and formation of the life materials. The breaking destruction of active life and water-rich planetary materials is fairly easy, but it requires considerable time to develop new materials continuously on the old Earth and life body after global establishment of single and multiple cyclic systems.

3) When the above idea of multi-processes is applied to the extra-terrestrial planets and space, an active life material cannot exist in global waterless extraterrestrial bodies of the moon and waterless planets. In-situ active life materials cannot be largely formed on the surface, even if the local fluid-layer formed by shock-wave process is triggered by a surface collision. On the Asteroids, a life precursor is difficult to form when there is no circularity of the water and atmosphere other than shocked-monomer inorganic and organic substances, because stable compounds of the supra- and giant-molecules should be formed at relatively fluid-rich condition.

4) Carbon cycle system with the active life body is based on the closed system for state changes. However, life materials can be remained especially at the collision with water planet. In this sense, the discovery of a life material as fossil minerals from the carbon cycle system is largely possible, if there are larger aggregates broken by the planetary collision. Therefore, planetary exploration including the Moon and planet Mars is significantly required now and in future by long-time planning.

5) Small cyclic systems of active life materials including our mankind can be moved to extraterrestrial world as short travel time to be involved in wide cycle system in the solar system, though present cycle system on water planet (as in same Earth-type system) should be involved due to its active combined multi-system.

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