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 CO2 and CH4 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. CO2, CH4). Most of them are stable at high pressures and/or low temperatures. Average temperature of Martian surface is about 210 K, the Martian atmosphere consists of about 95% CO2 and the average atmospheric pressure is about 0.56 kPa (Kieffer et al., 1993). From the observations of the Mars Express spacecraft, methane with 10-40 ppmv concentrations has been detected in the Martian atmosphere and on surface of the ground (Formisano et al., 2004; Mumma et al., 2009). In Martian conditions, it is suggested that CO2 and CH4 hydrates are formed in about 10 m below the ground and on the polar caps in winter (e.g. Max and Clifford 2001; Prieto-Ballesteros et al., 2006). Since water ice exists on Martian surface, the environment on the Martian surface should be enough to form CO2 and CH4 hydrates. In this case, Martian gas hydrates should be irradiated by natural radiation from radioisotopes in sediments as well as cosmic rays, which may cause radical formation in CO2 and CH4 hydrates.

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

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

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., Deinococcus radiodurans, and novel Deinococcal 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 planed 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


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

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

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

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

After the birth of life in such a localized area, the mother primordial continents have all gone into deep mantle remaining life on the deep-sea hydrothermal system. Plate tectonics has operated to clean-up ocean chemistry by the formation of ores at mid-oceanic ridges to transport them into mantle. Salinity was 3-5 times more in the Precambrian time, and plate tectonics was not effective to omit halogens from ocean into mantle. Continent-collision orogeny was critical to dilute salinity after the drop-down of sea-level at 800-600Ma.
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, $^{13}$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 \( \sim 2.7 \) Ga, but the atmosphere and oceans remained reducing (i.e., \( p_{H_2} > 1 \times 10^{-6} \text{ atm} > p_{O_2} \)) until the ‘Great Oxidation Event (G.O.E.)’ at \( \sim 2.45 \) Ga when the atmospheric the atmospheric \( p_{O_2} \) dramatically rose to \( \sim 10\% \) 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., \( \text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2\text{O} \) and \( 3\text{CH}_2\text{O} \rightarrow 2\text{CO} + 3\text{H}_2\text{O} \)). As the atmospheric \( \text{CO}_2 \) was converted to reduced C compounds (\( \text{CO}, \text{CH}_4 \), and \( \text{C} \)) 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 <\( \sim 100 \) 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 \( \sim 3.5 \) 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 \( d^{13}\text{C} \) values of carbonates and shales; (iii) the abundance of sulfate-rich rocks; (iv) the wide \( d^{34}\text{S} \) ranges for pyrite and sulfates in sedimentary rocks and ore deposits; (v) the common \( d^{15}\text{N} \) 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 anoxigenic 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.


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 idenpendently fractionated) isotopes of sulfur (AIF-S or MIF-S) in sedimentary rocks to UV photolysis of volcanic SO2 and to an O2-poor atmosphere. However, serious discrepancies exist between the AIF-S signatures in natural samples and those of the products (S0 and SO42-) of SO2 photolysis using a broad-band UV lamp which simulates the sun light. The produced S0 and residual SO2 possess only very small AIF-S signatures (i.e., delta33S/delta34S = 0.58 +/- 0.04). Based on theoretical and experimental investigations, we have proposed that the AIF-S signatures in some (if not all) Archean sedimentary rocks were produced by chemisorption-redox reactions involving solid phases (e.g., organic matter, iron oxides, carbonates, clays and aqueous S-bearing species (SO42- and H2S) during the diagenesis of sediments in hydrothermal environments. According to our model, the characteristics of AIF-S signatures may vary depending conditions of the chemisorption-redox reactions (e.g., type and surface area of the solid phase, concentration of the aqueous species, temperature, reaction time, open or closed-system). To evaluate the validity of our model, we have examined the relationships among the AIF-S characteristics (delta34S, Delta33S and Delta36S 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 +delta34S and +Delta33S values or -delta34S and -Delta33S 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 -delta34S and +Delta33S values for the sulfides and +delta34S and -Delta33S 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