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"The Role of Radiation in the Origin and Evolution of Life"

organized by
Research Reactor Institute, Kyoto University

in cooperation with
the Society of the Study of the Origin and Evolution of Life, Japan

Joint Meeting with the 23rd Annual Meeting of the SSOEL, JAPAN

ABSTRACT

The Society for the Study of the Origin
and Evolution of Life
JAPAN

生命の起原および進化学会 会則

地球上における生命の起原を科学的に解明することと，生物進化の攻究により，生命体の本質を明らかにしようとする。本学会は，関係諸分野の英知を集め，互の連繋によって新しい型の総合科学を確立・発展させることにより，上記の目的達成を期するものである。

第一条　本学会は，生命の起原および進化学会（Society for the Study of the Origin and Evolution of Life-Japan, SSOEL-Japan）という。

第二条　本学会は，会員の生命の起原および進化の研究の発展と，日本における当該研究の開拓・推進をはかり，関連学(協)会および，多くの人々の当該研究に対する理解を深め，もって学術・文化の発展に寄与するものとする。

第三条　本学会は，前条の目的達成のため次の事業をおこなう。

1．研究発表会・学術講演会の開催
2．学会誌等の出版物の刊行
3．其の他前条の目的達成のため必要な事業

第四条　本学会は前条の事業をおこなうため事務局をおく。

第五条　本学会の会員は，正会員と賛助会員とし，入会手続きは別途定める。

第五条の２　正会員は，第二条に示す研究に従事する個人で，学会が承認したものとする。

第五条の３　賛助会員は，本学会の目的に賛同し，その事業を援助する個人または個体で学会が承認したものとする。

第六条　会員は，別途定められた会費等の費用を前納しなければならない。定められた期間以上これらを滞納した場合は，会員の資格は消失するものとする。

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第八条　本学会は，会長１名，副会長１～２名および学会運営委員（以下委員と略す）を若干名，会計監査２名をおくものとする。

第九条　委員および会計監査は，正会員の互選による。選出された委員は学会運営委員会（以下委員会と略す）を構成し，学会運営の任にあたる。

第十条　会長・副会長は委員会が正会員の中から選出する。

第十一条　会長・副会長・委員・会計監査の任期は２年とする。

第十二条　委員会は，学会運営および学会事業をおこなうため，委員長１名，常任委員若干名を選出し，学会運営常任委員会（以下常任委員会と略す）を構成し，その任にあたらせるものとする。

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第十四条　常任委員会は，必要なとき委員会を招集し，本学会に関する諸事項を審議・決定する。

第十五条　常任委員会は，正会員の中から専門委員を委嘱し，本学会に関する諸事項を諮問することができる。

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第十七条　会員の退会届け者および会員資格消失者については，常任委員会は退会手続きをとるものとする。

第十八条　本学会は，年１回定期総会を開き，必要なときは臨時総会を開くものとする。

第十九条　本学会会則の改正は，会員の⅔以上の出席の総会において⅔以上の同意を要する。

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1．入会申し込み書に必要事項を記入し，常任委員会へ提出のうえ会員資格の承認をうける。
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4．本学会の入会は推薦によりおこない，委員会で承認する。

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1．入会金（正会員のみ）　1,000円
2．会費
　正会員　年額　5,000円
　賛助会員　年額（１口）　10,000円
3．学生のための入会金・会費
　正会員で，大学または大学院あるいはこれに準じる学校に在学する学生は，在学証明書の添付により，次の特典を与えるものとする。
　入会金 500円，会費（年額） 2,500 円
4．学会誌 Viva Origino 購読料　年額 5,000 円
　但し，会員には無料配布とする。
5．会費その他の費用の納入の猶予期限は１年以内とする。
6．会費払込振替口座
　（加入者名）生命の起源および進化学会
　（口座番号）大阪８－3673

Viva Origino

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京都大学国際会議
「生命の起源・進化における放射線の役割」

第２３回生命の起原・進化学会大会との合同会議

日時：１９９８年3月1日（日）～5日（木）

場所：ホテル「サンルート関空」; 大阪府泉大津市きららタウン
（南海線泉大津駅から徒歩１０分またはホテルシャトルバス５分）

参加登録費：１０,０００円　（アブストラクト、懇親会費含む）

組織委員長および２３回大会委員長
赤星　光彦（京都大学原子炉実験所）

〒590-04945 大阪府泉南郡熊取町野田
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Conference Schedule

	Sunday 1 March 1998	Monday 2 March 1998	Tuesday 3 March 1998	Wednesday 4 March 1998	Thursday 5 March 1998
9:00 am		Opening Ceremony			
9:30 am		O-1	O-9	O-13	O-21
10:00 am		O-2	O-10	O-14	O-22
10:30 am		Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:00 am		O-3	O-11	O-15	O-23
11:30 am		O-4	O-12	O-16	O-24
12:00 am		Lunch	Lunch	Lunch	Lunch
12:30 pm		Time	Time	Time	Time
13:00 pm	Bus from Kanku	O-5	Excursion to	O-17	O-25
13:30 pm		O-6	Castle Kishi-	O-18	O-26
14:00 pm		O-7	wada, Danjiri-	O-19	O-27
14:30 pm		O-8	kaikan and	O-20	O-28
15:00 pm	Bus from Kanku	Coffee Break	Kuboso-	Coffee Break	Coffee Break
15:30 pm		Poster Presentation	Museum	Poster Presentation	Poster Presentation
16:00 pm		From 2-P-1		From 4-P-1	From 5-P-1
16:30 pm		To 2-P-20		To 4-P-20	To 5-P-20
17:00 pm	Registration	Free		Free	On the bus to
17:30 pm					「Haya」
18:00 pm	Welcome-		Conference-		Farewell-
18:30 pm	Reception		Banquet		Reception
19:00 pm	at the hotel		at the Hotel		at Haya
19:30 pm	Site(Takoyaki		site		(Restaurant in
20:00 pm	Sushi-Party)[a]				Sakai-City)[b]

[a] sponsored by Prof. Y. Maeda, Director of KURRI [b] sponsored by SSOEL-Japan

SCIENTIFIC PROGRAM

The scientific program consists of Oral Sessions (O) and Poster sessions (P).

Monday, 2 March 1998

9:00~9:30 Opening Ceremony

Remarks: Akaboshi M. (Chairman)
Navarro-Gonzalez R. (Intern'l Executive Committee)
Ferris J. P. (Intern'l Advisory Board)
Harada K. (SSOEL-Japan)

CHEMICAL EVOLUTION (Extraterrestrial)

9:30~10:30 (Chairpersons:Navarro-Gonzalez R. and Saito T.)

10:30~11:00 Coffee Break

11:00~12:00 (Chairpersons: Noda H. and Kawamura K.)

CHEMICAL EVOLUTION (Terrestrial)

13:00~14:00 (Chairpersons: Ferris J. P. and Goto K.)

Tuesday, 3 March 1998

9:30~10:30 (Chairpersons: Yuasa S. and Harada K.)

10:30~11:00 Coffee Break

11:00~12:00 (Chairpersons: Brack A. and Munegumi T.)

13:00~1800 Excursion to Castle Kishiwada, Danjiri-Kaikan and Kuboso Museum.

Wednesday, 4 March 1998

Thursday, 5 March 1998

15:00~17:00 Coffee Break and Poster Session

Monday, 2 March

Chemical Evolution
(*Extraterrestrial and Terrestrial*)

O-1

Radiation chemical approaches to chemical evolution processes on earth and beyond

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Ionizing radiation is still taken as a minor partner in the group of energy sources available for chemical processes on early earth and in space. Justified when comparing its amount with those of other sources, this attitude neglects its advantage: the efficiency in producing free-radicals and radical-ions , promoters of chemical processes even in conditions hostile for chemistry like those in comets and other bodies in space, or in ocean depths and underground waters of early earth. The purpose of this review is to give a general picture of present radiation chemical approaches to the studies of extraterrestrial and endogenous origins of biogenic compounds .

We consider the types and amounts of ionizing radiation energy available for prebiotic chemistry in specific environments such as cosmic protons and radiations of radioactive aluminium (Al-26) in cometary nuclei, the radiation of radioactive potassium (K-40) in primitive ocean waters and mixed ionizing radiation of natural nuclear reactors in primitive underground waters.

Interaction of ionizing radiation with matter shows that the consequences depend on the type and energy of radiation, as well as on the physical state of irradiated matter. To present the basic facts we used as a model system the radiolysis of water (vapor, liquid and ice). Some routine techniques for sample preparation, irradiation and analyses, are described.

About sixty compounds are observed in radiation chemical simulation experiments. Their survey was beyond the scope of this work and is given elsewhere (1). Present study provides an insight into the specific contributions of radiation-induced changes to prebiotic chemistry. One is the modest, yet significant, intrinsic oxidizing capacity of primitive waters due to the radiolytic generation of various oxidizing free radical species in addition to molecules of oxygen and hydrogen peroxide. Other implications concern the consequences of radiation chemical processing of interstellar dust and comets.

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(1) Vujosevic S.I., Draganic I.G.: Biogenic compounds observed in radiation chemical simulation experiments. (This Conference) .

O-2

Radiation prebiotic syntheses in the solar system

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UV and high energy particles irradiation of the main atmospheric constituents of planetary environments can be a very important source of organics, including compounds of prebiotic interest, if the atmosphere is in a chemically reduced state. Indeed, the evolution of a CH_4-rich atmosphere under UV or electron irradiation leads to a chain of various organics, the complexity of which increases together with the number of pathways involved in their formation. Two complementary classes of products are obtained : volatile organics, such as HCN, H_3CN or HCHO, and non-volatile products, macromolecular organics, often called « tholins », including oligomers or co-oligomers of the low molecular products.

There are numerous places in the solar system where the formation of these starting ingredients is still going on. This is the case with comets. This is also the case with the outer solar system. Indeed, from Jupiter to Neptune and Triton and probably Pluto, organic chemistry is largely present in the outer planets, particularly in Titan.

Titan (1) has a dense atmosphere, mainly composed of N_2 and CH_4 and very rich in organic compounds, both in gas and aerosol phases. Because of the low temperature of Titan's environment, liquid water is currently absent from the satellite and compounds of low stability at the (Earth) laboratory temperature, and very reactive, are still or may be present.. However, Titan study (2) should provide information on prebiotic chemistry - at least prebiotic chemistry in absence of liquid water. This quasi-planet thus appears as a natural laboratory enabling to study prebiotic evolution toward complex organic systems in a planetary environment over a long time scale. A wide range of experiments simulating Titan's organic chemistry have been carried out. Very recent experiments performed within conditions closer to Titan's ones, (using, in particular, low temperatures) provide very new insights in this exotic prebiotic chemistry with crucial information on the gas phase and aerosols phase products (3).

A detailed study of this natural prebiotic laboratory is precisely one of the main objectives of the Cassini-Huygens mission (1,4). With the sending of the Cassini orbiter around Saturn and the Huygens probe in the atmosphere of Titan, this mission, successfully launched on October 15, 1997, for a Saturn arrival in 2004, will offer a unique opportunity to study in detail extra-terrestrial prebiotic processes, together with important implications in the field of exobiology and the origins of life.

The last laboratory data related to Titan's organic chemistry will be presented, together with the expected exobiological returns of the Cassini-Huygens mission.

References

(1) Lebreton J.P., European Space Agency (1997). Huygens : Science, Payload and mission, *ESA SP*- **1177**.

(2) Clarke D.W. & Ferris J.P. (1997). Chemical evolution on Titan : comparisons to the prebiotic Earth, *Origins of life and Evol. Biosphere*, **27**, 225-248.

(3) Coll P., Coscia D., Gazeau M-C.G. and Raulin F. (1997). New planetary atmopshere simulations : application to the organic aerosols of Titan, *Adv. Space Res.*, **19** (7) 1113-1119; Review and latest results of laboratory investigation of Titan's aerosols, *Origins of Life and Evol. Biosph.*, in press.

(4) Raulin F., Frère C., Paillous P., de Vanssay E., Do L. and Khlifi M. (1992). Titan and exobiological aspects of the Cassini-Huygens mission, *J. British. Interplanet. Soc.* **45**, 257-271.

O-3

Delivery of extraterrestrial organics to the primitive Earth: UV-processing of amino acids in Earth orbit.

Bernard Barbier, Marylène Bertrand, François Boillot, Annie Chabin, *Didier Chaput, Odile Hénin and André Brack
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Primitive terrestrial life - defined as a chemical system able to transfer its molecular information via self-replication and to evolve - probably originated from the evolution of reduced organic molecules in liquid water. Several sources have been proposed for the prebiotic organic molecules: terrestrial primitive atmosphere (methane or carbon dioxide), deep-sea hydrothermal systems and extraterrestrial meteoritic and cometary dust grains. The study of the carbonaceous chondrites that contain up to 5 % by weight of organic matter, has allowed close examination of the delivery of extraterrestrial organic material. Eight proteinaceous amino acids have been identified in the Murchison meteorite among more than 70 amino acids. Engel reported that L-alanine and L-glutamic acid were surprisingly more abundant than the corresponding D-enantiomers (L-enantiomer excesses of over 30 and 50%, repectively) in the Murchison meteorite. Cronin found also excesses of L-enantiomers for non-protein amino acids in the same meteorite. The presence of L-enantiomeric excesses in the Murchison meteorite suggests an extraterrestrial asymetric synthesis of amino acids, asymetry which is preserved inside the meteorite. A large collection of micrometeorites has been recently extracted from Antarctic old blue ice. In the 50 to 100 μm size range, the carbonaceous micrometeorites represent 80 % of the samples and contain 7 % of carbon. They might have brought more carbon than that involved in the present surficial biomass.

Space technology in Earth orbit offers a unique opportunity to study the behaviour of amino acids required for the development of life when they are exposed to space conditions, either free or associated with tiny mineral grains mimicking the micrometeorites. Our objectives are: i) to demonstrate that porous mineral material protects amino acids in space from photolysis and racemization (the conversion of L-amino acids into a mixture of L- and D-molecules); ii) to test whether photosensitive amino acids derivatives can polymerize in mineral grains under space conditions.

In ESA BIOPAN-1 flight experiment (June 14 - July 2, 1994), L-amino acids and one dipeptide were exposed to space conditions, free and associated with clays. Six amino acids found in the Murchison meteorite were tested with respect to chemical degradation and racemization. No detectable traces of D- amino acids could be found after the flight in any of the samples. Aspartic acid and glutamic acid exposed as free samples have been partially decomposed during exposure to solar UV. Decomposition was prevented when the amino acids were embedded in clays. In BIOPAN-2 flight experiment (October 8-23, 1997), photosensitive amino acids have been exposed. The analyses are in progress. The main limitation of these two exposure experiment was the relatively weak irradiation of the samples due to the short flight duration, the non synchronous orbits and the absence of an automatic sun pointing device. Nevertheless, significant degradation of exposed acidic amino acids indicates that the energy received was sufficient to induce chemical modifications. ESA Space Exposure Biology Assembly (SEBA) onboard the Space Station will offer an interesting facility for long duration exposures.

O-4

TITAN HAZE: CYANOACETYLENE AND CYANOACETYLENE-ACETYLENE PHOTOPOLYMERS

*James P. Ferris and Jeffrey Joseph (Department of Chemistry Rensselaer Polytechnic Institute Troy, NY 12180), David Clarke (Department of Basic Sciences, Albany College o Pharmacy)

The solar UV photolysis of the gases present in the atmosphere ofTitan is believed to be the source of the organic haze which obliterates the view of Titan's surface. The photochemical processes leading to this haze provides a model for how complex molecules may have formed from simple ones in the atmosphere of the primitive Earth. We have undertaken a study of the photolysis of cyanoacetylene and cyanoacetylene-acetylene mixtures since these are two of the atmospheric compounds which absorb solar UV strongly on Titan. Structure analysis of the polymers formed may contribute to the understanding of the data returned from the Huygens probe of the Cassini mission as it passes through the atmosphere of Titan.

Mechanistic studies established that the photodissociation of cyanoacetylene to a hydrogen atom and the cyanoethyl radical proceeds with a quantum yield of 0.09. Previous studies established that the photodissociation of cyanoacetylene into cyano- and ethynyl- radicals has a quantum yield of 0.05 so the formation of the excited state of cyanoacetylene must proceed with a quantum yield of 0.86. Free radical addition and abstraction processes predominate in the subsequent reactions following the photodissociation of cyanoacetylene present in the atmosphere of Titan.

Photolysis of acetylene in the presence of cyanoacetylene results in the polymerization of both monomers. Quantum yield measurements established that cyanoacetylene is 2-5 times as reactive as acetylene for polymer formation. The structure and morphological properties of polymers produced photochemically from the UV irradiation of cyanoacetylene and mixtures of cyanoacetylene with other gases have been examined in order to evaluate their possible contribution to the haze layers found on Titan. Infrared analysis, elemental analysis and thermal methods (thermogravimetric analysis, thermolysis, pyrolysis) were used to analyze polymers formed from cyanoacetylene by itself at 185 and 254 nm and in the presence of Titan's other major atmospheric constituents (CH_4, C_2H_6, C_2H_2 and CO). Of special significance is the copolymer formed from cyanoacetylene and acetylene since these are likely constitutents of the Titan haze. Scanning electron microscopy was used to visually examine the polymer particles.

These studies have been extended to a photochemical flow reactor where it is possible to use mixing ratios of gases comparable to those in the atmosphere of Titan and still obtain quantum yield data and sufficient product for structural analysis.

O-5

CHEMISTRY OF ARCHEAN VOLCANIC LIGHTNING

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More than 50% of the supracrustal rocks deposited during the Archean are of volcanic origin and indicates that volcanism was extremely active and wide spread globally. The more common eruption style was very likely explosive in nature on account of the higher content of volatiles present in the primitive magmas, the low viscosity of ultramafic and mafic lavas and the high mass eruption rate of a hotter and more active Earth's interior. The plinian and co-ignimbrite plume columns typical of explosive volcanic eruptions are characterized by the presence of reduced magmatic gases which are subjected to intense lightning discharges caused by the highly electrified ash particles billowed into the atmosphere. The products of these volcanic lightning discharges can escape from the high temperature of the eruption site at sonic or supersonic speeds (1).

Volcanic lightning may have played a role in chemical evolution prior to the emergence of life. Its importance was likely determined by the chemical nature of gases emitted by primitive volcanoes. The chemical composition of Archean volcanoes is not known although historically it is believed that it did not differ significantly from hot spot volcanoes, which originate from an undegassed primordial mantle reservoir (2). We examine here theoretically and experimentally the products formed by lightning discharges in an eruption cloud characteristic of Hawaiian volcanoes. The products of volcanic lightning are predicted based on thermodynamic equilibrium assumptions of the chemical species frozen out as the lightning channel rapidly expands and cools. Volcanic lightning is simulated in the laboratory by flowing the gas mixture into a microwave discharge cavity where the gases are excited and then the products are analyzed downstream by mass spectrometry using positive chemical ionization. Nitric oxide was found to be the only nitrogen containing compound formed by volcanic lightning.

Nitric oxide is not considered a potentially important compound in the context of the primitive atmosphere and the origin of life. NO would have been converted into nitric and nitrous acids and delivered to the early oceans as acid rain. Reduction of nitrate and nitrite ions to ammonia by Fe(II) could have been a source of reduced nitrogen in the early hydrosphere (3). We suggest that photolysis of NO in the lower and middle atmosphere would have provided a source of atomic nitrogen which could react with $^3CH_2$, from methane photolysis, to yield hydrogen cyanide.

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1. Navarro-González, R., Basiuk, V.A. and Rosenbaum, M.: 1996, in *Chemical Evolution: Physics of the Origin and Evolution of Life* (Chela-Flores, J. and Raulin, F., eds), Kluwer Academic Publ., Dordrecht, p. 123.
2. Basiuk, V.A. and Navarro-González, R.: 1996,*Origins Life Evol. Biosphere* **26**, 173.
3. Summers, D.P. and Chang, S.: 1993, *Nature* **365**, 630.

O-6

Irradiation Promoted Production of Organic Precursor Species in Inorganic Solids on the Prebiotic Earth

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Deposits of metallic carbonates have been widely distributed on earth for at least several billion years. The quantity of these carbonates is enormous, even when compared with other forms of carbon present in the biosphere. Thus, massive quantities of carbonates containing radioactive metal cations such as uranium, thorium and their decay products might have given rise to heavily irradiated solids containing large numbers of organic precursor species. These precursor species, stable in the solid state over geologically significant periods, could then enter the hydrosphere through weathering processes, giving rise to simple organic compounds which could contribute to the constituents of the origin of life on earth.

To test this concept, samples of carbon-14-labeled self-radiolyzed and gamma irradiated solid calcium and barium carbonates were dissolved in an acid solution and analyzed. The irradiation doses from self-irradiation were estimated from the storage times while the gamma doses were calculated from dosimetry information. The organic constituents contained in the aqueous solutions were determined, after separations using open column anion chromatography and both open column and high performance ion-moderated partition chromatography, by liquid scintillation counting of their carbon-14 contents. Identification of the compounds was made by comparing the retention times of the radiolabeled compounds with those of authentic (unlabeled) compounds detected after separation by either index of refraction or spectrophotometry.

Both self-radiolysis of carbon-14-labelled barium and calcium carbonates and gamma irradiation of recently prepared carbon-14-labelled calcium carbonate produced, after dissolution, significant quantities of formic and oxalic acids. Smaller quantities of glyoxylic, glycolic and acetic acids were seen while some samples also showed traces of methanol and formaldehyde. Experiments to reveal the presence of other small organic molecules were negative. The relative quantities of the observed products depended on the initial specific activity and storage time of the labeled compounds, with higher doses favoring the formation of the partially or fully reduced two-carbon acids. Thermal treatments cause most of the precursor species in the solid to revert to carbonate.

These results support the hypothesis that solid carbonates subjected to ionizing radiation could have been a source of carbon for organic synthesis on the prebiotic earth.

Financial support for this work from FAPESP, CNPq and CAPES (Brazil) and CONACyT (Mexico) is gratefully acknowledged.

O-7

Radiation induced reactions in compounds of biochemical relevance

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Studies in Radiation Chemistry can provide a deeper insight into the chemical processes that may have importance for prebiotic chemistry. Our aim has been to stress the relevance of ionizing radiation as tool for studying the behavior of compounds of potential interest in chemical evolution studies. Although the range of reactions that have been carried out by these means is extremely diverse, and much progress has been made, more work is required.

Many reactions induced by radiation have been examined in the context of primordial synthesis. They have been focused on different aspects:

a) Synthesis of monomers and polymers of biologically important molecules.
b) Heterogeneous catalysis (mainly with clay minerals) in the presence of ionizing radiation.
c) Reactions relevant to cometary chemistry and interstellar space.
d) Spontaneous nuclear recoil effects produce hot atoms. The reactions of hot atoms can be produced by collisions of interstellar gas and dust clouds, shock waves.

There are great theoretical achievements in Radiation Chemistry, that could be helpful in gaining a deeper insight into the chemical processes that may have importance for prebiotic chemistry. Since in dilute aqueous solutions the dominant paths are through the water, model systems for computer simulation also can be used. The energy deposition can be estimated rather easily.

The present work concerns with the analysis of some chemical reactions induced by ionizing radiation in aqueous media with compounds that may be relevant to chemical evolution studies, like carboxylic acids, and simple cyanides. Also the dependence of chemical changes on the adsorbed dose, the dose rate, the temperature and the presence of a clay mineral are examinaded. Do to the ubiquity of the radiation in the Universe, these studies are relevant in terrestrial and extraterrestrial environments.

O-8

Biogenic compounds observed in radiation chemical simulation experiments

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We present a review of biogenic compounds which are observed in radiation chemical simulation experiments of interest to prebiotic chemistry in waters of early earth and in cometary nuclei. Technical details, and theoretical approaches to aqueous radiolysis, are beyond the scope of this work and are considered elsewhere (1).

Radiolytic products in aqueous systems containing main biogenic elements (carbon, nitrogen, oxygen and hydrogen) are reviewed ; of particular interest are those found in simple cyanides and nitriles.

A survey is made of findings in radiation chemical studies of systems which chemical compositions are based on information on the constituents of comets, or the primitive atmosphere and hydrosphere of our planet.

About sixty molecules are reported: aldehydes, carboxylic acids, amino acids, heterocyclic compounds, polymers; also some data on free-radical intermediates observed during their formation .

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(1) I.G.Draganic: Radiation chemical approaches to chemical evolution processes on earth and beyond (This Conference).

2-P-1

Absolute Asymmetric Synthesis of Metal Complex Compounds achieved by the First Order Asymmetric Transformation

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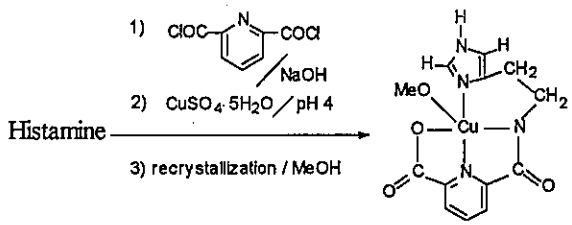
The first order asymmetric transformation has opened a channel to Absolute asymmetric synthesis of metal complex compounds, which is the macroscopic manifestation of molecular chirality in a solvent.

The present study has started to deny the Status, " Enantiomer could not turn to be Diastereomer". I had an idea that an enantiomer can turn to be diastereomers under a new mechanism of chiralitic "behavior" of an extra ligand on each enantiomer. This behavior causes the first order asymmetric transformation of each enantiomer and gives the equilibrium lying to either side of diastereomers favorably. It is detectable by the specific rotation analysis.

For taking shape the idea, I designed and prepared the penta-coordinated copper complex: [(6-carboxy-2-pyridilamide)histaminato]methoxocopper(II), Hst-pyr-Cu-OMe, using some achiral starting materials as shown in scheme 1. This complex has the equatorial tetradentate ligand which produces the atropo-S and/or atropo-R configurational frameworks, and which can be intra-transformed between atropo-S and atropo-R isomer owing to the bend of the methylen carbon neighboring the imidazole ring. This bending directions with respect to the apical methoxy group causes to give the *syn* or *anti* stereo-isomers at the same time. The asymmetric rotations of the fifth ligand of methoxy group attributes the enantiodifferentiation of the atropisomers in a solvent. This is to say that the enantiomers of the complex turned to be diastereomers by the asymmetric rotations {R,S} (Fig. 1).



Scheme 1 Hst-pyr-Cu-OMe

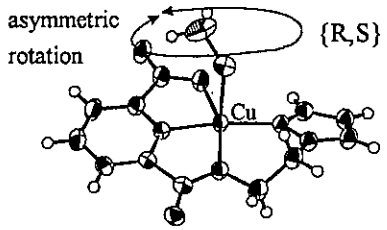


Fig. 1 Atropo-S-*syn*

An X-ray crystallography study revealed that Hst-pyr-Cu-OMe consists of the atropo-racemi complex. The $[\alpha]_D$ of the complex, however, indicated -980° as shown in Table 1, which includes the $[\alpha]_D$ data of the corresponding complexes derived from D, DL, L-histidine.

Table 1 $[\alpha]_D$[a] and the synchronous color changes

complexes	$[\alpha]_D$[b] MeOH[c]	$[\alpha]_D$ pH < 2[d]	$[\alpha]_D$[b] pH > 4[e]
Hst-Pyr-Cu-(OMe)	-980, (-1240)[f]	0, (0)[f]	-980, (-1240)[f]
D-His-Pyr-Cu	-750[g]	+41	-750
DL-His-Pyr-Cu	-560	0	-560
L-His-Pyr-Cu	-350	-41	-350
color of solution	blue	colorless	blue

[a] HORIBA, SEPA-200. [b] mutarotation. [c] MeOH(1.5 ml)+0.1M-NaOH(10 μ l), c 0.153, 0.241, 0.280, 0.220, 17°C. [d] 6M-HCl(10, 30[f] μ l).
[e] 6M-NaOH(10, 30[f] μ l). [f] 0.1M-NaOH c 0.154 20°C. [g] MeOH.

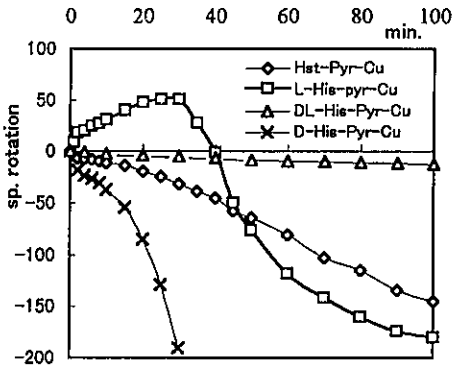


Fig. 2. Specific rotations allowing the crystals to dissolve into MeOH.

The solid crystal of L-His-pyr-Cu was found to consist of only the atropo-R enantiomer by X-ray analysis. Therefore, the transition of it's optically rotated polarity from plus to minus value implies that the atropo-S molecule of L-His-pyr-Cu is prevalent in a solvent (Fig. 2). Then, it is clear that Hst-Pyr-Cu-OMe and the series of corresponding complexes resulte in prevalence of atropo-S molecules in a solvent (Table 1 and Fig. 2).

This conclusion allows us to extend the new phenomena of the first order asymmetric transformation not only to the other metal complexes, but also to biological compounds and to some organic compounds produced through the five coordinated intermediates.

2-P-2

海底熱水噴出孔を擬した進化フローリアクター

A Flow Reactor for Prebiotic Synthesis Simulating Hydrothermal Vent

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原始地球上の熱水環境下において進行したと想定される, 自己複製分子出現に至る化学進化を模擬的に実現するため, 海底熱水噴出孔の環境を模した反応系を構築し, アミノ酸や核酸塩基を反応出発物質としてオリゴペプチド, オリゴヌクレオチドの生成を試みる. 海底熱水噴出孔は高温・高圧を特徴としているが, 噴出される熱水にはメタン, 水素, 硫化水素, アンモニアなどの還元性ガスの濃度が周りの海水に比べて高く, 鉄, マンガン, 亜鉛などの金属イオンが大量に溶け込んでいる. 海底から噴出する熱水およびその近傍は化学進化に適した環境と考えられる.

【進化フローリアクターの特徴】

閉鎖系において熱エネルギーを供給しただけでは, 有機合成反応が促進されるが同時に生成物の分解反応も起こり, そこでは熱平衡での生成・分解反応系が実現されるだけである. これに対して海底熱水噴出孔を擬した反応系(進化フローリアクター)は開放系であり, その特徴は次の二点に集約される.

①物質とエネルギーが不断なく供給されている.

②非平衡での化学反応の場が持続的に実現されている.

【進化フローリアクターの製作】

高圧を開放系で実現し, 高温の熱水を低温環境へ噴出する反応炉を製作した.

①無脈流ポンプを用い, 圧力損失の大きな細管(内径 0.1mm の管路)に反応出発物質を含む模擬海水を大量に送り込むことで, 細管上流に大きな圧力(最大 34MPa)を得た.

②細管上流に二つのチャンバーを設置し, 一方は電気炉で加熱し高温高圧環境を造り, 他方は低温水槽で冷却することで低温高圧環境を造った.

③双方のチャンバー間をノズルで接続し, 高温高圧の熱水を高温高圧環境下へ噴出させ, 海底熱水噴出孔に似た非平衡反応系を実現した.

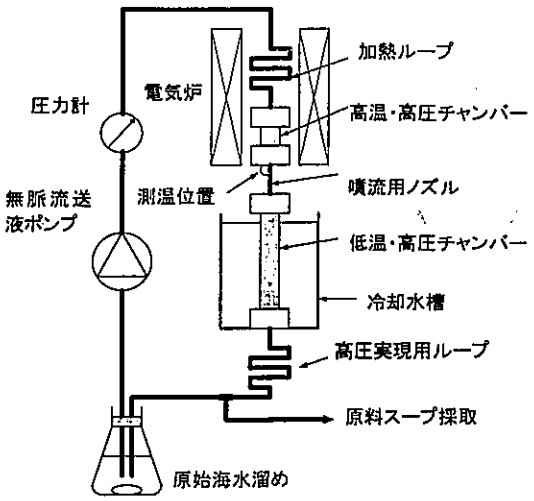

図　進化フローリアクターの構成

2-P-3

進化フローリアクターでの自己触媒型重合反応の出現
Autocatalytic Synthesis of Oligopeptides in a Flow Reactor

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物質進化における自己複製分子の出現に至るモデル実験を行った。海底熱水噴出孔の環境を模擬化した進化フローリアクターを用い、アミノ酸を出発物質として、オリゴペプチド生成に至る反応の実現を目指した。

【実験方法】

グリシンのみを反応出発物質とし、進化フローリアクターによる重合反応を試みた。高温高圧チャンバーは２５０℃、２４ＭＰａ、低温低圧チャンバーは０℃、２４ＭＰａの環境に設定し、無脈流ポンプで毎分１０㎖程度の流量で運転した。反応生成物は低温低圧チャンバーの出口より１分間隔で採取した。反応生成物の定量はＨＰＬＣを用い、標準物質のＨＰＬＣパターンの保持時間から生成物を同定し、ピークの面積から生成量を推定した。

【結果】

反応生成物はＨＰＬＣによる保持時間からグリシンの二量体、三量体と認められる。その生成量は高温高圧チャンバーが２５０℃に達した直後の反応初期段階においてdi-glycineおよびtri-glycine の生成量が指数関数的に増大した。この事実は自己触媒重合反応の可能性を示す傍証となる。

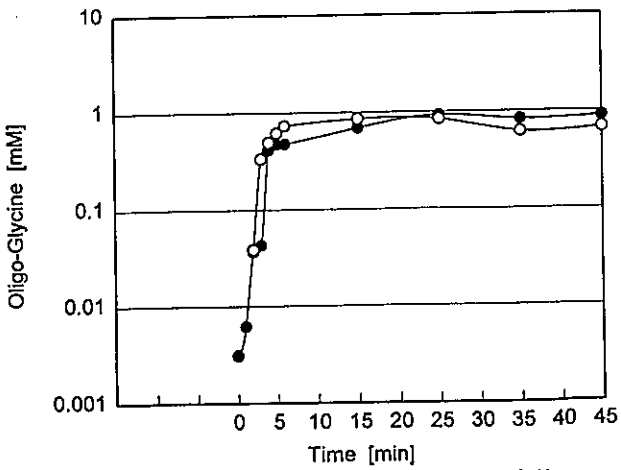

図　進化フローリアクターによる生成物
● Gly-Gly　○ Gly-Gly-Gly

2-P-4

Degradation of oligopeptides by contact glow discharge electrolysis

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Separation of homochiral peptides and heterochiral peptides may be an important step for the development of homochiral peptides and also for the formation of homochiral protein system in organisms. Heterochiral oligopeptides (for example D-Ala-L-Ala) composed of alanine are more hydrophobic than homochiral oligopeptides (for example L-Ala-L-Ala) baring same number of residues. Therefore, the solubility of heterochiral oligopeptides composed of alanine is lower than that of corrresponding homochiral oligopeptides in water.

In order to evaluate the concentration of these diastereomeric oligopeptides and the rate of separation of homochiral oligopeptides in the primitive hydrosphere, we have to know how the oligopeptides degrade or remain under speculated energy sources. In this study, contact glow discharge electrolysis which is knwon as a model reaction system of the lightning between atmosphere and hydrosphere was chosen as an energy source.

Contact glow discharge electrolysis was performed (480 V, 30 mA) in the solution containing L-Ala-L-Ala (1 mM) or D-Ala-L-Ala (1 mM) at pH 2. After 60 min's reaction, L-Ala-L-Ala decreased to c.a. 0.2 mM, while ammonia (0.46 mM), alanine (0.02 mM), alaninamide (0.01 mM), and several ninhydrin-positive compounds formed. The rate of degradation of D-Ala-L-Ala and main products were almost same as those of the reaction using L-Ala-L-Ala. However, the conversion of L-Ala-L-Ala to D-Ala-L-Ala and also the conversion D-Ala-L-Ala to L-Ala-L-Ala were not found in the reactions.

In the presentation, the postulated pathways of the reaction described above and the reactions using other peptide diastereomers will be discussed.

2-P-5

The organic-inorganic interactions as a geochemical origin of life

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Hokkaido UNIV. Earth and Planetary Sciences.

Many experiments have been conducted by using various energy sources such as ionizing radiation to study the origin and evolution of life. However, the role of abundant inorganic materials (minerals) on the earth's surface in the evolution of simple organic compounds into primitive biomolecules should also be considered.

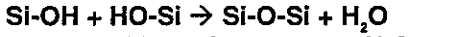
Based on our geohistorical backgrounds, banded iron formation (silica-iron oxides mixture layers) is one of possible geochemical environments of the first primitive life. Amorphous silica precipitated from solutions crystallizes into quartz in low temperature hydrothermal solutions. Our previous experiments at 180°C demonstrated that this is the dehydration process from the hydrated silica and is influenced by the presence of OH-bearing organic molecules. Amorphous ferric iron hydroxides precipitated from aqueous solutions dehydrate very rapidly into either Fe_2O_3 at lower pH and higher temperatures or FeOOH at higher pH and lower temperatures.

These hydrated amorphous silica and iron hydroxides are abundant colloidal particles in low temperature aquatic environments and have high surface area and surface active sites for chemical sorptions and reactions. The dehydration reaction of these materials proceeds spontaneously with a low to moderate heat energy sources (20-200°C). Considering that amino acides cannnot be polymerized spontaneously, the presence of silica and/or iron hydroxides can lower the free energy of overall polymerization reactions. Dehydration reactions of hydrous amorphous inorganic minerals such as silica and iron hydroxides can thus be expected to catalyze dehydration-polymerization of primitive organic molecules (amino acides and nucleoic acides) into precursers of bio-molecules (proteins and DNA). Therefore, we propose here a new working hypothesis of possible geochemical mechanism for the origin of life: coupled dehydration-polymerization-crystallization in the hydrous silica - iron hydroxides - amino and nucleoic acides systems (Fig.1).

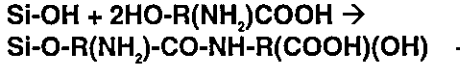
It should also be noted that the presence of transition metal ions in the above systems might play a crucial role in the energy transfer and enzymatic activities. Iron, again, is a most abundant transition metal ion on the earth having di- and tri-valent states. Iron and sulfur couple is known to mediate electron transfer for the photosynthesis as in the case of Fe-S-proteins (Ferredoxines). Iron sulfide mineral pyrite FeS_2 is then expected to be a key inorganic mineral in the co-evolution of mineral-bio-organic systems.

All these arguments permit us to propose a new point of view for the origin and evolution of life without any radiation energies: geochemical organic-inorganic interactions. These models will be tested by reaction experiments in the hydrous silica - iron hydroxides - amino and nucleoic acides systems.

Fig.1 A simplified schematic model in the co-evolution of organic-inorganic systems.
a) *Dehydration-crystallization of hydrated silica and iron hydroxides.*



b) Dehydration-polymerization in the silica-amino acid system to form polypeptides.



2-P-6

The role of organic-inorganic interaction in polymerization of amino acids

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Earth and Planetary Science. Hokkaido UNIV.

Over 45 years, researches for the origin of life have been done by organic chemistry and biology, mainly. But, it is also important to consider geochemical environments of evolution of simple organic compounds into primitive biomolecules. In other words, there is a possibility of polymerization of organic molecules through interactions with silicate minerals. Therefore, we checked this possibility, using silica gel and amino acids.

250mg of silica gel and 100ml of 0.1M amino acid aqueous solution were introduced into a PTFE-lined steal vessel, which was kept at 453K in a oven for 10 days.

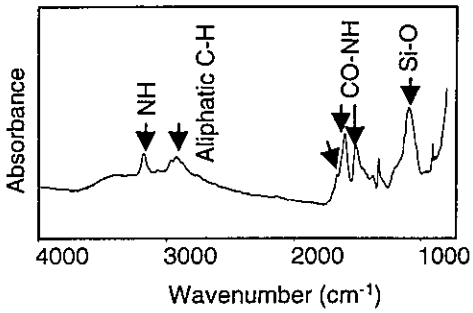

Fig.1: IR spectrum of the film product. Product was put on CaF_2 crystal.

Table1: several amino acids were reacted with silica gel. Concentration of amino acid solution was 0.1M,but Tyr was 0.1mM.

amino acid	film product	solution
Gly	x	no change
Ala	x	no change
Ser	appeaerd	turned brown
Val	x	no change
Thr	appeaerd	turned brown
Tyr	x	no change

In Thr(Threonine) run, a film-like product appeared on the surface of the solution. Fig.1 is IR spectrum of the film product showing existence of amide and ester bonds. In the same run, the solution turned into brownish color, and smelled bad. The same results were also obtained for Ser(Serine) run. However, for other amino acids, no changes or products were observed (Table1). This result indicates that amino acid's OH group is essential in the interaction of silica-amino acids. Since no change was found for Thr run without silica gel, OH of silica is also essential.

The following model was tentatively considered to explain the film formation: 1) dehydration between amino acid's OH group and silica gel's OH group. 2) amino acid bonded to silica surface then catches the dissolved amino acids. Amide bonds can also be formed between amino acids bonded to silica surface. Amino acids' layers thus grow by amide and ester bonds around Si-core forming a polymeric cluster. 3) these clusters aggregates into a film(Fig.2).

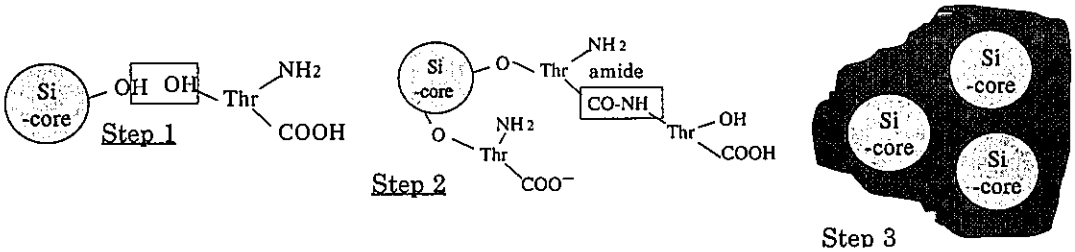

Fig.2: 1) Dehydration between amino acids and silica gel, 2) Formation of amide and ester bonds, 3) Aggregation into a film

This study indicates the importance of silica surface for the polymerization of amino acids. Further studies should then be focused on the surface reaction mechanisms.

2-P-7

水熱反応の速度論的解析：流通式反応器を用いるＡＴＰの加水分解反応速度の測定

Kinetic Analysis of Hydrothermal Reactions: Monitoring of ATP Hydrolysis by Flow Tube Reactor

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KAWAMURA Kunio (Osaka Prefecture University)

１．ＲＮＡは情報を保持する機能と酵素機能の両方を持つため，地球上において最初の遺伝情報を担った物質であると考えられている．一方，生命が誕生した環境は熱水鉱床のような高温の海水中であったと考えられている．ところが，生命が熱水中で出現したとする仮説が正しければ，ＲＮＡはそのような環境で化学進化したことになる．しかし，一般にＲＮＡは熱安定性が低く，高温水中では情報保持機能や酵素機能は発現できないと考えられるが，そうであればＲＮＡワールド仮説と熱水起原説は両立しない．著者らはこのような観点から，ＲＮＡ原料であるATPの高温水中（373～647K）での加水分解反応挙動を調べた［１］．その結果，ATPの分解は高温水中では速く，通常のバッチ法では追跡できなかった．そこで本研究では，フロー式反応器を用いて反応速度を測定することのできる新しい手法を開発した．今回は，この方法の評価と，この方法によってATPおよびアデノシンの加水分解反応を追跡した結果について報告する．

２．装置は，HPLC用ポンプ，ループインジェクター，加熱反応器，冷却および背圧管，および試料採取部からなる．試料は一定流速で送液され各温度で所定時間だけ加熱反応器中を通過する．したがって，流速を変えるあるいは加熱反応器中の配管の長さと管径を調節することによって，加熱時間を制御できる．加熱反応器内部の圧力は，背圧管に生じる圧損によって各温度における水の蒸気圧以上に保つことができた．この方法で，ATPあるいはアデノシン（各0.005 M)の加水分解反応を0.1 M NaCl, 0.05 M $MgCl_2$, 0.05 M Imidazole (初期pH=7.0)中で追跡した．生成物はHPLCで分析した．

３．背圧管の影響：背圧管としてテフロン(内径0.25 mm)製あるいはPEEK製(内径0.13 mm)チューブを用いて圧力と流速との関係調べた結果，この流れは層流であった．また背圧管の長さを変えて背圧を250kgcm^{-2}まで調整できた．加熱反応器中配管の影響：配管としてテフロン(内径0.25 mm, 長さ200 cm)およびSUS316 (内径0.25 mm, 長さ200 cm および内径 0.1 mm, 長さ100 cm)を用いた．テフロン管とSUS316管では基本的に同じ反応曲線が得られたので，これらの配管壁面での触媒作用はないものと考えられる．反応速度の測定：本法の性能を評価する指標として，398－523 K でATPの加水分解，532－ 573 Kではアデノシンの加水分解反応をそれぞれ追跡した．この方法で測定した473 Kにおける反応曲線を図に示す．反応は398－573 K において0.37－140 s の範囲で追跡できた．ATPあるいはアデノシンの減少の見かけの速度定数をアレニウスプロットした結果良好な直線関係となり，これらの範囲で熱伝達が正確に行われたことを確認できた．反応曲線をSIMFITで解析し，バッチ法を用いて373－423 Kの範囲で測定した結果と比較した結果，フロー法で測った結果と矛盾しないことが確かめられた．

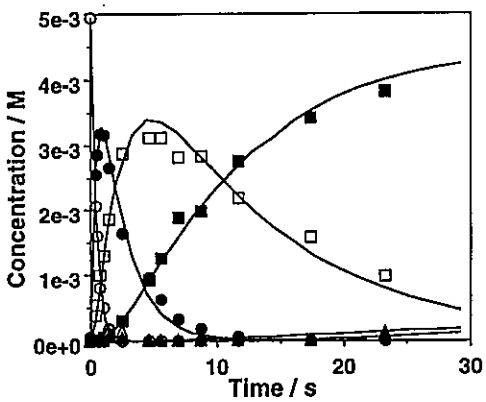

Fig. Reaction curves for the ATP hydrolysis using SUS316 tubing at 473 K. The lines drawn through the experimental points were fitted by SIMFIT.
○: ATP, ●: ADP, □ : AMP, ■: adenosine, △: adenine, ▲ : hypoxanthine.

[1]川村邦男，吉田晶子，松本修，Viva Origino, 25 , 177-190(1997).

2-P-8

中温水中におけるポリヌクレオチド類の加水分解反応挙動

Hydrolysis of Polynucleotides in Aqueous Solution at Elevated Temperatures

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1．　ＲＮＡは原始地球上で化学進化し最初の遺伝情報を担った物質であると考えられている。しかし、ＲＮＡの化学進化がおこった原始海水は高温で、ＲＮＡは生成すると同時に速やかに分解したと考えられる。したがってＲＮＡワールド仮説の信憑性を考察するためには、ＲＮＡの分解反応を系統的に調べなければならない。そこで今回は、60 ~ 120 ℃の範囲で種々の塩基を持つポリヌクレオチド(poly(N)) の加水分解速度定数を決定した。

2．　poly(N) は、市販のホモポリマー、またはポリヌクレオチドホスホリラーゼを用いて合成したコポリマーを用いた。反応条件は、2.5×10^{-4} M poly(N)をNaCl, $MgCl_2$,HEPES (pH=7)を含む水溶液に溶かし、プラスチックバイアル又は小型反応器に入れ、60 ~ 120 ℃で所定時間加熱した。生成物は高速液体クロマトグラフィーで分析した。poly(N) の加水分解速度定数は、結合の数の減少速度を1次プロットして、時間ゼロにおける傾きから決定した。

3．　poly(N) の加水分解反応の$MgCl_2$ の有無による影響を調べた。80 ℃, pH 7では、各ヌクレオチドの加水分解速度定数は$MgCl_2$ 非存在下で1.5×10^{-4}～1.7×10^{-3} min^{-1}であり、$MgCl_2$ 存在下では2.9×10^{-2}～2.4×10^{-1} min^{-1}であった。従って$MgCl_2$ の存在下で約50倍分解反応が加速されたことを示している。一方、ホモポリマーおよびコポリマーの塩基の種類を変えて調べたが、加水分解速度定数は80 ℃において最大10倍程度しか異ならなかった。これは、塩基の種類において加水分解速度定数はあまり影響されないことを示している。poly(A) の加水分解生成物を調べたところ、ポリヌクレオチド中のリン酸ジエステル結合は式（1）に従って切断されることが確かめられた。

$$\sim A^{3'}pA\sim \rightarrow \sim A^{3'}p + A\sim \quad (1)$$

poly(A) の加水分解速度定数をアレニウスプロットした結果、活性化エネルギーは64 kJmol^{-1} ($MgCl_2$ 非存在下) および45 kJmol^{-1} ($MgCl_2$ 存在下) であった。poly(A) は、$MgCl_2$ 存在下100 ℃ で10分間以内に完全に分解された。ＲＮＡが化学進化した環境がもっと高温であれば、ＲＮＡの分解速度はさらに大きかったと考えられる。従って、ＲＮＡが高温水中で化学進化したと考えるためには、①ＲＮＡの加水分解反応が抑制される条件、又は、②ＲＮＡの生成速度が分解速度に比べて充分大きい条件、を仮定しなければならない。

2-P-9

Synthesis of Amino Acids from Sodium Carboxylic Induced by keV Nitrogen Ions

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Nitrogen ions with keV energy were implanted into solid sodium carboxylic including sodium benzoate, sodium formate and sodium acetate. Some new chemical groups such as cyano-group ($-C\equiv N$), methylene group ($-CH_2-$) and radical of $COO^{-\bullet}$ were detected out after the implantation. It is especially significant that a number of amino group ($-NH_2$) was formed when the irradiated samples were dissolved in water. Hence , it has great possibilty for this kind of amino group to form some type of amino acid with the intrinsic carboxyl-group.

The samples were prepared as thin films, then were implanted. After the implantation. The samples were analyzed as follows:

1. With a FT-IR spectrometer, cyano-group (with characteristic wavenumbers of 2190 cm^{-1}) were observed in sodium acetate. It is well known that substances with cyano-group are precursor of amino acid, and the most important kind of precursor for biological bases as while.
2. Using ortho-phenbialdehyde as derivant, with a fluorescence detector, product containing α-amino group in sodium acetate was acquired in the spectrum of HPLC. The ninhydrin reaction further illustrated the production of amino group was proportional to the impalntation dose. Thus it can be deduced that the product has structure as sodium glycine $H_2C-COONa$.

$$\begin{array}{c} \\ | \\ NH_2 \end{array}$$

The experiment in present paper demonstrated that when nitrogen ions impact on small organic molecules, which have no nitrogen element, the rearrangement of deposited nitrogen ions, displaced atoms and intrinsic elements takes place, then amino group and cyano-group are formed. From this , a hypothesis is put forward that when low energy nitrogen ions generated in original atmosphere reached the surface of the earth and bombarded carboxyl salts in soil, amino acids could be synthesized. In one word, the interaction of low energy ions with solid substances may play an important role in the chemical evolution of life.

2-P-10

RADIOLYSIS OF CARBONATES AND RELATED ORGANIC SYSTEMS IN 3.8 Ga.

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Small molecules has been formed from simulated prebiotic synthesis using a wide variety of energy sources. The more reduced atmospheres favor the synthesis of organic compounds both in terms of variety as well as in the yields of the compounds. The energy sources considered here is ionizing radiation, which has been considered in the past as a minor contributor among the energy sources available for chemical evolution; the reason for this is that radiation sources were, in general, more abundant in rocks than in the atmosphere. However, due to its ionizing effects, we believe it must be considered a more significant source than it is currently accepted. The more important radionuclides from the interior of the Earth are potassium-40, and the uranium-238 and thorium-232 families, which, 3.8 X 10^9 years ago, supplied an estimated annual dose at the Earth's crust and shown in the following Table.

ESTIMATED ANNUAL DOSE (Gy/YEAR) 3.8 Ga AGO AT THE EARTH'S CRUST

MATERIA	POTASSIUM-40	URANIUM-238	THORIUM-232
Sedimentary rock carbonates	1.8 X 10^{-3}	1.04 X 10^{-3}	1.68 X 10^{-4}
Deep sea sediments carbonates	2.0 X 10^{-3}		
Sea water	2.5 X 10^{-4}	1.42 X 10^{-6}	1.98 X 10^{-9}

1 Gy = 1J/kg = 100 rad

At that time, this level of radioactivity might have been an important alternative energy source to induce chemical changes, reducing carbon compounds, such as bicarbonates in the ocean and carbonates in solid sediments, which could have co-precipitated with diverse cations including ^{238}U, ^{232}Th, and ^{40}K. Radiolysis of such carbonates has been studied and the G values have been calculated for the organic products formed from γ and from self- radiolyzed calcium carbonate. From this study, with doses of the order of MGy, the principal radiolytic products from self-radiolyzed $Ca^{14}CO_3$ are formic and oxalic acids with a G^0 values of 1.75 X 10^{-3} and 2.57 X 10^{-4} respectively. In addition, in O_2-free aqueous solutions of ammonium bicarbonate, the radiolytic products formed from kGy doses were formate (G^0 = 2.2), oxalate (G^0 = 0.059) and formaldehyde. Although the quantities of radiolytic products were small, they constitute important pathways for the formation of organic products on the primitive Earth. The resulting products are potential starting materials for the synthesis of more complex organic compounds.

In this work we will show that the quantities of organic products that might have been formed by this route may not have been negligible.

2-P-11

Quantum Mechanical Investigations of Fullerene, Photoactive and Organometallic Molecules, Complexes, Supramolecules, Supermolecules and Design of Basic Elements of Molecular Devices for the Electronically Genome Regulation

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Molecular implementation (MI) of logic functions, summators of neuromolecular networks, cells of molecular cellular automata, molecular trigger that are the basic elements of molecular devices for the electronically genome regulation were designed based on results ofsemiempirical and ab initio quantum chemical calculations of electron donor, electron insulator, electron acceptor and fullerene molecules, supermolecules, supramolecules and organometallic complexes. Complete set of sixteen MI of two variable logic functions was designed using MI of two variable molecular logic function initial basic sets. These two and three variable logic functions AND, NAND, OR, NOR analogs, four variable logic functions OR, NOR, AND, NAND analogs, molecular cell that simulates one of Life figures, summator of neuromolecular network that simulates sigmoidal behaviour of artificial neurone and RS molecular trigger were recalculated and found the optimal geometry and electron hoping probabilities.

2-P-12

Radiation induced stable fullerene radical anion

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The success of synthesizing macroscopic amount of fullerenes with a high purity e.g. > 99 % has brought about a variety of biological and medical application such as inhibition of the HIV-1 protease and antitumor effect by water soluble fullerene derivatives. At this stage we hypothesize that fullerene radical anions are more reactive to biological substances than neutral fullerenes, since the former interacts more strongly with molecules through coulombic forces between cationic species or charge transfer reactions, so that their application in biological and medical field is promising. Thus it is very important to elucidate physico-chemical properties of fullerene radical anions.

In this study, we report optical absorption and ESR characteristics of C_{60} radical anion embedded in γ-cyclodextrin which is produced by γ-irradiation of the aqueous solution.

The aqueous solution of C_{60} embedded in γ-cyclodextrin(C_{60} / γ-CD) of 1.6x10-4 mol・dm-3 was γ-irradiated at both 77 and 290 K. The optical absorption spectrum measured at 77 and 290 K consists of two bands at 935 and 1070 nm and is attributed to the radical anion C_{60}^- / γ-CD. The ESR spectrum measured at 77 K showed g = 2.0006 and $\triangle H_{pp}$ = 0.20 mT. The values are very close to those of pure radical anion of C_{60} produced in organic glasses such as MTHF and M CH,indicating that the excess electron density locates on the fullerene ring of C_{60} / γ-CD complex. The radical anion,C_{60}^- / γ-CD, was very stable at room temperature when it was produced at room temperature. When it was produced at 77K, however,the radical anion started to decay at about 200 K. The yield of C_{60}^- / γ-CD produced at 290 K was about 50 times as high as that at 77 K. The temperature effects on the stability and yield can be explained by the thermal behavior and reaction of OH radical which is concomitantly produced in the aqueous solution. The OH radical produced in aqueous solution decays faster than e_{aq}^- so that the survived e_{aq}^- reacts with C_{60} / γ-CD to yield C_{60}^- / γ-CD. On the other hand, the reaction between e_{aq}^- and C_{60} / γ-CD becomes less efficient at 77 K because of the low mobility of e_{aq}^-. The OH radical is also stably trapped in the aqueous solution at 77 K. On annealing the irradiated aqueous solution at 200 K, the OH radical becomes mobile and encountes the radical anion to oxydize it.

2-P-13

Experimental studies of chemical evolution using nuclear reactions and their associated radiations

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In the experimental approach to the origin of life, the simplest working hypothesis holds that the the molecules that are fundamental now were fundamental at the time of the origin of life. It is conceivable that the nucleic acids or at least their precursors appeared at a very early stage in the evolution of this planet. The energies available for the synthesis of organic compounds under primitive earth conditions have been considered to be mainly ultraviolet, electric discharge and heat from volcanoes. However, in our laboratory, we have performed several experimental studies of chemical evolution using nuclear reactions and their associated radiations. This report reviews such trials in brief. At first, the recoiled ^{31}P atoms derived from the b-decay of ^{31}Si were used to synthesize AMP from adenosine[1], and ATP from ADP[2]. Recoiled ^{32}S atoms derived from the b-decay of ^{32}P were also available to convert alanine to cysteine[3]. In connection with the works concerning the use of hot atoms derived from b-decay, it was of particular interest to find out that there was significant difference in the radical formation of D- and L-alanines irradiated with the β-rays induced from the β-decay of ^{90}Y[4] and ^{3}H[5].

The fact that racemization reaction of amino acid, alanine took place both in the free state and in alanine oligomers after γ-irradiation[6], indicates the importance of further analysis of the mechanism and the biological meaning. Another observation was also made on the selective radio-decompositi on of amino acids irradiated in mixed aqueous solutions. Namely, alanine was 5-fold more radiosensitive when it was irradiated with glycine than it alone[7]. From another evidences which were obtained from the experiments in which irradiation was carried out in various concentrations of these amino acids and at different pH, the result was explained by supposing a direct interaction of the glycine radicals and alanine molecules[8]. Similar phenomenon was found between L-alanine and L-aspartic acid[9]. Namely, the asymmetric field induced by L-alanine might affect the radio-decomposition rate of either aspartic acid. Recently our attention is focussed on the enzyme-like activities induced by radiation on the non-enzyme proteins, gelatin, polyglycine,and peptides[10].

1) Akaboshi *et al.*, *Biochim Biophys. Acta*, 238, 5 (1971). 2) Akaboshi *et al.*, *ibid*, 246, 194 (1971).
3) Akaboshi *et al.*, *Origin of Life* (ed. by Noda H., Acad. Publ. Center, pp. 343 (1978)).
4) Akaboshi *et al.*, *Origins of Life*, 9, 181 (1980). 5) Akaboshi *et al.*, *ibid*, 12, 339 (1982).
6) Kawai *et al.*, *Viva Origino*, 15, 148 (1987). 7) Akaboshi *et al.*, *Viva Origino*, 16, 154 (1988).
8) Akaboshi *et al.*, *Viva Origino*, 19, 147 (1991).
9) Akaboshi *et al.*, *Origins of Life*, 20, 111 (1990).
10) Akaboshi *et al.*, Abstracts of the 11th International Conference on the Origin of Life, July, 7-12 , Orleans , France (1996).

2-P-14

Survivability of small biomolecules under high temperatures

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After several decades of progress in the area of origins of life, it is still difficult to convincingly explain how emerged the simplest biomolecules, amino acids and nucleic acid bases, on the primitive Earth. Two extreme points of view are their endogenous production and extraterrestrial delivery (by comets, meteorites and interplanetary dust particles).

Geological record and photochemical models point to the Earth's primordial atmosphere to be composed mainly of carbon dioxide (probably with a small percentage of carbon monoxide), nitrogen and water vapor. Organic compounds can hardly form, especially in significant amounts, in such a non-reducing environment. That is why the alternative idea of extraterrestrial delivery of organic matter to the early Earth is especially attractive at present. A strong argument on its favor is the identification of a large variety of organic compounds, including amino acids and nucleic acid bases, in carbonaceous chondrites, as well as the detection of numerous organic species in interstellar medium and comets. However, one of the problems is how temperature labile biomolecules can survive the high temperature regimes developed during atmospheric passage and on impacts of space bodies to the terrestrial surface.

Although some indirect estimates of simple biomolecules' survivability have been reported, there is an evident lack of experimental data. Some results have been reported demonstrating that amino acids decompose at temperatures about 500 °C giving CO_2, H_2O, NH_3, CO, and a variety of relatively simple organic compounds (amines, nitriles, amides, hydrocarbons, *etc.*), as well as undergo simultaneously intermolecular condensation into cyclic dipeptides diketopiperazines. The latter class of compounds is very important in our context since diketopiperazines preserve amino acid residues intact: amino acids can be regenerated again under diketopiperazine hydrolysis. Semi-quantitative estimates of their yields at the 500 °C pyrolysis give 5-20%. However no data are available on whether amino acids and nucleic acid bases decompose completely under those high temperatures, that would have the most direct relation to the problem of biomolecule survivability in space bodies entering the Earth's atmosphere and impacting its surface.

To provide some insights, we have undertaken the present study. Particular goals were to estimate (1) how much amino acids and nucleic acid bases can survive without chemical alteration being subjected to a rapid heating; (2) what happens to optical activity of chiral amino acids; (3) yields of diketopiperazines formed; (4) what other compounds form that can produce amino acids again upon hydrolysis. As a result, we have found that (1) simple amino acids, purines and pyrimidines do not decompose completely even under temperatures >500 °C, with the percentage of recovery of the order of 1-10%; (2) major products of amino acid intermolecular condensation are diketopiperazines with the yields normally of the same order of magnitude as amino acid recovery; (3) other products containing intact amino acid residues, formed in smaller amounts than diketopiperazines, are bicyclic amidines and hydantoins; (4) racemization of amino acid residues is significant to total.

2-P-15

THE PREBIOTIC SYNTHESIS : THE URANIUM AS A UNIVERSAL ENERGY SOURCE

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We establish the hypothesis according to which the Archean uranium deposits (UDs) were the most suitable environments to achieve the monomers and polymers prebiotic synthesis and, consequently, the origin of Life on Earth. The UDs provided thermal energy, ionizing radiation and fission energy. Ionizing radiation was the most effective in the synthesis of monomers, and the nuclear fission, localized in certain UO_2 mineralized volumes (aggregates), was responsible for the synthesis of biopolymers (Garzon, 1996). On the other hand several experimental and/or observational facts are coherent with the environments and /or mechanisms proposed :

1.- The presence of carbonaceous matter in certain uraninites (Grandstaff,1980;Schidlowski, 1981;Robinson ,1984).

2.-The content of some carbonaceous matter in the large pitchblende lenses in the Oklo deposit (Nagy et al.,1993).

3.-The existence of some carbonaceous radioactive minerals, being THUCHOLITE the most relevant of them.

4.-The presence of organic compounds in certain meteorites (Shimoyama,1996). There is also and acceptable correlation between the geographical distribution of the Archean microfossils and that of the early uranium deposits.

Garzon ,L.:1996,El Origen de la vida.Un nuevo escenario.Servicio Publicaciones.Universidad, Oviedo (Spain).
Grandstaff,D.E.:1980,Precambrian Res,13,1-26.
Nagy,B. et al.:1993,Geology,21,655-662.
Robinson,A. and Spooner,E.T.C.:1984,Economic geology, 79,297-321.
Schidlowski,M.:1981,US Geological Survey,Prof.Paper 1161-N,29p
Shimoyama,A.:1996, Abstracts of the 11th International Conference on the Origin ofLife, Orleans ,France 5,12 J1

Tuesday, 3 March

Chemical Evolution
(*Terrestrial*)

O-9

Surface chemical reactions during the irradiation of solids: Prebiotic relevance

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Surfaces reaction phenomena among organic compounds adsorbed into alumino-silicates can be enhanced if they are irradiated with a very penetrating radiation. In this work is hypothesed that such combination of interactions (which include facets as excitation, storage and transfer of energy), is considered to serve as a substrates for the prebiotic evolution of molecules. In particular, the interaction of these alumino-silicates with nuclear gamma rays and its relationship to surface chemistry is discussed in terms of the optical-spectroscopic properties of these non-conductive solids.

Firstly, the potential contribution of the natural radioactive nuclei as a prebiotic energy source, is studied as the only energy source capable of penetrate a condensed matter. From these point of view a conservative estimate to place a lower limit on their prebiotic abundance of these nuclei is intended.

Secondly, a comparison of some of the properties of these energy sources, relative to solar energy, must be pointed out in order to give a particular suitability for driving reactions occurring under geological conditions. However, the importance of the interaction of gamma-rays with solids, must be supported within a framework of the capabilities of minerals to serve with its behavior, (under for example electronic excitation, and surface reactivity), to the evolution of organic molecules.

With these in mind, it was then necessary to find some properties that fit with the exposed above. These were found within the luminescent properties of solids, which give an indication of storage and transfer processes of energy. Thus, the spectroscopic properties of the solid-adsorbate system provide a basis for estimating the potential significance (in the occurrence of solid surface chemistry) of storage and transduction of energy. From this should be enough to realize its importance during the primitive Earth.

Therefore, the interaction of these condensed phases with gamma-rays, conduces to some commonly accepted concepts of heterogeneous catalysis, and some means by which surface activity might be enhanced with the presence of this energy inputs.

O-10

Chemical evolution on the dust grains in the dark clouds: Experimental Approach

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The reactions of H atoms with N, C, O, CO, and organic compounds in solid phase at 12 K were investigated by temperature-programmed desorption mass spectrometry. The solid matrices, containing atoms were formed by depositing plasma-activated gases over the surface of a cryocooler at 12 K. The deposited film was reacted with H atoms by spraying plasma-activated hydrogen gas over the surface of the deposited sample films.

When N_2 film containing N atoms was reacted with H atoms, it was found that the H atoms diffuse inside the N_2 matrix and react with N atoms to form NH_3 molecules. The diffusion of H atoms in N_2 and H_2O matrices at 10-30 K and the absence of H atom abstraction from H atoms of NH_3 were confirmed by an electron spin resonance experiment.

In the reaction of H atoms with C atoms trapped in the CO matrix, H atoms migrate in the CO matrix and react with trapped C atoms selectively to form CH_4. This indicates that the reactivity of H with the matrix CO is much lower than that with the C atom.

D_2O was the major product from the reactions of D atoms with O atoms trapped in a N_2O matrix.

The formation of formaldehyde and methanol has been confirmed in the reaction of H with solid CO., i.e., the occurrence of consecutive H atom addition reactions, $CO \rightarrow HCO \rightarrow HCHO \rightarrow HCHOH \rightarrow CH_3OH$. The rather low yield of the reaction products suggests either the small rate constants of the H atom addition reactions to CO and/or the occurrence of the hydrogen abstraction reaction, $H + HCO = CO + H_2$. CH_4 was found to be one of the final products from the reactions of H atoms with solid CO. The precursor for the formation of CH_4 may be CH_2OH radical.

No products were detected from the reaction of H atoms with CH_3CN, indicating that the nitrile group is not amenable to the hydrogenation reactions by H atoms at $\approx$10 K.

In conclusion, The H atoms play a role for the formation of fundamental molecules as well as that for the destruction of complex molecules formed on the dust grains through the hydrogen abstraction reactions followed by the disproportionation reactions.

O-11

Chemical Synthesis of Biomolecules in the Origin of Life Simulated by Ions Implantation

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The synthesis of biomolecules is an important step in the origin of life. In the early period of the earth, H_2, CH_4, H_2O, NH_3 etc. constituted the atmosphere. Frequent energizing impacts, such as ultraviolet ray, discharge, ionizing irradiation, could synthesize some important biomolecules like amino acids, bases or their precursors from the simple gases mixture. Then the products formed in the atmosphere deposited onto lands or into oceans with rain dropping. Those into oceans could evolve continually with the help of water. How about those onto lands, which may be in the form of salts or other compounds reacting with elements in soil. In the above energizing process, simple molecules absorbed the energy to give rise to electrons, ions, ionized molecules (atoms), radicals and free atoms, which are all active particles. These active particles acted on each other or on neutral molecules, to form more complex molecules.

It is well known that ion irradiation has the same energizing effects. So it is possible to produce new complicated molecules or even biomolecules when ions impact directly on molecules in soil or oceans. In the original period of the earth, the energetic particles which generated from discharging, irradiating or emitting of the abundant radioactive elements in the earth crust could reach the surface of the earth or oceans to react on molecules in soil or water.

To prove the hypothesis, implantation of energetic nitrogen ions into water, simple organic or organic salts has been conducted. Using FT-IR, NMR, HPLC, EPR, and chemical methods to analyze the products. Some results have been obtained. New substances with UV absorption were found when nitrogen ions impacted on sodium formate (HCOONa) and sodium actate (CH_3COONa), and methylene group ($-CH_2-$) and radical of $COO^{\cdot}$ also were detected out in HCOONa. New cyano group was formed both in sodium actate and sodium benzoate (PhCOONa), and when the samples were dissolved in water, amino acids were formed. These two kinds of products contain the extra nitrogen element. By the way, when nitrogen ions with hundreds eV injected directly into water, amino group was detected out in this water.

So it demonstrates that when energetic ions act on simple organic molecules, they cause ionizing, exciting and rupture of molecules through energy transferring; then the fragments rearrange or synthesize non-symmetrically into new more complex molecules, in this step, the extra element has possibility to insert into the new products. Thus the implanted ion has energy and mass deposition dual effects in chemical synthesis of biomolecules. This chemical synthesis effects induced by ion implantation may play an important role in the chemical evolution of life.

O-12

Versatile Chemical Reactions of Carbon Compounds by Using Water Molecule Under High Energy Conditions

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ABSTRACT

The plasma generated by glow-discharge, arc-discharge and burning flame induce various organic reacatins in aqueous solution, such as oxidation, dehydrogenation, carboxylation, amination, coupling reaction and fixation of nitrogen molecules etc. The main active species are considered to be hydroxyl and hydrogen radicals generated by the decomposition of water molecules under high energy conditions. The reactions induced by plasma are very strong processes without using any other chemical reagent. Considering the composition of the reaction products, the reactions proceed relatively controlled stepwise way. The new type of chemical reaction in aqueous solution induced by plasmas is an unusual reaction which could not be carried out by the convertional chemical ways, and is considered to have great potentialities in its application to many organic compounds in aqueous solution. These reactions are also interesting in connection with the abiotic formation of bio-organic compounds during the course of chemical evolutional processes on the primitive Earth.

Wednesday, 4 March

Chemical Evolution (*Terrestrial*)
and
Radiation and Origin of Chirality

O-13

Studies on mechanisms of amino acid formation in plasma by optical emission spectroscopy

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There are many questions about mechanisms of amino acid formation by electric discharge. Are amino acid precursors formed in plasma, in water, or in other places? Are those formed from hydrogen cyanide or from other molecules?

In this study, plasma produced by magneto-plasma dynamic arc-jet (MPD arc-jet) and spark discharge was characterized by optical emission spectroscopy, and the mechanisms of amino acid formation by electric discharge were considered.

MPD Arc-Jet Method

A large amount of energy was instantly supplied into a CO-N_2-H_2O gas mixture. Highly activated plasma was produced, spouted ahead and collided inner surface of a reaction tube. A thin film deposited on the surface was scratched and hydrolyzed, and then, amino acids were given.

Atomic spectra, such as N, O, H, were observed in the plasma and the plasma temperature was estimated at 10000 K. This hot plasma was quickly cooled to room temperature by colliding against inner surface of the reaction tube, and an amorphous film was deposited on it. In this case, amino acid precursors seemed to be formed directly from excited atoms on the surface of the reaction tube, which indicates that intermediates, such as hydrogen cyanide, may not necessarily be important on amino acid formation. This corresponds to the results of our previous report.[1)]

Spark Discharge Method

This is a typical method of amino acid synthesis by electric discharge. A CO-N_2 gas mixture and water were set in a flask. After spark discharge was caused with a Tesla coil for several hours, the water was hydrolyzed and then, amino acids were given.

Not atomic spectra but CN molecular spectra were observed in the plasma. After cooled sufficiently, some kinds of molecules dissolved in water. In this case, amino acid precursors seemed to be formed by chemical reaction and polymerization of molecules, such as hydrogen cyanide, in gas or water.

1) S. Miyakawa, *Appl. Phys. Lett.*, in press.

O-14

The possible role of radiation in biogenesis: A system approach

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The origin of life process may be divided, somewhat arbitrarily, into a first stage of prebiotic synthesis of the building blocks of biology and their (relatively) simple interactions, and a second stage characterized by the emergence of more complex chemical entities distinguished by central attributes of life, such as metabolic cycles and template-directed syntheses. So far the great majority of studies on the role of radiation in biogenesis have focused on isolated reactions of the first stage. This is the result of both the complexity of the processes under study on the one hand, and the lack of detailed theories of the second stage, on the other. The "coevolution theory" (Lahav and Nir, 1997; Nir and Lahav, 1997), is a rather detailed biogeochemical scenario for the emergence of central attributes of life during the second stage of the origin of life process. Based on this model system it is possible to evaluate the role of radiation in the context of the "self-organization" (second stage) of the origin of life processes. The goal of the present work is to demonstrate the need for using a system approach in order to explore the possible role of UV radiation in a prebiotic scenario dealing with the latter evolutionary stage. The discussion focuses on (1) Screening effects by means of minerals and water, and (2) Robustness of the coevolution scenario with respect to UV radiation.

1. Screening Vulnerability of organic molecules to UV radiation is an important consideration in the evaluation of the coevolution scenario for the chemical evolution processes. The presence of minerals in the vicinity of these organic entities, or shadowing such as by rocks and cliffs, or a thick layer of water, might be critical for the survival of these processes and their primordial organic entities.

2. Robustness The coevolution theory makes it possible to study the robustness of the whole evolutionary system rather than isolated prebiotic reactions. Thus, according to the coevolution theory the minimal system necessary for the computer-modeling of the emergence and establishment of template-and-sequence-directed (TSD) syntheses comprises two amino acids, two proto-mononucleotides, proto-ATP, amphiphilic molecules, a mineral and several metal ions, in a fluctuating environment. Assuming a central role for small peptide catalysts and under appropriate conditions, this system is characterized by autocatalysis and feedback loops and is gradually enriched by TSD molecules of both proto-RNA and catalytic peptides in a TSD-reactions takeover process. In order to evaluate the effect of UV radiation the whole system should be analyzed. Calculations simulating certain aspects of the radiation effects on TSD syntheses have been carried out. For instance, an increase in the decomposition rate of proto-tRNA molecules can be compensated by increased concentrations of peptide catalysts or proto-RNA molecules. Preliminary results suggest that the coevolving system is rather robust, thus enabling the evolution of TSD syntheses, and probably many other attributes of life, under a range of environmental conditions and reaction parameters.

References

Lahav, N., and Nir , S. (1997). Emergence of template-and-sequence-directed (TSD) syntheses: I. A bio-geochemical model. *Origins of Life Evol. Biosphere.* 27: 377-395.
Nir, S., and Lahav, N. (1997). Emergence of template-and-sequence-directed (TSD) syntheses: II. A computer simulation model. *Origins of Life Evol. Biosphere.* (in press).

O-15

Non-equilibrium processes in prebiotic chemical evolution

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Cosmic evolution is characterized by a manyfold of non-equilibrium processes, beit in the first moments of cosmogeny, in prebiotic chemistry and in biological evolution. In prebiotic chemistry five types of non-thermal-equilibrium or suprathermal reactions contribute essentially to the built-up of biomolecule precursors and complex organic molecules, 1) photodissociation and reaction of the recoils with some eV energy, 2) ion- or atom implantation from the outside as well as knock-on processes within gaseous or solid systems e.g. by the action of solar wind or cosmic rays with energies ranging from eV to some 10^9 eV, 3) impact of small paticles with velocities exceding 500 ms^{-1} , 4) explosions (e.g. of solid C_2H_2), and 5) impact of bolides (meteorites, comets). As specific mechanism of these suprathermal processes in solids a multicenter reaction has been postulated. The collision cascade or shock wave changes the site of final reaction of implants by knock on, dislocation and excitation in order to loosen bonds and decrease lattice energy. Thus the formation of complex molecules such as PAHs or DNA-precursors from molecular fragments, radicals, metastable insertion products, etc. within a chocked zone is facilitated. Non-equilibrium chemistry is an important step to increase complexity of prebiotic matter. Especially within solids, these processes are typical examples for phenomenological determinism,, which Christian de Duwe has postulated for evolutionary reactions. From the great variety of product forming processes of suprathermal chemistry the interaction of the neighbourhood preselects typical pathways leading to incorporation of the implanted ions, atoms, fragments in larger molecular units which are newly formed.

O-16

SYNTHESIS OF RNA OLIGOMERS AND THEIR TEMPLATE PROPERTIES

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The RNA world was proposed as the first step in the emergence of life, where catalysis and storage of information was performed by RNA. According to this postulate, RNA oligomers were formed by the polymerization of mononucleotides present in the prebiotic world.

We have been studying the formation of RNA-like oligomers from activated monomers using montmorillonite, a clay mineral with layer structure, as catalyst. Self condensation of 5'-imidazolides of nucleosides in pH 8 aqueous electrolyte solution at room temperature produced oligomers up to 14 monomer units in length. The regiospecifity, composition and the length of the longest oligomer formed on montmorillonite varied with the base attached to ribose.

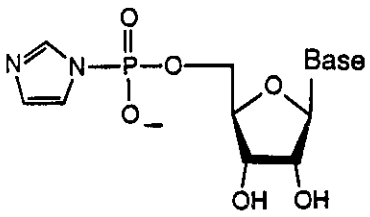
Reaction of ImpA in the presence of montmorillonite produced oligomers containing 2:1 ratio of 3',5'- to 2',5'-linked phosphodiester bonds. Addition of diadenosine diphosphate ($A^{5'}pp^{5'}A$) to the reaction mixture at a ratio of 9:1, ImpA:$A^{5'}pp^{5'}A$, increases the regiospecifity of 3',5'- to 2',5'-linkages to 3:1.

The extent of catalytic activity of montmorillonite varies with exchangeable cation used. Montmorillonites saturated with alkaline metal ions, NH_4^+ and Ca^{2+} are the most effective catalysts for the formation of oligoadenylates.

Oligocytidylates formed from the self condensation of ImpC on montmorillonite contain mainly 2',5'-phosphodiester bonds. We have studied the template properties of these oligocytidylates [oligo(C)] for the non-enzymatic template directed synthesis of oligoguanylates [oligo(G)]. The self condensation of guanosine 5'-phospho-2-methyl imidazole (2-MeImpG) is catalyzed by oligo(C)s containing both 3',5'- and 2',5'-linkages. An oligo(C) template containing exclusively 2',5'-linkages also serves as template for the synthesis of oligo(G)s. The oligo(G)s formed on templates containing both 3',5'- and 2',5'-linked phosphodiester bonds, and exclusively 2',5'- linked phosphodiester bonds produce oligo(G)s containing both 3',5'- and 2',5'-linkages.

Bases:

A: Adenine
C: Cytidine
G: Guanine
U: Uracil



Structure of 5'-phosphorimidazolide of nucleoside

These studies establish that RNA oligomers prepared by mineral catalysis, or other routes on the primitive earth, did not have to be exclusively 3',5'-linked to catalyze template-directed synthesis, since oligo(C)s containing a variety of linkage isomers serve as templates for the formation of complementary oligo(G)s. These findings support the postulate that origin of the RNA world was initiated by RNA oligomers formed by polymerization of activated monomers present in the prebiotic world.

Our most recent work demonstrated that the reaction of mixtures of two activated monomers yield oligomers containing both monomer units. The reaction of A- and U- or A- and C-containing monomers on montmorillonite result in the preferential formation of the dimers pApU or pApC, respectively. This finding suggests that the hydroxyl groups of purine nucleotides react preferentially with the activated phosphates of pyrimidine nucleotides on montmorillonite. The reaction of C- and U-containing monomers also lead to the formation of phosphodiester bonds between the two kinds of monomers. However, unlike A- and C- or A- and U-pairs, there is no difference in the reactivity of one monomer kind towards the other.

O-17

Radiation as the advantage Factor in the Prebiotic Formation of Enantiomeric Excess

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There are considered all the three variants of the appearance and increase of enantiomeric excess (EE) under the illumination of racemic mixtures of enantiomers by circularly - polarized light (CPL) or due to the β -radiolysis of such mixtures. Main dimensionless characteristics of the value of EE and of the dynamics of its accumulation are the chiral polarization (CP) $\eta = (D - L)/(D + L)$ (D and L are the concentrations of enantiomers) and the advantage factor (AF) $g = (K_D - K_L)(K_D + K_L)$ (K_D and K_L are the rate constants of mirror-conjugated reactions with the participation of D and L enantiomers).

There are presented dynamical equations $\dot{\eta}(\tau)$ for asymmetrical processes of destruction of enantiomers, of their racemization and for their synthesis from achiral substrate. The existence of racemizing processes ($\dot{\eta} = -æ\eta$) causes strong limitations of stationary values of CP: $\eta^{(s)} \leqq g \sim 10^{-2}$ (for CPL; for β -radiolysis $g \ll 10^{-2}$), at $g \gg æ$ it becomes possible the formation of transition states with η max $\gg \eta^{(s)}$. It is emphasized the cardinal difference between the accumulation of EE, i.e. the transformation of racemic state to the mixture of "dominant" and "recessive" enantiomeres and the attainment of chiral purity of optically active system.

Under the typical actual conditions - i.e. under the domination of racemizing processes ($g \ll æ$) over the effect of AF - the attainment of chiral purity is possible only by the bifurcational mechanism, via the spontaneous breaking of mirror symmetry. Such peculiar phase transition can proceed even at $g = 0$. Evolutionary attainment of chiral purity by gradual accumulation of EE (even with the account to various amplification processes) is possible only at practicully complete suppression of racemizing processes ($g \gg æ$).

In this connection it seems to be of particular interest the investigation of the influence of local or global AF on the system which can undergo the optical activation at very low temperatures, when all thermally activated processes are suppressed and - in addition - the tunneling racemization is strongly inhibited due to the interactions of chiral molecules with cold environment.

O-18

New Concepts on the Role of Physical Parameters Inducing Homochirality for the Evolution of Biosphereres

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In this paper an overview is given on the concept of homochirality in the context of life as such, on the mechanisms operating in generating homochirality in living systems, and on the significance of homochirality outside Earth in the search for extraterrestrial life. Under the term „homochirality" we understand the abundance of only one possible chiral structure within an investigated system. (This would by definition then automatically exclude the coexistence of the other chiral, the antipodic or enantiomer compound in the same system!) This condition is obviously a unique feature of our terrestrial biosphere (where only the L-amino acids and D-sugars predominate in the biopolymers) and manifests certainly not only an accidental property, but a necessary building principle that allows sufficient complexity of the biological system required. In the literature many models have been worked out on the various mechanisms capable of generating such an homochirality during terrestrial evolution from prebiotic elements into the recent biosphere. The dispute within the scientific community has not been settled in so far as the result (as it appears to us today!) was a purely chance decision or the consequence of uni-directed pressure leading to the actual homochiral structure. Among the physical parameters discussed acting on the evolution of biosphere are the so called parity violation of weak interaction, gravitation, and selectively acting radiation, to name only the most mentioned ones. Although there are many theoretical paperson the possible mechanisms in the literature, only rather meager experimental evidence is published which would be able to support unambiguously the one or the other theoretical model ruling this process. In spite of these deficiencies one thing at least seems to be clear beyond any doubt: The homochirality as such is a specific signature of life, not only on Earth, but also on any extraterrestrial body to be investigated in detail. Hence a systematic search for homochiral structures outside Earth would necessarily serve as a central tool for the search of extraterrestrial life. Recently some evidence of this kind has been reported, some work is in progress and some sound research proposals dealing with the study of chiral structures on extraterrestrial bodies have been submitted, which will be discussed here in this paper.

O-19

Radiation on the causal origin of homochirality

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The cause for the great preference in life for L-amino acids and D-sugars over their corresponding enantiomers has been extensively studied. Based on a series of experiments, it is found that elementary particles interact differentially with enantiomers of amino acids. The difference of inelastic scattering section of D and L type molecules under irradiation of β electron caused an asymmetry of reaction rates of chiral molecules when the system is far from equilibrium at low temperature. The helicity of the polarized β electron (left or right) which may stereoselectively decompose one of the two configurations (D or L) decided by the rotatory strength sign of different amino acids. According to the theoretical prediction, the disputation and suspicion about the controversial results between Garay(1968) and Darge(1976) could be explained. It might be attributed to the fact that the rotatory strength sign of L-tyrosine ($R_{\pi\pi^*} > 0$) and L-tryptophan ($R_{\pi\pi^*} < 0$) are of opposite sign at experimental condition. Based on the theoretical study and experimental results, a new classification of twenty amino acids is proposed. The first kind L-amino acids are Ala,Val,Ile,Asp,Glu,Gln,Arg and Lys as their rotatory strength sign are positive. The necessary condition of L-amino acid surviving under β irradiation is ($R_{\pi\pi^*} > 0$). It may be the first stage of the formation of biochirality.

In 1991 A. Salam proposed a new hypothesis: the subtle energy difference of chiral molecules induced by Z^0 interaction combined with Bose-Einstein condensation may cause biochirality among the 20 amino acids at critical temperatureT_c ,which is analogous to that of BCS superconductivity. Four kinds of experiments have been carried out in attempting the phase transition of single crystals of D-,L-alanine and valine. (1) An obvious λ phase transition at 270 ± 1 K was shown in the specific heat measurement of alanine and valine enantiomers by differential scanning calorimetry. The biologically dominant L-enantiomer was found to have lower energy. (2) Magnetization of the single crystals of D-,L-alanine and D-valine were measured as a function of temperature using the SQUID magnetometer. Magnetic transition temperature seems coincident with that of λ transition. The difference of the $\chi \sim T$ curve between the D- and L-alanine is attributable to the variation of intramolecular geometry of chirality density in the presence of an external magnetic field. (3) Laser Raman spetra of D-,L-alanine at different temperature (100K, 250K, 260K, 270K, 280K, 290K) showed that the second order C-H streching frequencies at 2606 cm^{-1}, 2724 cm^{-1} of D-alanine vanished at 270 K but reappeared at 100K In the same condition,L-alanine has no such phenomenon. We propose a weak effect arises in the period of λ phase transition at which the hydrogens of α carbon oscillate between the lower and higher energy states and stay for a relatively long time in the higher state before they are recorded. (4) Nuclear Magenetic Resonance Spectroscopy of D-, and L-alanine powders were measured as a function of temperature using Bruker DRX 300 wide bore with 5 mm probe. Carbon-13 cross polarization spectrum and one pulse proton spectrum were shown that D-alanine and L-alanine play different behaviour at the λ phase transition point 270 K. It means the mechanism of phase transition of alanine enantiomer is different. We present our experimental results involving the possible relevance of Salam's putative phase transition. The putative transition was suffered from the difficulty of implying large activation energy barriers for the production of optically pure amino acid .It is possible to account for this problem by assuming that the principal effect of ionizing radiation on the alanine in solid state as in aqueous solution produced an α-radical from the amino acid zwitterion by abstracting a hydrogen atom. Three resonance hybrid of α-radical anion obtained from the zwitterion . It may be possible to implement the transition from D- to L-types which have lower ground state energies.

O-20

UV Processes Leading to Prebiotic and Chiral Organics in Interstellar Dust

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The mantles of interstellar dust which are accreted at temperatures of 10K in molecular clouds are photoprocessed by the ultraviolet radiation from distant stars and also by the ultraviolet radiation generated by the cosmic rays. Ultraviolet photons break the bonds of the simple frozen molecules such as water, carbon monoxide, methane, and ammonia. Warmup and recombination of the frozen radicals leads to the formation of complex organic molecules(ref 1). Laboratory experiments as analog to the interstellar processes provide evidence for the presence of a wide variety of prebiotic molecules in interstellar dust. Some of these molecules, including several identified amino acids in the laboratory created organics, are mirror image molecules. When an interstellar cloud of dust passes in the neighbourhood of a neutron star, the circularly polarized ultraviolet radiation from such a star, of which the crab nebula is the canonical example, destroys either one or the other of the mirror image mantle molecules (depending on the direction of circular polarization) and this leads to a cloud of dust with chirality in its organic mantles (ref 3). Quantitative laboratory experiments combined with the distribution of neutron stars inferred from X-ray pulsars have been combined to suggest that a large fraction of interstellar clouds should be dominated by as much as or greater than a factor 2 in the handedness of their organic molecules (ref 2). Our solar system appears to have formed from the contraction of such a cloud as indicated by the recent evidence for such a high level of enantiomeric excess ($L/D \approx 2$) in the Murchison meteorite (ref 4). This appears to confirm the prebiotic source of chirality in interstellar space. Since comets are presumed to consist of the dust of the primitive solar nebula it will be extremely important for the future space probes, such as the Rosetta mission to comet Wirtanen, to study *both* the chemical and chiral properties of the nucleus and dust.

1. Greenberg, J. M., 1984, Scientific American, 250, 124-135.
2. Greenberg, J. M., Kouchi, A. Niessen, et al, 1994, J. Biol. Physics,20, 61-70.
3. Bonner, W. B.,1991, Orig. Life, 21, 59-111.
4. Engel, M. H., Macko, S. A., 1997, Nature, 384, 265-268.

4-P-1

Property of active site for D-tryptophan on tryptophanase

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The origin of homochirality has intrigued scientists ever since *Pasteur's* discovery of the optical activity of amino acids. It has been so far discussed from the viewpoint of physics and chemistry, but there is still no general consensus. The stereospecificity of enzyme is very important for asymmetric biological world, because enzymes serve to select L-amino acids dominant in contemporary biological world. It is necessary to study the origin of homochirality on the basis of enzymology. The enzymological first step is to investigate the difference between the reaction with L type and D type on the same enzyme.

Tryptophanase (TPase), which is one of the most extensively studied PLP-dependent enzymes, has the very strict stereospecificity to L-tryptophan (L-Trp). TPase is not active to D-tryptophan (D-Trp) at all. However, TPase becomes active to D-Trp in highly concentrated diammoniumhydrogen phosphate solution (DAP). The reaction process of D-Trp degradation has been studied in terms of kinetics. It shows the significance of TPase・DAP・D-Trp complex, which is essential to gain access of D-Trp to the catalytic site of TPase through steric structural change. We here investigate the relation between active site for D type and one for L type. It is examined, first of all, how D-Trp acts on the active site for L-Trp. Secondarily, the active site for D-Trp is competitively deactivated with D-histidine (D-His) which has no effect on the active site for L-Trp, and then the inhibition type of D-Trp in the reaction of L-Trp degradation is analyzed in terms of kinetics.

The inhibition type of D-Trp as an inhibitor transits from competitive to non-competitive inhibition with increasing DAP concentrations. The switch of the inhibition type is probably responsible for indole ring of tryptophan, because potassium pyruvate and indolepyruvate serve as competitive and noncompetitive inhibitors in the reaction of L-Trp degradation, respectively. On the other hand, the activity of D-Trp degradation is maximal at the DAP concentration of 3.1 M, in which D-Trp acts as noncompetitive inhibitor. Additionally, D-Trp serves only as competitive inhibitor when the activity for D-Trp degradation is completely halted with D-His. This suggests that the catalytic site for D-Trp should be remote from the active site for L-Trp.

4-P-2

On the Origin of Saccharides: biology meets chemistry

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Statistics show that more than 60% of so far reported lectins (carbohydrate-binding proteins) are Gal-specific. Why such uneven distribution occurs beside a number of theoretical monosaccharides (see Fig.) ? A possible answer for this basic question is that Gal was selected as an important "recognition" saccharide especially in higher organisms. In fact, Gal is used more prominently in higher organisms like mammals, while Glc and Man represent microorganisms such as bacteria and fungi. From a glycochemical viewpoint, Gal has inherent nature distinct from those of Glc, Man and Fru. Latter three monosaccharides are related by "Lobry de Bruyn-Alberta van Ekenstein transformation". It is well established that in N-linked oligosaccharide biosynthesis Gal is incorporated at later stages after removal of Glc and Man residues from the common precursor $Glc_3Man_9GlcNAc_2$. Gal is exposed at outermost spaces of cells unless it is masked by sialic acids, so that it is easily recognized by various communication molecules by homophilic carbohydrate-carbohydrate or heterophilic carbohydrate-protein interactions.

Extensively observed rules on saccharide utilization are summarized: i) Life systems choose only stable saccharides, which have the least number of axial groups in an assumed C1 conformation of aldohexoses. ii) Glc and Man are used maximally as starting materials for biosynthesis of saccharides (e.g., L-fucose, L-rhamnose, sialic acids, and more unusual dideoxysaccharides), while Gal is never used for such a purpose. iii) Glc, Man and Fru are enzymatically convertible to one another essentially by the mechanism via enediol intermediate, which mimics "Lobry de Bruyn-Alberta van Ekenstein transformation", while Gal is produced via 4-keto intermediate by the action of UDP-Gal-4-epimerase.

From these observations, the author has proposed a possible scenario on the origin of saccharides, which consists of i) "folmose reaction", ii) "aldol condensation" between glyceraldehyde and dihydroxyacetone, iii) "Lobry de Bruyn-Alberta van Ekenstein transformation" (these processes generate first triplet saccharides, Glc, Man and Fru), and iv) "bricolage" by using Glc and Man to produce various saccharides including Gal. Thus, biological phenomenon of "galactose-recognition" is considered to be an inevitable result based on glycochemistry.

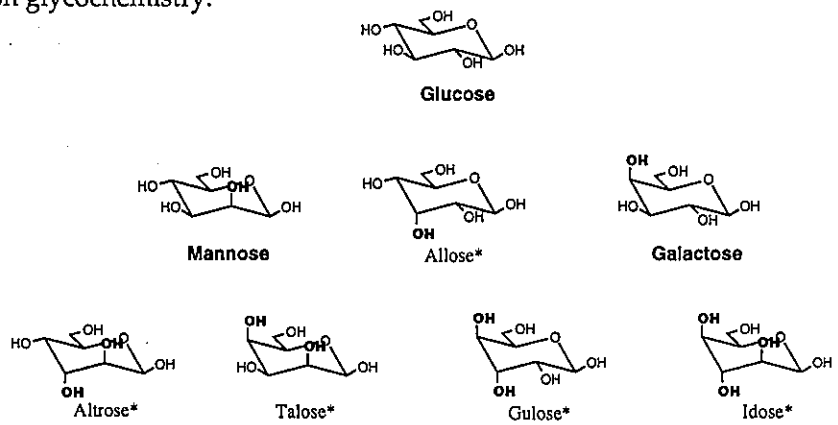

FIG. Theoretical D-aldohexoses. All the conformations are drawn as C1 form, where C5-CH_2OH group has the equatorial configuration. Sterically unfavored axial OH groups are emphasized by thick bonds.

1) Hirabayashi, J (1996) *Quart. Rev. Biol.* **71**, 265-380

4-P-3

Molecular Diversity and Evolution of the Galectin Gene Family in *C. elegans*

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Lectins are non-immune-origined proteins which specifically bind saccharides[1]. Among lectins, galectins are unique in that all members belonging to this family are galactose-specific. Although physiological functions of galectin are not well understood, they are implicated in various phenomena fundamental for multicellular animals[2] Galectins are found not only in vertebrates, but also in much lower animals, such as nematode and sponge. On the basis of protein architecture, they are classified into three structural types; i.e., proto, chimera and tandem-repeat types (see FIG.) .

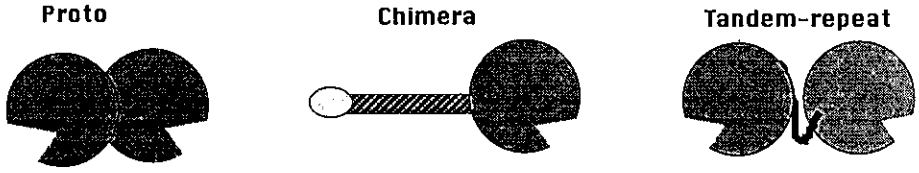

FIG. Galectins are classified into three distinct groups based on their structural architectures.

Caenorhabditis elegans is a small (1 mm) and simple (1,000 cells) model animal to investigate complicated multicellular systems. As a result of recent progress of genome project for this organism (80% of 1 x 10^8 bp completed), a number of galectin-related genes have been found. Main purpose of this study is analyze functions of these candidate genes and give insight into molecular mechanism of gene evolution, through i) cDNA cloning, ii) bacterial expression iii) and gene targeting experiments. So far, 10 galectin genes have been investigated. Among them, 5 were found to fall into tandem-repeat type galectins (tentatively designated CeLec-I-V), but their amino acid similarities differed variously (35-80%). The second group can be classified as proto type (CeLec-VI-X), though CeLec-VII, VIII and X show closer relationship to one another in their size (18 kDa), amino acid identities (45-70%) and high content of His (14%). Surprisingly, mRNA for CeLec-VII was not spliced as predicted by GeneFinder. This alternative splicing results in frame shift, and only short peptides are to be translated. CeLec-VIII gene, located close to CeLec-VII gene on chromosome X, can be a product of gene duplication as well as CeLec-VII, but as regards sequence homology it showed closer similarity to CeLec-X (70%) mapped on chromosome V. Binding to immobilized asialofetuin was examined by using recombinant galectins. CeLec-I, II, III (tandem-repeat type) and CeLec-VI (proto type) had stronger binding activity than CeLec-IV and VIII, while CeLec-IX had only very weak binding activity (activity of CeLec-V and X has not yet been checked).

In conclusion, most galectin genes were found to be functional (transcripts are identified) and exhibited galactose-binding activity. However, individual members showed significantly diverse features, such as RGD motif (CeLec-IV, V), high His content (VIII, X), extra exon-coded loop region (V), longer C-terminal tail (VII, VIII, X), etc. The results of the functional analyses should be valuable for considering biological significance of molecular diversity and life evolution, as well as for obtaining clues to a possible mechanism for gene duplication, pseudo gene formation, and generation of a novel gene.

1) http://www.dtinet.or.jp/~nao/glycoforum/science/word/wordE.html
2) Kasai, K., and Hirabayashi, J. (1997) *J. Biochem.* **119**, 1-8
3) Hirabayashi, J., Arata, Y., and Kasai, K. (1997) *Trends Glycosci. Glycotechnol.* 9, 113-122

4-P-4

Origin and Evolution of the Endogenous Double-Stranded RNAs in Plants

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Many plants often harbor the endogenous double-stranded RNAs (dsRNAs) at defined low levels. These dsRNAs transmit essentially via cell division and fusion. The host plants exhibit no sign of infection. With these respects, these dsRNAs are plasmid-like RNA replicons. In addition to the above properties, these endogenous dsRNAs have the key enzymes involving the replication, an RNA-directed RNA polymerase (RdRp) and an RNA helicase (Hel). These enzymes are also encoded by the conventional positive-stranded RNA viruses. The origin of the endogenous dsRNAs and the evolutionary relationship between these dsRNAs and the positive-stranded RNA viruses are unknown. Using the sequence data of the dsRNAs in *japonica* rice and green alga, we carried out the phylogenetic analysis of their replication enzymes and the comparison of their genomic organization with the conventional RNA viruses. The rice dsRNA (RDR) is about 14 kbp in length and has a single large open reading frame (ORF). Phylogenetic analyses indicated that RDR has an RdRp of superfamily (SF) III and a Hel of SF I and some consensus motifs of type I methyltransferase (MTR) which cap 5′ terminal of its genome. These properties are similar to those of some positive-stranded RNA viruses such as rubi-, tobamo-, potex-, closteroviruses. It suggests that RDR and some positive-stranded RNA viruses have evolved from the same ancestor. The green alga, *Bryopsis* sp., contains five dsRNA species in its mitochondria and chloroplasts. The mitochondrial dsRNA (BDRM) is 4,520 bp in length and has two overlapping ORFs. Northern hybridization data and the nucleotide sequence suggest the occurrence of a −1 ribosomal frameshift. The gene expression strategy and the classification of its RdRp indicate that BDRM is similar to totiviruses such as yeast L-A virus. These phylogenetic analyses of RDR and BDRM suggest that these dsRNAs do not originate from a single ancestor. The certain groups of the endogenous dsRNAs and the conventional RNA viruses may have evolved from a same ancestral RNA replicon. The endogenous dsRNAs may have spread as widely as the conventional RNA viruses.

4-P-5

Role of the Terminal Base-Pair of Acceptor Stem and CCA Sequence of tRNA in Aminoacylation Activity

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The CCA sequence is common to all the 3' ends of tRNAs. In principle, aminoacyl-tRNA synthetase attaches the proper amino acid to the 3' terminal adenosine of its cognate tRNA species. The geometry of the CCA sequence intrinsically close to the active site in aminoacyl-tRNA synthetase implies an important role in the catalytic process of aminoacylation. In addition, more than half of the tRNAs possess the G_1-C_{72} base pair at the end of acceptor stem. In general, the discriminator base, N_{73}, and certain base pairs within the first four of the acceptor stem (1-72～ 4-69) are needed to confer aminoacylation and to determine specificity. To study the role of the universal CCA sequence at the 3' end of tRNA and its vicinity in the aminoacylation process, not only the substitutions of these bases but also the nucleotide-additions at the 5' end of tRNA were introduced into many kinds of *Escherichia coli* tRNA transcripts and the effects on the aminoacylation activity with cognate aminoacyl-tRNA synthetase were investigated.

The results showed that all examined tRNAs basically possessed their own requirement of CCA in aminoacylation. However, the aminoacylation activity for the base substitution mutants of A_{76} was somewhat correlated with the hydrophobicity of the corresponding amino acids. Among the tRNAs investigated here, the aminoacylation activities were not influenced by the exchange of G_1-C_{72} to A_1-U_{72} except the cases of $tRNA^{Ala}$, $tRNA^{Thr}$ and $tRNA^{Gly}$. G_1-C_{72} might function as negative identity for the other species. One nucleotide-addition to the 5' end of tRNA, which resulted in the Watson-Crick base pairing at the position of discriminator base, did not affect the aminoacylation activity. Two nucleotide-addition decreased the activity for Watson-Crick type base pairing design (C_{-1}-G_{73}, G_{-2}-C_{74}), while the case of non base pairing at position 74 (C_{-1}-G_{73}, A_{-2}-C_{74}) showed no drastic decrease of the activity. These results suggested that proper spatial arrangement and flexibility were important for aminoacylation reaction.

4-P-6

May we ignore static geomagnetic field as the cause of chirality and helicity?

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Possible effects of magnetic force (e.g., Lorentz force) are considered toexplain the right-handed nature of DNA. Although the static magnetic field itself can cause only very weak asymmetry in molecular reactions compared to the already-weak atomic weak-interaction force, it may cause a systematic and strong asymmetry if a second force (e.g., gravity, convection electric field, or centrifugal force for gyrating ions) exists. We consider two possible occasions when the Lorentz force might have played some role during the formation of initial DNA/RNA. In both cases, we must assume that life is formed in a restricted geophysical area (such as volcano on either hemisphere). (1) To polarize the elementary molecules to D-type chiral ones: Under the influence of external forces (e.g., gravity), molecules are aligned to a different axis than the geomagnetic field direction, and the chiral-electrons in such molecules are expected to show an asymmetric distribution. In fact previous observation in space has shown magnetic field-dependent crystal forms. (2) To assemble the molecules to right-handed spiral forms: Helical duct structures being caused by whistler waves in the ocean (where the waves are strongly polarized) may act as a catalyst for nucleoside to be organized.

4-P-7

Role of Inorganic Phosphorus Compounds in Life Evolution: Molecular Recognition and Hydrolysis of Polyphosphates by Natural Enzymes

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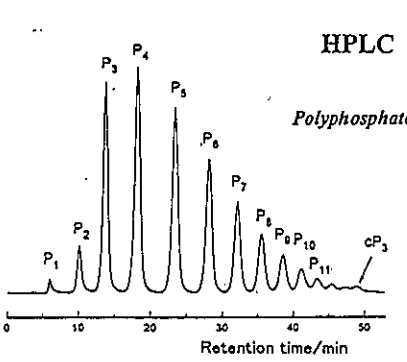
Inorganic polyphosphates of linear (Pn) and cyclic (cPn) structures, as exemplified by linear triphosphate P_3 and *cyclo*- triphosphate cP_3, consist of high-energetic P-O-P bonds analogous to those of ATP. This paper was undertaken to elucidate the molecular recognition by natural enzymes of Pn (n = 2 ~ 20), and cPn (n = 3 ~ 8), with a view to indicating the possibility that polyphosphate ions might have played a bioenergetic role in earlier life evolution before the emergence of ATP-world. High-performance liquid chromatography(HPLC), flow injection analysis (FIA) and P-31 NMR were employed to monitor the kinetic processes of enzyme-catalyzed hydrolysis of polyphosphate ions.

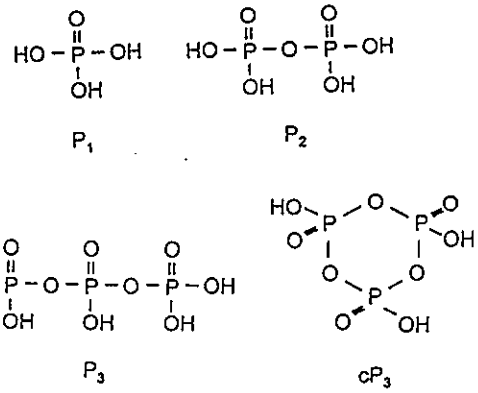
Strong analogy between ATP and diphosphate (pyrophosphate, P_2) with respect to their thermodynamic and kinetic parameters of P-O-P bond hydrolysis has been demonstrated[1-4]. A striking feature was that inorganic pyrophosphatase (EC3.6.1.1) from baker's yeast recognized P_2 as a specific substrate and accelerated the hydrolytic conversion of P_2 to orthophosphate P_1 by a factor of ten billion (10^{10}). The enzyme did not catalyze the hydrolyses of higher Pn and cPn, providing a strict ability to discriminate P_2 from the immediate homologue P_3.

On the other hand, alkaline phosphatase (EC3.1.3.1) from bovine intestine indicated quite different aspect of substrate specificity. It catalyzed the hydrolyses of all linear Pn, from P_2 up to P_{20}, but was inactive towards all cyclic cPn, from cP_3 to cP_8. The enzyme-catalyzed hydrolysis of Pn was likely to proceed according to a terminal phosphate clipping mechanism, not the cleavage at internal groups.

[References]

(1) N. Yoza, S. Onoue and Y. Kuwahara, Chem. Lett., **(6)**, 491(1997); (2) N. Yoza, S. Nakashima and T. Nakazato, Chem. Lett., **(1)**, 53(1997); (3) N. Yoza, Y. Akazaki, T.Nakazato, N. Ueda, H. Kodama and A. Tateda, Anal. Biochem., 199, 279(1991). (4) N. Yoza, H. Hirano, Y. Baba and S. Ohashi, J. Chromatogr., 325, 385(1985).





4-P-8

ポリシチジル酸を鋳型とするオリゴグアニル酸生成反応の
中温水中における速度論的解析

Kinetic Analysis of the Poly(C) Template-Directed Synthesis
of Oligoguanylates in Aqueous Solution at Elevated Temperatures

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Umehara masatosi, Kawamura Kunio

(Osaka Prefecture Univercity)

1．ＲＮＡは情報を保持する機能と酵素機能との両方をもつためにＲＮＡワールドを形成し、生命の起源に重要な役割を果たしたと考えられる。一方で、生命が出現した環境は熱水中であったとする根拠が得られつつある。そこで、ＲＮＡワールドが熱水中で成立したかどうかを調べるために、今回はpoly(C)存在下でoligo(G)が生成する反応を40～80 ℃の範囲で調べた。

2．活性化したグアニル酸モノマー（ImpG）及びpoly(C)を含む反応溶液 80 μＬをプラスチックバイアルにとり、あらかじめ所定の温度に設定したヒーターで加熱した。反応は液体窒素で急冷して停止した。生成物中に残存するpoly(C)をリボヌクレアーゼＡで選択的に加水分解して、HPLCでoligo(G)を分析した。

3．poly(C)を鋳型としてImpGからoligo(G)が生成する反応を反応温度 40～80 ℃で 24 時間まで追跡した。oligo(G)（４鎖長以上）の生成量は、40 ℃で 6 h反応させたとき約 30%であり、70 ℃で 10 min反応させたとき 1 %以下であった。反応温度の上昇に伴ってoligo(G)の生成は困難になったが、70 ℃でも微量のoligo(G)が生成した。これは、ワトソンークリック型の水素結合が弱くなり、oligo(G)の見かけの生成速度が小さくなったためと推定される。oligo(G)の生成量は、時間の経過に伴っていったん増加し続いて減少した。これは、生成したoligo(G)が加水分解されたためであると考えられる。最大の長さをもつoligo(G)が生成した反応時間は、40 ℃のとき 18 hであり、70 ℃のとき 10 minであった。また、このときの最大鎖長は 40 ℃で 30 鎖長、70 ℃で 13 鎖長であった。現在、この反応曲線をもとにoligo(G)生成の速度定数の解析を行っている。

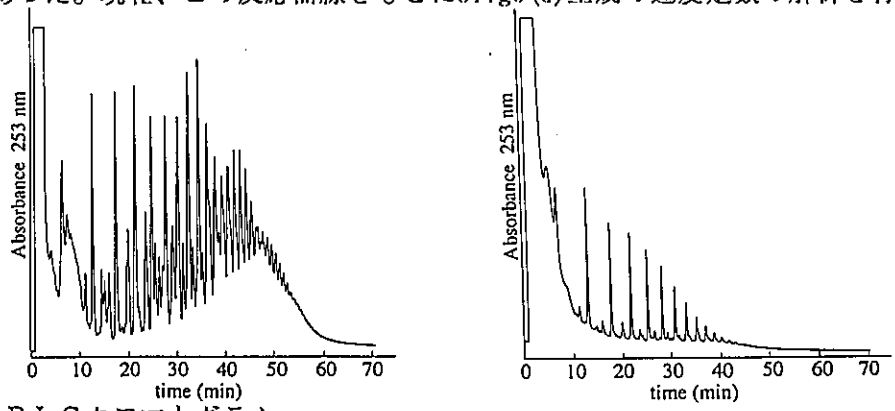

Fig. 1. ＨＰＬＣクロマトグラム

(a) 40 ℃,　18 h　　(b) 70 ℃,　10 min

Reaction conditions ; [ImpG]= 0.015 M, [poly(C)]= 0.025 M, [HEPES]= 0.1 M, [MgCl2]= 0.2 M, [NaCl]= 1.0 M, pH= 8.0.

4-P-9

Molecular evolution of aminoacyl tRNA synthetases and origin of universal genetic code

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The living things are thought to have appeared on the primitive earth 35 hundred years ago. At that time, only a primitive protein synthesis mechanism should exist, and after that, a genetic code system had evolved and the universal genetic code system had been established. Aminoacyl tRNA synthetase must have co-evolved with the genetic code system.

Every living thing in urkingdoms, Archea, Bacteria and Eucaria, utilizes the universal genetic code. Thus , three urkingdoms are supposed to be branched off after the universal genetic code system had been established. The present study aims to clarify how the universal genetic code system had been established, and to estimate the evolutionary paths of urkingdoms, by comparing the diversity of amino acid sequences of aminoacyl tRNA synthetase in various organisms.

4-P-10

SELECTION OF RNA-BINDING PEPTIDES FROM COMBINATORIAL LIBRARIES

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The arginine-rich RNA-binding motif (ARM) is a short RNA-binding peptide motif (15-20 amino acids in length) which has been identified in viral proteins such as HIV Rev, HIV and BIV Tat, as well as a number of bacteriophage (λ , ϕ21, and P22) antiterminator N proteins. Studies of the interactions of ARMs and their RNA sites have shown that both the structure of the peptide and the RNA targets that they recognize are diverse, and that the ARM may be a particularly versatile motif. Many of the amino acid determinants of these interactions have been determined, and it appears that other than arginine, very few other amino acids (predominantly hydrophilic amino acids) are required for tight and specific binding. This low sequence complexity and versatility of the ARM lead us to hypothesize that arginine-rich RNA-binding peptides may have arisen readily from random peptide mixtures of relatively low complexity early in evolution and played a role in the transition from an RNA world to an RNA-protein world.

In order to test how readily RNA-binding arginine-rich peptides may have been selected from random peptide mixtures, we created a number of relatively small combinatorial libraries and attempted to identify peptides that bind to the HIV RRE hairpin. We used a bacterial system based on λ N antitermination, that consists of an N-expression plasmid and a reporter plasmid containing the RNA site and transcriptional termination elements upstream of LacZ, so that peptide-RNA binding and resulting antitermination can be visualized by β-galactosidase activity. We were able to select WT Rev-like peptide from one library consisting of four amino acids (R, S, N, and H), and novel peptide sequences from another library consisting of three amino acids (R, S, and G). We have also used an evolutionary approach consisting of a mutagenesis and selection to identify variants of one RSG peptide (identified from the three amino acid library) into a stronger RRE-binder. These results demonstrate the low sequence complexity needed to select specific RNA-binding peptides, therefore suggesting the relatively high abundance of such peptides early in evolution. The possible evolution of such ribonucleopeptide complexes in a predominantly RNA-based world will be discussed.

4-P-11

Glutamyl tRNA synthetase of halophilic archaebacterium *Haloferax volcanii*

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Introduction

Aminoacyl tRNA syntheses (ARS) play an important role in the translation step by correctly charging tRNAs with their cognate amino acids.

We have studied glutamyl tRNA synthetase (GluRS) of halophilic archaebacteria *Haloferax volcanii*. We reported that GluRS of *H. volcanii* was eluted from various chromatography in the same position of aspartyl tRNA synthetase (AspRS) and that partial amino acid sequences of purified GluRS had similarities to those of AspRS of *Methanococcus jannaschii.*

Here we report the primary structure of *H. volcanii* GluRS and aminoacylation of fractionated tRNA with purified GluRS.

Method

Degenerate PCR primers were designed from reverse translation of partial peptide sequences. GluRS gene was cloned from *H. volcanii* genomic DNA using the PCR products as probe. The sequence of the gene were determined.

tRNAs were fractionated by Mono Q column and used for aminoacylation experiments with purified enzyme.

Result

We cloned 1302 bp of GluRS gene from *H. volcanii,* which coded for a protein of 433 amino acid with calculated molecular weight of 48689. The GluRS contained 12.2% aspartate and 8.8% glutamate, which is characteristic composition of halophilic proteins. Amino acid sequences obtained from purified GluRS were included in deduced amino acid sequence. The deduced amino acid sequence didn't contain HIGH and KMSKS sequences which are signature sequences of class I ARS, but did motif 1 , 2 and 3 which are signature motifs of class II ARS. Homology search showed that GluRS of *H. volcanii* didn't have similarities with known GluRS ,but did with known AspRS. These results suggested that *H. volcanii* AspRS charged aspartate and glutamate to tRNAs.

Currently, we are examining whether the enzyme can discriminate tRNA.

4-P-12

The origin of ribonuclease P RNA (M1 RNA), as viwed from poly-tRNA Theory

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The origin of RNase P RNA is yet an unsolved problem, although one of us (K.O.) formerly pointed out some sequence similarity between RNase P RNA and virusoids (Ohnishi, 1992). Eigen hypothesized that tRNA is the first gene from theoretical standpoint. On the other hand, we have postulated poly-tRNA theory (Ohnishi; Endocytobiology V, 407: 1993; Ann. N.Y. Acad. Sci. 707: 524, 1993;; Ohnishi et al.; Genome Informatics Workshop-93, 325; GIW-96, 238), in which most primitive mRNAs began to evolve from primitive tRNA(s), and at least some mRNAs (e.g., for glycyl tRNA ligase) have evolved from a poly-tRNA ribozyme closely kin to the poly-tRNA region of the *Bacillus subtilis trrnD* operon transcript. Here we report a possibility that RNase P RNA might have evolved from some tRNA or oligo-tRNA region of the *rrnB*-type poly-tRNA.

E. coli and *B. subtilis* RNase P RNA's were compared, by dot-matrix (Harr Plot) method (using Genentyx Software, Genentyx, Tokyo), with poly-tRNA regions of rrnB and trrnD operons, and also with rRNA regions of these operons. Most similar sequence segments found by this method were further analyzed by aligning the entire 377-base-region of RNase P RNA. The resulting alignment (n-base-long, m-base-match) was statistically evaluated by computing base-match probability by chance, $P_{nuc}(m,n)$.

Dot-matrix method showed three closely similar segment-pairs between *E.coli* RNase P RNA and *B. subtilis rrnB* operon poly-tRNA region; denoted here by matrix-homologies A, -B, and -C. Based on the homology-C, the entire region of the RNase P RNA was aligned against bases 5672-6032 of the *rrnB* poly-tRNA region, tRNA(Leu)-tRNA (Gly)-tRNA(Leu)-tRNA(Arg)-tRNA(Pro) (Fig.1). Base match level is 47.4 %(= 166/350, excluding gap positions), giving P_{nuc} (166, 350) = 0.11×10^{-18} in this alignment (*rnpB* bases 1-377). The homologies A and C satisfy this alignment, in which homologies A and B correspond homology relationships among different tRNA homologs in M1 RNA. Homology search in GenBank database further revealed that Thermus thermophilus dnaJ gene (DNA region encoding aa's 98-215) is most plausibly homologous to RNase P RNA (bases 14-377) [45.3% base match, $P_{nuc}(160,353) = 0.33^{-18}$)].

4-P-13

Origins and molecular evolution of prokaryotic cell-dividion genes

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The *E. coli fts* operon possesses *ftsQ*, *ftsA*, and *ftsZ* genes, which are known to be typical prokaryotic cell-division genes. The origins of these genes were alalyzed from the viewpoint of molecular evolution. Amino acid (aa) sequence segments similar to those of these three cell-division gene products were searched for from PIR Database, by Lipman-Pearson method using Genentyx Software (Software Development Co., Tokyo). Thus found possibly homologous sequence segments were re-analyzed by dot-matrix method (Harr-Plot), and the corresponding base-sequence alignments (m-base-match in n-base-alignment) were statistically evaluated by computing base-match probability by chance, $P_{nuc}(m,n)$ (Ohnishi, Origins of Life 14: 707-715, 1984). Sequence data were obtained from GenBank.

Homology search from database resulted in finding close aa sequence similarities between *ftsQ* (aa's 116-171) and *Thermomyces lanuginosus* actin (aa's 98-153), between *ftsA* (aa's 39-103) and *D. melanogaster* insulin-receptor (Ins-R) (437-501), and betwen *ftsZ* (aa's 50-125) and *S. cervisiae cdc* cell-division gene product (aa's 1148-1224). Based on these similarities and further matrix analyses, aa and base sequence alignments were obtained, in which similarity levels are; 16.9% aa-match (45.0 % base-match, P_{nuc} (192, 427) = 0.29×10^{-19}) for ftsQ (aa's 61-202)-actin (43-186) comparison, and 24.7% aa-match (35.7% base-match, $P_{nuc}(104,291) = 0.51 \times 10^{-4}$) for *ftsA* (aa's 8-104)-Ins-R (410-502) comparison. Similarly, *ftsZ* (aa's 16-180) and *cdc39* (aa's 1015-1281) were found to show a 22.9 % aa-match (22.9 % base-match), giving $P_{nuc}(208,491) = 0.35 \times 10^{-16}$. From these results and Harr-plot graphics, genuine homology relationships were concluded for every comparisons described above.

Accordingly, *ftsQ* protein is considered to have originated from actin-like molecule of primitive contractile system. The *ftsA* protein is a homologue of Ins-R and tyrosin-kinase, both functioning as elements of tyrosin-kinase-mediated signal-transmitting system. *ftsZ* protein is related to the yeast *cdc* cell-division protein, whose exact function being unknown.

4-P-14

Poly-tRNA-mediated origin of mRNAs and genetic codes

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The *Bacillus subtilis trrnD* operon has a structure of 5' [16S rRNA-23S rRNA-5S rRNA-$(tRNA)_{16}$] 3'. The tRNA cluster in this operon includes 16 tandemly repeated tRNA genes (denoted by "poly-tRNA structure"), in which ordering of amino acid (aa) specificities of these tRNA is "NSEVMD FT YWHQ GCLL". An ancient "*trrnD* -peptide" possessing this aa sequence was hypothesized, and protein sequence regions similar to trrnD-peptide were searched for from PIR Proein Sequence Database. The aa's 139-156 in the *E. coli* Gly-tRNA synthetase (GlyRS) a subunit was found to be most similar to this peptide. Further analysis revealed that not only the GlyRS gene encoding GlyRS a, but also the *a* gene of *Synechococcus* 6301 encoding F_0-ATPase a subunit, are both true homologues of the *B.subtilis trrnD* -poly-tRNA region. Leghemoblobin exon-3 (encoded the module) and vertebrate immunoglobulin J_H exons were also found to be homologues of portions of the trrnD-poly-tRNA region. A *trrnD* -type pseudo-tRNA gene cluster was also found in the downstream region of the *E. coli* 5S rRNA gene.

The *Bacillus subtilis* rrnB operon has a structure of 5' [16S rRNA-23S rRNA-5S rRNA-$(tRNA)_{21}$] 3', and this *rrnB* -type poly-tRNA structure was also analyzed from the standpoint of the poly-tRNA theory. Aa and corresponding base sequences were aligned against hypothesized rrnB-peptide (comprizing 21 aa-specificities of rrnB-tRNAs) and rrnB-mRNA (comprizing 21 codons complementary to 21 tRNA-antocodons). Gene segment coding for the helix 2-turn-helix 3 DNA-binding domain (aa's 30-57) showed a 54.0% base-match and a matching-probability by chance, $P_{nuc}(46,87) = 0.24 \times 10^{-7}$ to the tRNA-His region of the *B. subtilis rrnB* operon. Corresponding gene-segments of the *E. coli* adenylate kinase and the*Saccharomyces cervisiae* glutaraldehyde 3'-phosphate dehydrogenase (GAPDH) showed 51% (Pnuc = 0.24×10^{-4}) and 45% (0.59×10^{-3}) base-matches. Sponge homeoprotein 1 showed 30% aa match and 47% base0-match($P_{nuc}=0.59 \times 10^{-9}$) to GAPDH in DNA region coding for aa's 50-107, elucidating close evolutionary relationship between these proteins. Based on matrix analysis, the entire 377-aa-encoding region of the lambda-repressor gene (cI) was found to be homologous to the hexa-tRNA-region, "tRNA(Phe)-spacer-tRNA(His)-sp.-tRNA(Gly)-sp.-tRNA(Ile)-sp.-tRNA(Asn)-sp.-tRNA (Ser)", in the rrnB operon, showing 48.1% base-match and $P_{nuc}(204,424) = 0.14 \times 10^{-19}$. Accordingly, these genes were concluded to have evolved from a *rrnB*-like poly-tRNA structure, as proposed by poly-tRNA theory.

These findings strongly support the recently proposed "poly-tRNA theory" (Ohnishi, 1993) on the origin of mRNA and genetic codes. Thus it has now been concluded that both the *B. subtilis trrnD* -type and rrnB-type poly-tRNA regions are relics of most primitive RNA molecules capable of synthesizing *rrnD* -peptide-like or *rrnB*-peptide-like primitive peptides in early life. The most paradoxical problem on the origin of genetic codes seems to have been basically solved from the aspect of poly-tRNA theory.

4-P-15

Formation of Amino Acids from Simulated Planetary Atmosphere by Radiation

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A number of experiments have been performed to synthesize bioorganic compounds in simulated planetary environments based on chemical evolution hypothesis. Energy sources, such as spark discharge, ultraviolet light and heat, were used in previous experiments, which suggested that bioorganic compounds like amino acids could be easily formed abiotically if reduced-type starting materials were used. Nowaday it is suggested, however, that the primitive earth atmosphere was not strongly-reduced as was previously considered. It was reported that abiotic formation of bioorganic compounds were difficult when non- or mildly-reduced types of starting materials were used. In the present study, we irradiated mixtures of CO, CO_2, N_2 and H_2O with high energy protons, electrons or gamma ray to examine possible formation of amino acids in primitive earth.

Experimental: A gas mixture of CO (350 Torr) and N_2 (350 Torr) over liquid water was irradiated with (i) 3 MeV protons from a van de Graaff accelerator (TIT), (ii) 15 MeV electrons from a linear accelerator (INS, Univ. Tokyo), or (iii) gamma ray from a ^{60}Co source. In some experiments, mixtures of CO, CO_2, N_2 and H_2O were used as starting materials. Amino acids in hydrolysates of aquous phase products was determined by HPLC and/or GC/MS.

Results and Discussion: A wide variety of amino acids were detected in all the products. Glycine was predominant among them. Fig. 1 shows correlation between energy deposition to the gas mixture and glycine amount found in the product when a 1:1 mixture of CO and N_2 was used. It is proved that the amount of glycine is proportional to the deposited energy. Yield based on energy (G-value) was ca. 0.02 molecules per 100 eV when a 1:1 mixture of CO and N_2 was irradiated with particles, which was independent from the kind of particles. In the case that the mixture was irradiated with high flux of gamma ray, the yield was less than others, which suggested to be due to decomposition of the products.

Amino acids could be also formed when mixtures of CO, CO_2, N_2 and H_2O was used; particularly, CO/N_2 ratio is *ca.* 1, yield was considerably high. The present results suggested that prebiotic formation of amino acid was possible in primitive earth atmosphere by cosmic radiation.

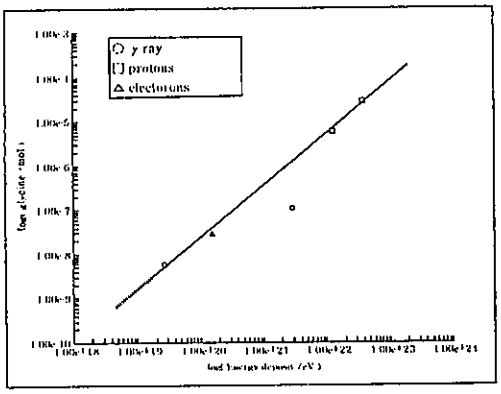

Fig. 1. Correlation between energy deposition to the gas mixture and glycine found in the product.

4-P-16

Rate of racemization and degradation of amino acids during acid-hydrolysis of synthetic peptides

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Homochirality, the total predominance of one enantiomer, is necessary for present-day life. DNA and RNA are constituted of L-sugars; proteins and peptides are of D-amino acids. The reason and cause of biological homochirality is not known although many researches have been done on this matter. We have noticed a phenomenon that the rate of a D-amino acid concentration to the corresponding L-amino acid (D/L ratio) in proteins from tissue extracts occasionally decreased with the time length of hydrolysis, in spite that the D/L ratio was low.

To confirm the phenomenon we synthesized two peptides using F-moc method and a peptide synthesizer: 1) a peptide composed of 1 D-serine molecule and 9 other L-amino acid molecules; 2) a peptide composed of 4 L-serine molecules and 16 other L-amino acid molecules. Determination of D- and L-amino acids was performed by high-performance liquid chromatography with a reversed-phase column as described previously (Nagata et al., J. Chromatogr. 575, 147-152, 1992), after modification of amino acids with 1-fluoro-2,4-dinitrophenyl-5-L-alanine amide. The results of hydrolysis of the first peptide and the mixture of the two peptides in 6 M HCl at various temperatures and for various time lengths showed that the amount of D-serine liberated and the D/L ratio of serine decreased with the time length of hydrolysis. Hence, it has been suggested that D-serine is prone to decompose by heat in 6 M HCl, comparing to L-serine. The phenomenon appears to concern with the origin of amino acid homochirality in organisms.

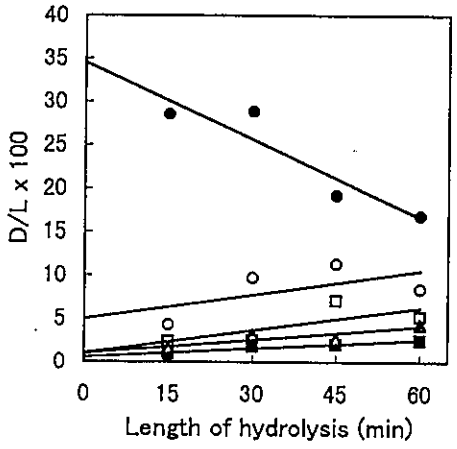

Fig. A hydrolysis carried out at 160°C. Linear regression lines are shown. Symbols are: ●, Ser; ○, Asp; □, Glu; △, Pro; ■, Ala

Thursday, 5 March

Radiation and Origin of Chirality, Energetics for Chemical Evolution

and

Biological Evolution

O-21

The role of isotope effects in radiation-induced selection processes

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The radiation-induced decarboxylation of phenylalanine-1-^{13}C and of leucine-1-^{13}C show sigmoid dose effect relations, typically for the radiation damage in organic solids. The decarboxylation of D-enantiomers is more effective than that of L-enantiomers. This is valid for ^{60}Co-radiation, which is not polarized at the place of irradiation, but also for the autoradiolytic decarboxylation of leucine-1-^{14}C.

Therefore it can be assumed that not the nature of radiation is responsible for the generation of the D/L-asymmetry of amino acids, but the effects induced by the absorbed radiation dose.

Of special interest are recent findings concerning the decarboxylation and deamination of L-leucine-1-^{13}C by ^{60}Co-irradiation. The formed carbon dioxide and ammonia had to be separated and prepared for mass spectrometric analysis individually. Comparing the results one can state that the yield of deamination is 4-5 times greater than that of decarboxylation. The dose-dependent isotope fractionations during decarboxylation (^{12}C/^{13}C) and deamination (^{14}N/^{15}N) amplify the radiation effects in the relatively low dose range. Both reactions lead to a loss of an asymmetric centre.

The importance of these results for the abiotic origin of chirality is discussed.

O-22

Search for asymmetric reaction of amino acids by circularly polarized radiation using a polarizing undulator at the Electro-technical Laboratory

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Evaporated thin films of D/L-phenylalanine and water solution (pH = 1, 4, 8) of D, L-aspartic acid were irradiated by circularly polarized undulator radiation in an attempt to detect asymmetric decomposition or asymmetric oligomerization reactions.

New technique to make evaporated thin films of amino acids was developed. Thickness of the films were estimated with a crystal oscillation type deposition controller to be about 50 nm. Absolute values of optical absorption coefficient μ(hv) and circular dichroism CD(hv) of these films were successfully measured at the first time within the photon energy range of 5<hv<9.5 eV and 5<hv<7.1 eV, respectively.

Experiments of thin films were performed mainly at the polarizing undulator beamline of the NIJI-II in the Electrotechnical Laboratory ETL (Tsukuba). The BL-28A helical undulator beamline of the Photon Factory in the National Institute of High Energy Physics KEK-PF (Tsukuba) was also used. Evaporated thin films were irradiated with 8 eV (at ETL) and 35 eV (at KEK-PF) photons. Irradiated samples were analyzed by a high pressure liquid chromatography HPLC. Although some peaks due to new products were observed and small fragments were found to evaporated into vacuum, asymmetries in decomposition and oligomerization reaction was found to be smaller than the detection error 0.3 % of chromatography.

Experiments for water solution (pH=1, 4, 8) of D, L-aspartic acid showed similar results with the thin film experiments.

We also examined photodecomposition of D, L-aspartic acids irradiated with a 225 nm excimer lamp. From the HPLC analysis, we conclude that the quantum efficiency of the decomposition of aspartic acid was about 0.48 and the quantum efficiency of creation of alanine from aspartic acid was about 0.17.

We believe that these quantitative information are valuable to make a quantitative model of origin of life. At the conference, we will discuss about our project to measure the circular dichroism in the vacuum ultraviolet region (4<hv<30 eV) using the polarizing undulator at the Electrotechnical Laboratory.

O-23

Contribution of Cosmic Ray, Radiation, Lightning and Geothermal Heat to Prebiotic Synthesis on the Primitive Earth

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Although there could have been a wide variety of energy sources driving prebiotic synthesis on the primitive earth roughly around 3.8 billion years ago, autocatalytic oligomerization and polymerization of the then available monomers supposedly leading to the emergence of life there would have required somewhat tailored energy sources for their onset. Needless to say, cosmic ray and radiation could have played a major role for driving the synthesis of small organic molecules in the interstellar space. Lightning in the atmosphere on the primitive earth could have supplied a sufficient amount of energy for further synthesis of those small molecules carried and transferred in the form of cosmic dusts and outgassing. Nonetheless, those energy sources of cosmic ray, radiation and lightning could be too sporadic and intermittent to drive the autocatalytic processes on a continual fashion since their evolutionary onset.

One more possibility of the energy sources for driving continual autocatalyses could be geothermal heat, especially in the form of submarine hydrothermal vents. Hot springs from hydrothermal vents could certainly be continual in supplying heat energy to their neighborhoods ever since they were formed in the Archaean ocean. Submarine hydrothermal vents on the primitive earth have been proposed as most likely locales for synthesizing various monomers and polymers of prebiotic and protobiological significance among others. A rationale for this scenario rests upon the ease with which the systems could make available the activation energy for synthesizing those monomers and polymers prebiotically while continuously preventing themselves from approaching a thermal equilibrium.

We constructed a flow reactor simulating a submarine hydrothermal system and used the flow reactor for examining a likelihood of oligopeptide synthesis from amino acids alone without having recourse to any of condensing agents, templates or even metallic ions. When amino acid glycine was chosen as an initial reactant, we demonstrated that the flow reactor could synthesize both di- and tri-glycine. The initial buildup of the yields of both the oligopeptides was found to be exponential with the elapse of time. The oligopeptide synthesis from glycine in the flow reactor could be autocatalytic. The present observation suggests that evolutionary emergence of autocatalytic oligopeptide synthesis could have been quite likely in the Archaean ocean on the primitive earth. Of course, autocatalytic reactions that may be possible in the flow reactor could not be limited only to oligomerization of amino acids.

O-24

Energetics, Formation Rates and Densities in Chemical Evolution

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A number of experiments, which have been performed for several tens of years, indicates that any kinds of energy sources can easily create the bioorganic compounds from a simple chemical mixture, not depending on the states of gases, liquid and solid. Amount of the bioorganic compounds contributed on the primitive Earth can be estimated by multiplying the two parameters of the formation rates obtained in the laboratory experiments and the energy flux of each energy source. As shown in Table 1, the interactions of cosmic rays with gases on the primitive Earth had produced the highest amount of bioorganic compounds, which is 4 order higher than that by comets. However the most important parameter in chemical evolution process should be a density of bioorganic compounds in the soup, not a total amount of the compounds. It is difficult to expect the next chemical steps from the density of 10^{-9} kg/m^2 of bioorganic compounds formed by cosmic rays. The next steps in chemical evolution, after creating the bioorganic compounds, should be expected only in the density formed by comets.

Table 1. Energy fluxes, Formation Rates and Density

	Effect.Energy in cal/cm^2 yr.	G-value for Gly	Products/year on Earth kg	Density kg
Cosmic Rays on gases of primitive Earth	10^{-2}	10^{-2}	2×10^{6}	4×10^{-9} /m^{2}yr
Discharge on gases of primitive Earth	3×10^{-1}	10^{-7}	1.4×10^{3}	3×10^{-9} /m^{2}yr
Cosmic rays on Cometary Ices*	10^{-4}	10^{-2} ~10^{-4}	10^{2}	20 / m^3 shot
Microsphere Formation of Bioorganic comp. in Laboratory			1 spoon chemicals in 100cc	10 /m^3

* A Comet of 1 km Φ with >85 degree incidence per 10^7 yr.

O-25

DNA REPAIR AND EVOLUTIONARY CONSERVATION OF STRESS RESPONSE GENES IN ARCHAEBACTERIA

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Archaebacteria constitute a unique class of organisms which represents the evolutionary stage immediately succeeding that of the universal ancestor. These include three major phenotypes confined to a few ecological niches such as thermal habitats for extreme thermophiles, saturated brine for extreme halophiles and strict anaerobic environment for methanogens. In terms of genetic distance eubacteria and archaebacteria are as different from each other as either is from eukaryotes. Archaebacteria have unique metabolic pathways and their proteins have been adapted throughout evolution to work under the unusual physiological conditions. The ability to function and remain stable in the extreme environment is often achieved by evolutionary tricks such as insertion of metal ions into the structure, increase of external salt bridges, presence of stabilizing cofactors or by introduction of some peculiar amino acids in their proteins. The metabolism, physiology and molecular biology of archaebacteria exhibit some traits which are unique and others which may be considered either 'eubacterial' or 'eukaryotic' in nature. Studies on DNA repair and stress response in these organisms would help to understand the evolution of cellular responses most essential for survival in living organisms.

The archaebacterial halophile *Haloferax mediterranei* was found to be highly resistant to gamma-radiation. The number of radiation induced strand breaks in cellular DNA of this bacteria increased with increasing dose of gamma-radiation. Post irradiation incubation of the cells in growth medium resulted in repair of most of the radiation-induced strand breaks due to the presence of an efficient DNA repair system. Cloning and sequencing of *recA* like genes from archael species (*Haloferax volcanii, Methanococcus jannaschii* and *Sulfolobus sofataricus*) with putative protein products similar to that of yeast Rad51 and Dcm1 strongly indicate the presence of homologous recombination events that have been documented in several eubacteria and eukaryotes. These results suggest the presence of radiation stress inducible genes in archaebacteria.

In response to stresses such as heat shock, archaebacteria synthesize increased amounts of stress inducible proteins called heat shock proteins (HSPs) similar to eubacteria. The sequence of the genes encoding heat shock proteins show significant homologies in organisms as diverse as Drosophila, *E. coli*, yeast, mammals and plants. The sequence conservation of these genes implies that the HSPs perform a universally important physiological function. Among the various HSPs, HSP70 (DnaK) is the most abundant and highly conserved during evolution and this protein is also present in archaebacteria. Most of the HSPs function as 'chaperones' and help in refolding the cellular proteins that have been denatured during stress. HSP70 along with its co-chaperones, viz. HSP40 (DnaJ) and GrpE bring about the renaturation of proteins and restore normal cellular activity. These co-chaperones are reported to be present in archaebacteria. Our studies on cloning and sequencing of the *hsp70* locus have elucidated the organization of the genes encoding these chaperones in the archaebacterial halophile, *Haloferax mediterranei*. The organization of this locus in *H. mediterranei* is **5'- *grpE - dnaK - dnaJ - 3'***. This organization is similar to the organization of the *hsp70* locus of the archaebacterial methanogen *Methanosarcina mazei S6* and to that of Gram positive eubacteria.

O-26

Induction of macromutations with gamma-rays in rice plant (*Oryza sativa* L.)

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It is well known that there are many groups in animal and plant kingdoms showing that primitive forms have higher DNA values (C-values) than advanced forms. Then the phylogenic tree of animals which is depicted in consideration of genome size is a " weeping willow type" tree as shown in Fig.1. The strangeness of finding is expressed in the words " C-value paradox".

By watching the phylogenic tree closely, it is inferred that, in the course of evolution, the genome size increased discontinously when animals obtained new body plan and decreased continously when animals specialized their phenotypes without changes of their body plan.

In the field of breeding science, the research on the induction of mutation in crops has mainly dealt with the induction of gene mutations (micromutations) for many years. With the advances of molecular genetics and DNA techniques, however, a more fundamental reorganization of genes, chromnosomes and genomes (macromutations) has become the center of interest. Based on the findings in evolutionary biology mentioned above, it is expected that macromutations are induced through irradiation of plants which are artificially increased in genome size.

Artificial aoutoteraploids of rice plant were exposed to gamma-rays in order to obtain fully fertile rice plants exhibiting gross phenotypic changes induced through the reorganization of reduplicated chromosomes after irradiation. Plants which were diploid in their appearance occurred occasionally in the irradiated tetraploid population. And progeny of the diploid-like plants were examined. The results showed that the structure of genes and chromosomes in the oridinal diploid plant were changed through the reduplication of genome and irradiation. Based on the obtained results, the driving forces of evolution will be discussed.

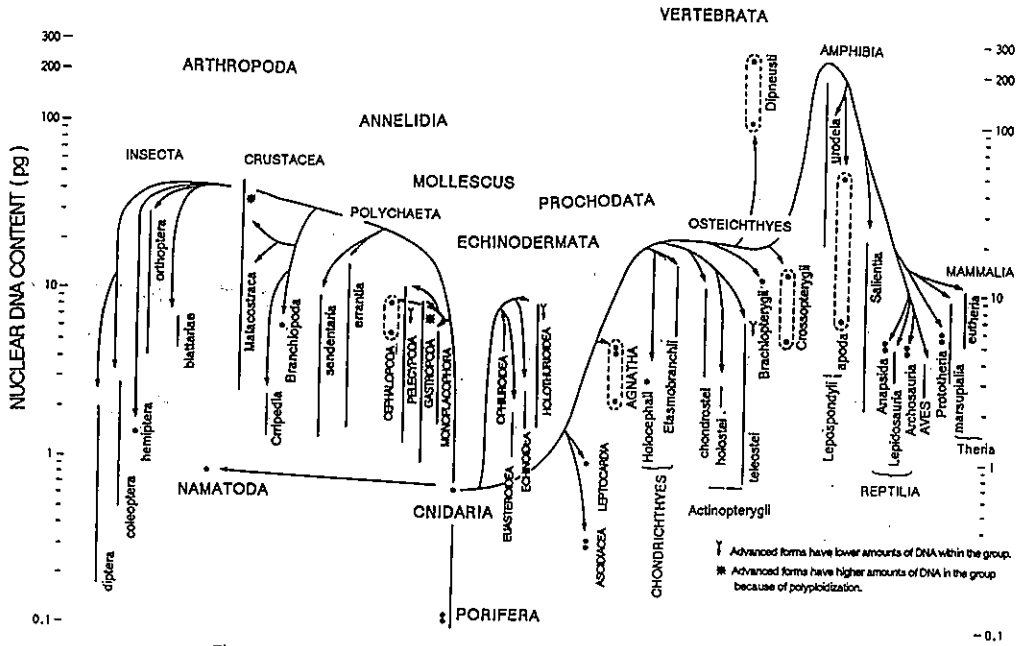

Fig. 1 The phylogenic tree of animal depicted in consideration of genome size

O-27

Tunneling reaction in γ-irradiated mammalian cells and their model system at 295 K

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It is confirmed that a hydrogen-atom-transfer reaction in solid hydrogen at very low temperature takes place by quantum-tunneling, in which a reaction takes place by passing through a potential energy barrier for the reaction by wave character of an atom. Since most of reactions in biological systems including the reaction of vitamin C are a transfer of a hydrogen atom or a proton that has a large wave character, it is generally expected that the tunneling reaction may play an important role in biological systems at room temperature. In order to examine a tunneling reaction in mammalian cells and their model system, the study consists of the three stages. The first stage is a direct measurement of reaction in mammalian cells and their model system. The reaction of vitamin C and the long-lived radicals produced by γ-irradiation of the cells was studied by ESR. The second stage is to examine the correlation between the reactions in the biological system and biological effects. The third stage is to study the isotope effects on the reaction, which will give an information on the contribution of a tunneling reaction.

When golden hamster embryo (GHE) cells or concentrated albumin solution (0.1 kg dm^{-3}) that is a model system of cells is irradiated with γ-rays at 295 K, organic radicals produced can be observed by ESR. The organic radicals survive at both 295 K and 310 K for such a long time as 20 hr. The long-lived radicals in GHE cells and the albumin solution react with vitamin C by the rate constants of 0.007 $dm^3\ mol^{-1}\ s^{-1}$ and 0.014 $dm^3\ mol^{-1}\ s^{-1}$, respectively. The long-lived radicals in mammalian cells cause gene mutation and cancer, which are suppressed by addition of vitamin C. The isotope effect on the rate constant (k) for the reaction of the long-lived radicals and vitamin C has been studied in the albumin solution by use of protonated vitamin C and deuterated vitamin C. The isotope effect (k_H/k_D) was more than 20～50 and was interpreted in terms of tunneling reaction.

O-28

Activity for D-tryptophan on γ -irradiated tryptophanase

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Although tryptophanase (TPase) is well defined as a catabolic enzyme involved in degradation of L-tryptophan (L-Trp) by a beta elimination reaction, it is also known to act over a wider range of beta elimination substrates and even in replacement reactions, including the condensation of cysteine and serine to form tryptophan. It is of great significance to choose TPase as an object of study for enzyme evolution, because such wider reactivity to L-tryptophan derivatives is consistent with the evolutionary relationship of tryptophanase with other pyridoxal 5'-phosphate - dependent enzymes, which suggests that the primitive regio - specificity of this family of catalysts evolved prior to substrate specificity. The regio-specificity probably involved the stereospecific mechanism which was closely related to the occurrence of homochiral biological world. Accordingly, it is essential for elucidation of the origin of homochirality to study the stereospecificity. We compare the activity towards L-Trp and D-Trp for studying the stereospecificity of TPase. Generally speaking, the stereospecificity of enzymes is very rigid. TPase cannot also react with D type of tryptophan derivatives at all irrespective of such wider reactivity to L-Trp derivatives. We explored proper control with which TPase can react with D-Trp.

TPase becomes active to D-Trp in diammoniumhydrogen phosphate solution (DAP). The inhibition of indolepyruvate and potassium pyruvate towards TPase was non-competitive and competitive, respectively. D-Trp in the reaction of L-Trp degradation transitionally behaviors from as a competitive to as a non-competitive inhibitor with increasing DAP concentrations. These results suggest that the activity for D-Trp may be basically responsible for the heterocyclic moiety of tryptophan. The inhibition type of D-Trp at L-Trp degradation is thus analyzed when the activity of D-Trp is halted. TPase is irradiated with γ - ray to sterilize the activity for D-Trp, and irradiation dose is prepared to be active to only L-Trp. The inhibition type of D-Trp in γ - irradiated TPase is competitive but fails to switch from competitive to non-competitive inhibition. This shows an uncompetitive binding site in the presence of DAP is necessary to the activity for D-Trp. Perhaps DAP makes D-Trp bind at a binding site apart from the active site for L-Trp through stereostructural change of TPase. It is suggested that the active site for D-Trp may be independent of that for L-Trp.

5-P-1

Accumulation of energy for development in starfish eggs.

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The animal pole of fully grown starfish oocyte is recognizable by the eccentric position of the germinal vesicle, and in mature eggs by the position of the polar bodies that are formed at the animal pole after germinal vesicle breakdown. Fertilized eggs divide equally throughout the cleavage stage and in the first two divisions the cleavage planes are formed to include the animal-vegetal axis. Ristricted distribution of the determinant for archenteron at the vegetal pole has been reported, in which vegetal region-deprived eggs (about 7% of whole egg) develop to the so-called permanent blastlae. In contrast, animal pole cytoplasm does not contain the determinant, at least in the localized state. An important property of the animal pole cytoplasm is revealed when animal half-deprived vegetal egg fragments alone are allowed to develop for longer period. Whole eggs were bisected either perpendicularly or obliquely to the animal-vegetal axis so that possibly localized cytoplasm near the animal pole or around the equatorial region were excluded, and the remaining vegetal fragments were allowed to develop. In the remaining vegetal halves, the squamous ectoderm tended to be thicker for longer duration than in those of normal embryos and their mouth opening appeared smaller in size in particular during early bipinnariae, they could form archentera and metamorphose to juvenile starfish .

Although both vegetal and animal cytoplasm are necessary for further development in starfish, each propertiy is apparently different. The essential property of the vegetal cytoplasm is its potential to cause the cytoplasm-endowed cells to become the esophagous and mesoderm such as mesenchymal cells and coelomic pouches, and animal cytoplasm does not.

Blastomeres at 2-cell stage or 4-cell stage can undergo metamorphosis when they are separated and allowed to develop. When blastomeres at 8-cell stage are similarly separated, howevere, they can not metamorphose even if they can form archentera and become bipinnariae. The size of animal pole side blastomeres that rescue the developmental deficiency of the isolated vegetal blastomere of 8-cell stage was up to the size of cells of 64-cell stage. Therefore intact eggs of starfish eggs can be regarded that they accumulate more than sufficient energy for the developmental continuation about 7 fold than the minimam size (1/8 + 1/64 = 14%) of blastomeres that can undergo metamorphosis.

The size of the larvae that began to metamorphose was almost similar even if they differently in sizes started their development. Interestingly, the periods which were required for the larvae to reach the size was significantly different, the larveae started from smaller size, the longer the period.

5-P-2

Significance of phospholipid bilayer in origin and evolution of the cells

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The unit of all living systems is a single cell. Cells are surrounded by cell (or plasma) membranes which are constructed from phospholipid bilayer as skeleton. Therefore, the living system is essentially a closed system which is border on the environment with a phospholipid bilayer, although much material and information is exchanged between the inside and outside of the system. Lipids comrise a diverse class of chemical substances characterized by their solubility in non-polar organic solvents and low dielectric regions, namely fatty acids as long hydrocarbon chains and thus are extensively hydrophobic, although their carboxylic acid groups strongly polar because it can ionized by losing a proton in water. Consequently, fatty acids have both hydrophobic and hydrophilic characteristics. On the other hand, phospholipids contain phosphoric acid which is esterified by free -OH group of diglyceride as phosphatidic acid. Most biologically important phospholipids are derivatives of phosphatidic acid. A small amount of phospholipid can be spread over the surface of water to form a monolayer of the molecules. When the phospholipid-water system is agitated, the phospholipid molecules form a configuration known as liposome, a sphere of phospholipid bilayer. Liposome is the skeleton of the cell membrane. Simulation experiments of chemical evolution have demonstrated to be able to synthesize fatty acids and trioses as components of phospholipid. The phospholipid bilayer is impermeable to ions and thus can form ionic concentration difference, i. e., an ionic gradient, between the inside and outside of the phospholipid bilayer of biomembrane. The ionic gradient generates a spontaneously electro-chemical potential within the membrane. The cell uses this potential as an energy source for various functions, including ATP synthesis. The extant cellular energy is produced by the pumping of protons across mitochondrial cristae and chloroplast thylakoids to generate that potential. Proto-cells had to acquire the energy from the potential of the cell membrane, in which the ionic gradient was spontaneously generated. Therefore, it is reasonable are a prebiotic product of chemical evolution.

5-P-3

RAPD analysis of local populations of a mayfly species, *Epeorus ikanonis*

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Polymerase chain reaction (PCR) with a short DNA primer often generates some polymorphic DNA fragments detectable on the gel electrophoresis (1). These polymorphic DNA, called RAPD (random amplified polymorphic DNA), have been used to characterize genetic relationships among intra-specific populations (2,3). Here we report the results of the RAPD analysis on the local populations of a mayfly species, *Epeorus ikanonis* TAKAHASHI in northern Kyoto City, Japan.

Mayfly male individuals were collected at three locations termed Station D, Station E, and Station K in the year of 1995, and Station K, Station L, and Station O in the year of 1997. The stations D and E located at the Kibune Stream, and the stations K, L and O located at Kumogahata Stream. Genomic DNA samples were prepared from the sperm vesicles of mayfly according to Perbal (4). They were subjected to the amplification with a 12-mer DNA primer, which consisted of a potential core sequence for repetitive DNA (5). The amplified DNA samples were fractionated on the agarose gel and visualized by ethidium bromide staining.

Each individual sample showed 5 to 14 DNA bands on the agarose gel. The pair-wise comparison of electrophoretic patterns was carried out to estimate the RAPD identity among individuals by calculating the ratio of the number of common DNA bands versus the total number of DNA bands observed in two samples. The results suggested that the population in the Station K retained lower identity score than the others. These RAPD may provide a useful molecular marker for the ecological and evolutionary analysis of the local populations of mayflies.

References
1. Williams, J. G. *et al.* (1990) Nucleic Acids Research **18**, 6531-6535.
2. Foo, C. L. *et al.* (1995) Zoological Science **12**, 535-541.
3. Tamate, H. B. *et al.* (1995) Zoological Science **12**, 669-673.
4. Perbal, B. (1988) *A Practical Guide to Molecular Cloning* (second edition), John Wiley and Sons, New York.
5. Kato, M. (1996) Journal of Theoretical Biology **180**, 121-124.

5-P-4

Structure and molecular evolution of satellite DNA isolated from a saltwater fish *Sillago japonica*

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Eukaryotic genomes have arrays of large number of identical DNA sequences, called satellite DNA. Since the satellite DNA sequences often exist in or close to the centromeric regions of the chromosomes, they are considered to be involved in the chromosome construction.

We have previously identified a member of satellite DNA in a saltwater fish *Sillago japonica* (Percoidei, Sillaginidae), which is homologous to Sparidae EcoRI family centromeric satellite DNA. The repeating unit of the satellite DNA is about 180 bp and A/T-rich. The monomer unit of *S. japonica* satellite contains two inverted repeats, a consensus core for fish satellite families, and the A-T clusters. We have performed the enzymic probing of DNA conformation on the satellite sequence, and propose a novel model of the altered DNA structure. Potential role of the unusual DNA structure in the evolutionary process of the centromeric satellite will be discussed at the time of the Meeting.

5-P-5

Sequence polymorphism of *Sillago japonica* EcoRI family satellite DNA

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Many types of measures are applied to evaluate the genetic distance among closely related species or intraspecific populations, such as RAPD, diversity of mitochondria DNA sequences, and minisatellite fingerprinting. Satellite DNA sequences are also known to have higher diversity in their members. We have identified a member of satellite DNA in a saltwater fish *Sillago japonica* (GenBank accession number U37027), which is considered to be a homologue of Sparidae EcoRI family satellite DNA. There are observed two inverted repeats, A-T clusters, and a consensus motif for repetitive DNA in the monomeric unit. In the present study, we have analyzed sequence diversity of the consensus motif regions of *S. japonica* satellite units.

S. japonica individuals were obtained from Osaka Bay and Seto Inland Sea by angling, and genomic DNA was extracted from their liver tissues. The DNA region flanked by two inverted repeats in repetitive unit was amplified from genomic DNA by polymerase chain reaction (PCR). The PCR products were cloned, sequenced and compared in each individual and between individuals. The results suggested that the sequence similarity of amplified DNA may be an effective measure for the genetic distance of *S. japonica*.

5-P-6

Lamination and lithification in living stromatolites, phototrophic bacterial mats from Yumomine-Onsen Hot Spring, Hongu, Wakayama Prefecture Japan.

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Stromatolites are calcareous sedimentary rocks (limestones) having internal laminated structures (laminae). According to the definition presented by S.M. Awramik and L.Margulis (1974), stromatolites are organosedimentary structures produced by sediment trapping, binding and/or precipitation as a result of the growth and metabolic activity of microorganisms principally cyanobacteria; that is, the process of stromatolite formation is so biological. Then, it is probable that the Archean stromatolites, built by ancient prokaryotic microbes, have a strong resemblance of the structure and the function to the recent stromatolites, bacterial mats developed under thermoextreme aquatic conditions of hot springs. Since few eukaryiotic grazer can live to destroy physical structures of bacterial mats under these conditions, the bacterial community, a bacterial ecosystem, is well preserved, so that we can examine the formation process of internal structures (lamination) of the mats and the licification by biomineralizations within the mats.

Using two tyes of phototrophic bacterial mats (oxygenic cyanobacterial mats and anoxygenic Chloroflexus mats) obtained from Yunomine-Onsen Hot Spring, Hongu, Wakayama Pref., we will present some results of morphological examination with SEM on the lamination of bacterial mats and of X-ray analyses of mineral particles on and in the mats, and will discuss allochthonous and autochthonous biomineralization, actively proceeded by bacteria of the mats.

5-P-7

Macro cellular structure of acidothermophilic archaebacterium *Thermoplasma*.

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Thermoplasma is an acido-thermophilic archaebacterium. The organisms in the genus grow optimally at pH 1-2 and between 50 and 60C. There is no cell wall around cytoplasmic membrane. The organisms form multi nucleate macro cellular structures. We have recently isolated new strains of the genus. We analyzed macro cellular structures of these new isolates by optical and electron microscopes. We will also discuss the significance of the structure in the evolution of eukaryotic cells.

5-P-8

A Molecular View of Microbial Diversity in Marine and Terrestrial Hot Water Environments.

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Isolation and cultivation of extremely thermophilic or hyperthermophilic microorganisms have contributed to our knowledge about the presence and diversity of microbes capable of growing at extraordinary temperatures and about their novel biochemical machinery. However, molecular phylogenetic surveys of naturally occurring microbial community in Yellowstone National Park hot spring environments indicate that the phylogenetic diversity of thermophilic microorganisms is far greater than previously proposed by such methods[1, 2]. Here we report the further phylogenetic characterization of diverse microbial community in hot water environments by the PCR-mediated small subunit rRNA gene (ssu rDNA) sequencing. The mixed population DNA is directly extracted from the effluent hot water or sediment of a shallow marine hydrothermal vent at Tachibana Bay, or the pooled hot water of Unzen hot spring, in Nagasaki Prefecture, Japan. Based on the partial rDNA sequences amplified with Bacteria-, Archaea-specific or universal primers, the microbial population are varied in each sample and subject to its environmental conditions. For instance, nitrogen fixing group of Bacteria such as *Rhizobium*, *Bartonella* and *Agrobacterium* are detected as the major microbial population from 128 °C of effluent vent water even though they are not viable. From adjacent sediments, however, high abundance of unidentified marine bacterial or low G+C members occupy the majority instead of the nitrogen fixing species. Thermophiles are a small faction of microbial population in all samples but thermophilic archaea are predominant in archaeal population. In addition, the large number of archaeal rDNA sequences obtained from hot waters are the uncultivated and unidentified archaeal types of sequences and reveal distant relationship to the crenarchaeotal and korarchaeotal species found in a Yellowstone National Park hot spring. The findings extend our view of archaeal diversity in hot water environments and phylogenetic organization of Archaea.

5-P-9

Strategy for identifying the initial system of life

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A method for identifying the essential system of life is described. The system of life is extremely difficult to model in terms of physics because of the large complexity gap between elegant theories of physics and complicated biological phenomena. Since we must accept the existence of this gap, we start by modeling actual biological transitions, and then reconstruct the system from these models.

We identify the system as a formula of density $\rho(t)$, which is a basic indicator of statistical physics. The ρ of life will be obtained through the following approximation cycle (Fig. 1). (1) We first describe physical criteria for life by translating the consensus of biologists into physical constraints. For example, 'increase in free energy F' can be translated into $\langle\, \hat{F}(r;\rho)\,\rangle^{\tau} > 0$, where τ denotes the characteristic time for local equilibrium. Those criteria are arranged into a detector functional $\Psi[\rho]$. (2) Then we model the biophysical transitions common in organisms, such as potassium ion flow. (3) After reconstructing ρ from j's, (4) we test whether the obtained ρ meets the criteria $\Psi[\rho] > 0$. (5) If it is not, we repeat refining j's and ρ until it is met.

The emergence of life is formulated as transition $D = \phi \rightarrow D \neq \phi$, where $D = \{r \mid \Psi[r;\rho] > 0\}$, since the existence of a life-like subsystem can be shown as $D \neq \phi$. Evolution, which is the emergence of a higher-order system, can also be shown as this kind of transition by preparing several criteria Ψ's corresponding to the evolutionary stages from a single cell to more complex organisms.

This method also allows us to discuss initial conditions and natural laws for the origins of life by analyzing the parameters of an identified system ρ.

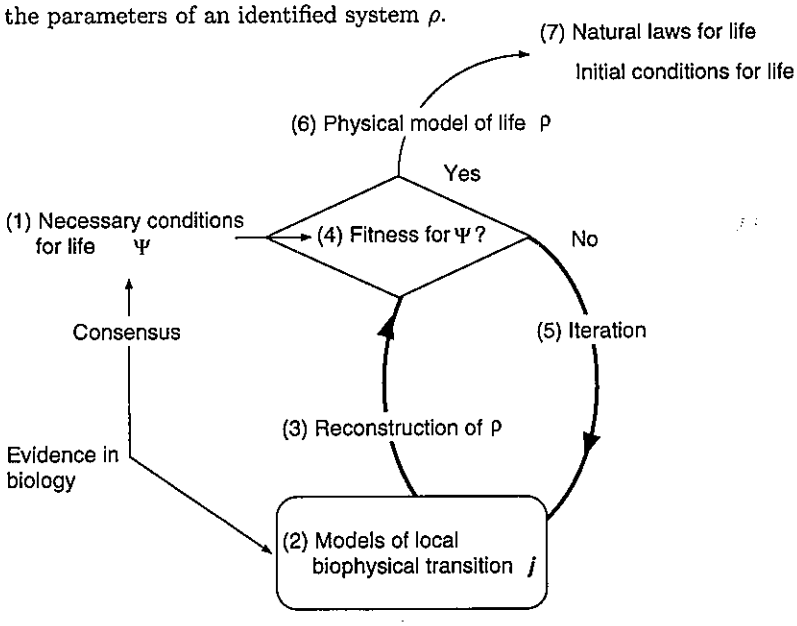

Fig. 1. Strategy for approximating the system of life.

5-P-10

SNS hypothesis on the origin of the genetic code

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The genetic code represents the relation between the base sequences written as triplets on DNA or its RNA transcripts and the amino acids in proteins. The meaning of each codon is the same or universal in all known organisms except for several organelles in eukaryotic cells and some microorganisms. As the hypotheses for the origin of the genetic code, the RNY or [(G/A)N(C/U)] and the WWW or [(A/U)(A/U)(A/U)] hypotheses have been presented by Eigen and Schuster (1) and by Jimenez-Sanchez (2), respectively, so far. However, the authors disregard several essential aspects for the primeval genetic code, such as potentials for formation of native-like proteins and probability of occurrence of long nonstop frame (NSF) under the respective genetic coding system.

Contrary to that, we found that NSFs on GC-rich antisense sequences (GC-NSF(a)) are favorable for producing new genes (3) and that imaginary proteins from the GC-NSF(a)s well satisfy the conditions for formation of native-like three-dimensional protein structures in a region of more than 60% GC content. (SNS)n or [(G/c)N(C/g)]n sequence was deduced as an extrapolated form of the GC-NSF(a) to GC-rich side. In fact, extremely GC-rich actual genes with around 75% GC content possess approximate SNS coding pattern. To confirm the coding ability of the SNS repeating sequences further, we randomly generated base compositions composed of SNS by a computer. Out of the computer-generated base compositions in the codon, favorable ones were selected out under the conditions of the seven structural index values (hydrophobicity, acidic and basic amino acid contents, [neutrality], helix, sheet and turn formations) required by actual proteins. The imaginary proteins encoded by the SNS code actually satisfied the seven conditions for the corresponding amino acid sequences to be folded into three-dimensional structures similar to that of present-day native proteins. Taking defects of the previously proposed RNY and WWW coding systems together into consideration, we propose here the SNS hypothesis as the origin of the genetic code.

(1) Eigen, M. and Schuster, P. (1978) *Naturwiss.*, **65**, 341-369.
(2) Jimenez-Sanchez, A. (1995) *J. Mol. Evol.*, **41**, 712-716.
(3) Ikehara, K., Amada, F., Yoshida, S., Mikata, Y. and Tanaka A (1996) *Nucl. Acids Res.*, **24**, 4249-4255.

5-P-11

A possible evolutionary pathway of the genetic code deduced from the SNS hypothesis

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We have provided the SNS hypothesis for explaining the origin of the genetic code as seen in the accompanying paper. It was examined whether an evolutionary pathway from the SNS hypothesis to the present-day genetic code (the universal genetic code and the mitochondrial codes) can be reasonably deduced under the following conditions in order to show that the hypothesis would be correct. (i) Nonassigned GC-rich and AT-rich codons can not be formed from the previously assigned codons in GC-rich and AT-rich bacteria, respectively. In other words, GC-rich and AT-rich nonassigned codons can not be produced under the strong GC and AT mutation pressures, respectively. (ii) It is impossible to divide a previously existing four-codon box into two two-codon boxes, since either of two codons cannot become nonassigned codon by similar reasons described above. (iii) Since amino acids encoded by U-initiated codons, such as Phe, Tyr, Cys and Trp, would be synthesized through the more complicated metabolic pathway, U-initiated codons should be captured after formation of the A-initiated codons.

It was found that an evolutionary pathway can be reasonably deduced from the possible primeval SNS code to the universal genetic code and the mitochondrial genetic code without meeting any large difficulty as described below. (i) Pro-SNS (SNG) primeval code was established. The code could be a precursor form of the SNS primeval code, since His codon would be added to the SNG code to complete the primeval SNS code. (ii) As a next step, the SNN code would be produced by expanding the SNS code accompanied by addition of SNW code under AT mutation pressure. The expansion must be carried out through "wobblings" of the codons at the third codon position. (iii) The (SNN + (ANN - AUR)) code were created by codon-capture of the A-initiated codons except of AUR codons. (iv) Next, the (SNN + (ANN - AUR) + (UNN - UAR -UGR)) code was formed by further codon capture of U-initiated codons except UAR and UGR codons. (v-1) At the final step, AUA, AUG and UGG codons were assigned into Ile, Met and Trp codons, respectively, to produce the universal genetic code, and three codons (UAR and UGA) were left as translational termination codons. (v-2) On the other hand, AUR and UGR codons were used as Ile and Trp codons, respectively, in mitochondria of many mammlian cells to create the mitochondrial code under an extremely high AT pressure and genome size-reducing pressure.

The reasonable deduction of the evolutionary pathway from the possible SNS primeval code to the universal and the mitochondrial genetic codes supports our idea that the SNS code would be the primeval genetic code.

5-P-12

Organic compounds in the condensed water from the MIR space station.

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Microflora Investigation Experiment was one of the first MIR utilization space experiments. In relation to the experiment, we analyzed for amino acids and hydrocarbons in the condensed water (C1, C2 and C3) form the MIR space station. These water samples were collected at three different sites in the MIR space station by two Russian crew on 27th February, 1997. Approximately 1 ml for each sample was extracted with benzene and the extract was analyzed by gas chromatograph combined with mass spectrometer (GC-MS). The residual water was hydrolyzed and divided into two portions. One was analyzed by amino acids analyzer for quantification and the other by GC-MS to determine the D/L ratios after derivatized with 2-propanol and trifluoroacetic acid anhydride.

Sixteen protein amino acids were found. Concentration of each amino acid in the C1 sample ranged from 1 to 40 nmol ml^{-1}. Compositions of protein amino acids in the C1 and C3 are similar to those in the common microorganisms. D/L ratios of 10 amino acids determined by GC-MS were less than 0.1. These ratios indicate that racemization have not proceeded significantly by cosmic ray in orbit.

Non protein amino acids, such as N-methylglycine, β-alanine, γ- and α- aminoisobutyric acids and isovaline were found in the C1 sample. It is difficult to specify the sources of the first three amino acids because they are found in many sediment samples such as the Tokyo bay sediment. However, latter two amino acids are extremely rare and used as maker amino acids of fungal peptide antibiotics. Microorganisms identified in the condensed water samples by other investigators belong to new genus or new species. Therefore, the two amino acids might be included in these microorganisms.

Many kinds of organic compounds were detected in the benzene-extracted fractions. However, polycyclic aromatic hydrocarbons were found very little, indicating little polycyclic aromatic carbons probably formed by the fire on 23rd February, 1997 were trapped in the condensed water in the MIR space station. Aromatic alcohols, aldehydes and ketone were detected in all three condensed water samples. They might have accumulated from long time usage of fragrants and/or disinfectants in the MIR space station.

5-P-13

A Hypothesis that Advent of Membrane Phospholipid with Enantiomeric Glycerophosphate Backbone Caused the Divergence of Archaea and Bacteria

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One of the most remarkable biochemical differences between the members of two domains *Archaea* and *Bacteria* is the stereochemistry of the glycerophosphate backbone of phospholipids, which are exclusively opposite. The enzyme responsible to the formation of archaea-specific glycerophosphate was found to be NAD(NADP)-linked *sn*-glycerol-1-phosphate (G-1-P) dehydrogenase and it was first purified from *Methanobacterium thermoautotrophicum* cells and its gene was cloned. This structure gene named *egsA* (enantiomeric glycerophosphate synthase) consisted of 1041 bp and coded the enzyme with 347 amino acid residues. The amino acid sequence deduced from the base sequence of the cloned gene (*egsA*) did not share any sequence similarity except for NAD-binding region with that of NAD(P)-linked *sn*-glycerol-3-phosphate (G-3-P) dehydrogenase of *Escherichia coli* which catalyzes the formation of G-3-P backbone of bacterial phospholipids, while the deduced protein sequence of the enzyme revealed some similarity with bacterial glycerol dehydrogenases. Because G-1-P dehydrogenase and G-3-P dehydrogenase would be originated from different ancestor enzymes and it would be almost impossible to interchange stereospecificity of the enzymes, it seems likely that the stereostructure of membrane phospholipids of a cell must be maintained since the time of birth of the first cell. We propose here a hypothesis that archaea and bacteria were differentiated by the occurrence of cells enclosed by membranes of phospholipids with G-1-P and G-3-P as a backbone, respectively.

5-P-14

Modification of αA-Crystallin obtained from aged and X-ray Irradiated Mouse Lenses

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Proteins have been considered to consist exclusively of L-amino acids in living tissues. However, we found biologically uncommon D-aspartyl (Asp) residues at specific sites in αA- and αB-crystallin from the aged human lens (mean age: 80 years). D-Asp increased with age and ultraviolet irradiation. Our purpose was to elucidate the correlation between lens opacities, lens protein aggregation and aspartyl residue racemization in αA-crystallin obtained from spontaneously aged and irradiated mouse lenses.

Methods. αA-Crystallin was isolated from X-ray irradiated and non-irradiated mouse lenses and digested with trypsin. Tryptic peptides (T1-T20) were identified by amino acid sequence and mass analysis. Amino acids, from hydrolyzed peptides, were derivatized to diastereoisomers and the D/L ratios determined by RP-HPLC.

Results. In non-irradiated lenses, α-crystallin has αB and αA subunits. RP-HPLC resolved the αA-crystallin T18 peptide into 2 peaks (T18' and T18). Only the aspartyl (Asp)-151 residue of the T18' peptide exhibited racemization. The Asp-151 D/L ratio increased with aging. However, α-crystallin obtained from lenses 8 weeks after irradiation, unlike non-irradiated lens, were separated into 3 peaks (αB-, αA- and αAm-crystallin). Increased αAm and decreased αB-and αA-crystallins were found in lenses obtained more than 12 weeks after irradiation. In addition, mature cataracts and HMW proteins, the main component being αAm, appeared in lenses 12 weeks after irradiation. The T18 peptide of irradiated lenses also yielded T18' and T18 peptides by RP-HPLC. Only the Asp-151 residue exhibited racemization, however the D/L ratio was lower than the control.

Conclusion. The racemization of the αA-crystallin Asp-151 residue increased during aging. X-ray irradiation induced cataract, formation of HMW and αAm and suppressed Asp-151 residue racemization.

5-P-15

Determination of rare earth elements in cultured HeLa cells using ICP-MS

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Though it is known that a trace amount of rare earth elements (REEs) is accumulated in organisms, little is known about the biological effect and meaning of these elements. The present experiment is a part of our study which was designed to estimate the implication of the bioaccumulation of REEs in organisms. In order to examine the bioaccumulation of REEs exactly, we employed cultured mammalian cells as the experimental material and inductively coupled plasma-mass spectrometer (ICP-MS) as the observatory means. Namely, HeLa cells grown in minimal essential medium (MEM) supplemented with 10% culf serum were collected by centrifigation, and the dried materials were used as the samples. The present analysis revealed that the total REE content (for 14 kinds of REE measured) in the cells was 25.13 ng/g). The range of REE content varied from 0.178 ng/g (for Lu) to 9.65 ng/g (for Ce). The REE-values (ng/g) obtained for the dried cell materials were compared with those of the cultured medium, *viz.*, MEM and culf serum which were used to culture the cells. The results demonstrated that the cells accumulated REEs within the cells in individually different manners. Namely the accumulation ratio was the higher in the lighter REEs (for Ce the ratio was 31.8, while 14.7 for Lu). The source of these REEs in the medium was considered not to be H_2O and serum but MEM reagent. The meaning of the accumulation is a problem to be further investigated.

5-P-16

The Creation of the Living Organisms by the Solar Radiation Why are They against Thermodynamics?

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The mysterious features of the living world as distinguished from the nonliving world, namely, its tendency toward building up an order apparently against the second law of thermodynamics, and its abnormally high free energy inaccessible in thermal equilibrium on this earth, are ascribed to the solar radiation as the driving force which has been incessantly creating and evolving the living organisms for these billions of years. Being an open system exchanging matter as well as energy with the outside, the living world has been and is kept in nonequilibrium (with metabolism) and nonstationary (with chemical and biological evolution) state.

The biomolecules are considered to be metastable compounds with their own lifetimes for their oxidization or disintegration into stable inorganic compounds. It is known that the chemical energy released thereby amounts to 1.2 eV (in carbohydrates and proteins) ~ 2 eV (in lipids) per atom, which correspond to 1/2~ 3/4 of a typical photon energy of the solar radiation (the intensity peak at 2.6 eV) and is hundred times as great as the thermal energy (kT~0.02 eV) on the earth. This indicates that the biomolecules can be formed from inorganic matter under the sunlight by multistep photochemical reactions (with one atom attached to the growing polymer per one absrobed photon on the average if a reasonable fraction of energy loss due to relaxation is taken into account), but that they can hardly be formed by thermal fluctuations.

The incessant metabolic turnover of all living organisms on the earth indicates that the enormous amount of chemical energy released thereby must be supplied by a huge and stationary energy source, the only conceivable candidate of which is the solar radiation. The photosynthesis by plants is now bearing an important role of harvesting the solar energy, while in the prebiotic age only the direct photosynthesis from inorganic matter could open the doorway to the living world, and presumably it is still going on.

"One atom attachment per one photon absorption" is a typical process known in the photochemical study; photoexcitation of an electron in an atom or a molecule generally gives rise to a new bonding. In order that the multisteps of these processes proceed efficiently to generate enough numbers of biopolymers, there must be some mechanism suppressing the radiative and nonradiative de-excitation processes (which would render the preceding photoexcitation futile) and favoring for the population inversion. While only a few examples of such a long-lived "relaxed excited states" (with the absence of radiative de-excitaiton and the small rate of nonradiative de-excitation) are known among inorganic solids, the same situation will be more readily realized in aqueous solution of inorganic molecules in which the atoms are quite mobile to form a new chemical bond with the photoexcited atom.

Solving the rate equations describing the growth of successive higher polymers through the photochemical bond formation under competition with the nonraditive dissociation, we find, in typical situations, that an appreciable amount of simplest biomolecules can in fact be formed in less than a billion years, being in consistence with the fossile study. An experiment is proposed elsewhere [1] which simulates the chemical evolution on the earth but reduces the geological time to a laboratory time by intensifying the solar radiation without changing its spectral shape. Through this argument one realizes the importance of water as heat absorber (large heat capacity and low temperature as it is on the earth) for the birth of the living organisms under the sunlight.

Since the energy of photon absorbed which corresponds to the electronic transition energy differs from step to step, the continuous spectrum of the solar radiation is essential for the multistep photosynthesis to proceed so as to generate the biomolecules.

The metabolism in the living organisms is consdidered to originate from the finite lifetimes of the metastabe biomolecules, although the actual metabolic turnover rates of the respective tissues formed later have been regulated to higher values by the relevant enzymes in order to keep suitable balance for the survival of the whole organism.

Reference: [1] Y.Toyozawa: J.Phys.Soc.Jpn. 66 (1997) 3737.

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ウ）a），b），c），・・・

各見出しのゴチ指定，改行等は既刊の実例にならう．

5．図，表，写真は所定の位置に貼る．図，表，写真の番号，表題，説明は和文原稿の場合にも英文で記すことが望ましく，そのまま写真製版出来るよう図，写真の下，表の上および下に記す．

6．和文原稿の場合には英文要旨をつける．

英文要旨冒頭には，表題，著者名，所属機関，その所在地（郵便番号付記）をこの順で記す．続いて，4行あけた後，ABSTRACT, KEY WORDS （10語以内）を記す．

7．英文要旨は英文原稿作成の手引きを参考にして記す．

8．英文要旨は表題から KEY WORDS まで含めて1頁以内に納める．

☆ 和文原稿作成の手引き

1．原稿は400字詰め原稿用紙に横書きで記す．ワープロを使用の場合は，25字×16行とする．

2．第1ページに和文表題，著者名，所属機関，その所在地（郵便番号を付記）を，この順序に記す．第2ページには英文要旨を記す．第3ページ以下に本文を記す．

3．見出しは，区切りの大きいものから順に下記ア）～ウ）の通りとする．各見出しのゴチ指定，改行等は，既刊の実例にならう．

ア）1，2，3，・・・

イ）1－1，1－2，・・・，2－1，2－1，・・・

ウ）a），b），c），・・・

4．図，写真および表は別紙とし，原稿中にはそれぞれの挿入箇所を指定する．

5．和文原稿の場合にも，図，写真および表の表題および説明文は英文で記すことが望ましい．

6．英文要旨冒頭には，表題，著者名，所属機関，その所在地（郵便番号を付記）を，この順序で記す．

7．英文要旨の後に KEY WORDS （10語以内）を記す．（日本語でのキーワードは不必要．）

生命の起原および進化学会

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Kyoto University International Conference on
"The Role of Radiation in the Origin and Evolution of Life"
Joint Meeting with the 23rd Annual Meeting of the SSOEL, JAPAN
at
Hotel "Sunroute Kanku"
Kirara-town, Izumiohtsu City, Osaka
March 1-5, 1998

CONFERENCE SCHEDULE

(ICRROEL Joint Meeting with the 23rd SSOEL- Japan)

Sunday, 1 March
16:00~17:00 Group Meeting in Japanese (Editorial Committee, "Cattleya")
17:00~ Registration Desk Open (the 2nd floor)
18:00~20:30 Welcome Reception (Main Hall "Crystal Rose", the 2nd floor)

Monday, 2 March
9:00~9:30 Opening Ceremony
9:30~10:30 Plenary Session (O-1, O-2)
10:30~11:00 Coffee Break
11:00~12:00 Plenary Session (O-3, O-4)
12:00~13:00 Lunch Time
13:00~15:00 Plenary Session (O-5, O-6, O-7, O-8)
15:00~17:00 Coffee Break and Poster Session (2-P-1~2-P-20)
17:00~18:00 Group Meeting in Japanese (Executive Committee, "Cattleya")

Tuesday, 3 March
9:30~10:30 Plenary Session (O-9, O-10)
10:30~11:00 Coffee Break
11:00~12:00 Plenary Session (O-11, O-12)
12:00~13:00 Lunch Time (General assembly of the SSOEL, Japan, Main Hall)
13:00~18:00 Excursion to Castle Kishiwada, Danjiri Kaikan and Kuboso Memorial Museum (by Bus)
18:00~20:30 Conference Banquet (Sky Banquet Room 20F)

Wednesday, 4 March
9:30~10:30 Plenary Session (O-13, O-14)
10:30~11:00 Coffee Break
11:00~12:00 Plenary Session (O-15, O-16)
12:00~13:00 Lunch Time
13:00~15:00 Plenary Session (O-17, O-18, O-19, O-20)
15:00~17:00 Coffee Break and Poster Session (4-P-1~4-P-20)

Thursday, 5 March
9:30~10:30 Plenary Session (O-21, O-22)
10:30~11:00 Coffee Break
11:00~12:00 Plenary Session (O-23, O-24)
12:00~13:00 Lunch Time
13:00~15:00 Plenary Session (O-25, O-26, O-27, O-28)
15:00~17:00 Poster Session (5-P-1~5-P-20)
18:00~20:30 Farewell Reception at "Haya" (Restaurant in Sakai-City)