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ABSTRACTS OF ISSOL 2005, THE 14TH INTERNATIONAL CONFERENCE ON THE ORIGIN OF LIFE, HELD IN BEIJING, FROM JUNE 19–24, 2005

TABLE OF CONTENTS*

---

*I – Invited talk; O – Oral presentation; P – Poster presentation.

I-12. Mineral Catalysis and Prebiotic Synthesis
James P. Ferris, Prakash Joshi, Michael Aldersley, Shin Miyakawa, Wenhua Huang and Kong-Jiang Wang

I-13. Beyond TNA
Ram Krishnamurthy

I-17. The simplest cellular life
Doron Lancet, Ariel Solomon, Ran Kafri and Barak Shenhav

I-18. Locating the root of LUCA through tRNA and aminoacyl-tRNA synthetase genes
J. Tze-Fei Wong

I-21. Evolutionary geomics approach to the core of minimal bacterial gene set
Vicente Pérez-Brocal, Amparo Latorre, Rosario Gil, Juli Peretó and Andrés Moya

I-22. Working towards the "minimal cell": a bottom-up proposal
Kepa Ruiz-Mirazo

I-23. Functional phylogeny: a consistent classification of organisms based on translation inhibition response
Carlos Briones

I-24. The last common ancestor: what's in a name?
Luis Delaye, Arturo Becerra and Antonio Lazcano

I-26. The role of virus in the origin of DNA genome and early cellular evolution
Patrick Forterre

I-28. Mediation of early microbial evolution and ecology by cyanide inhibition?
Christopher H. House

I-29. Three-dimensional optical and molecular- structural imagery of Precambrian microscopic fossils
J. William Schopf

I-33. Lithopanspermia, a mode of natural distribution of life in the Solar System?
Gerda Horneck

I-34. Searching for a second genesis of life: why, where, how
Andre Brack

I-35. Astrobiology and the exploration of Gusev Crater by the Mars Exploration Rover Spirit
David J. Des Marais and the Athena Science Team

I-36. A new astrobiological vision of Titan from the Cassini-Huygens data
Francois Raulin

I-37. Some philosophical remarks concerning the origin of life
Alvaro Moreno

I-38. Catholic critics of early synthetic biology experiments: Agostini Gemelli, Jaume Pujiula and Jean Maumus
Juli Peretó and Català

I-39. An epistemological synthesis concerning the status of prebiotic experiments in 20th century studies of the origins of life
Stéphane Tirard

O-1. The reduction of nitrogen to ammonia by ferrous hydroxide
David Mauzerall

O-2. Remnants of early Archean (circa 3.5 Ga) seawater in BIF from Caozhuang Formation, Qian'an County, Hebei Province, North China
Meng Fanwei, Zhou Chuanming, Yuan Xunlai

O-4. Investigation of interactions between cyclic triribonucleotides and alpha-amino acids
Carole Anastasi

O-5. Chemical Chaos on Primitive Earth Leading to the Biological Evolution
Yu-Fen Zhao, Jing-Ping Xiao

O-7. RNA Evolution by Recombination and Selection
Qing S. Wang and Peter J. Unrau

O-8. The origin and early evolution of membrane proteins
Andrew Pohorille, Karl Schweighofer and Michael A. Wilson

O-9. Nucleotide-like coenzymes in the formation of primitive metabolic systems
Milhail S. Kritsky, T.A. Telegina, M.P. Kolesnikov, T.A. Lyudnikova, Yu.L. Zemskova, E.A, Sviridov A.N.

O-10. Origin and evolution of photosynthetic reaction center II (PSII) subunit proteins: Evolutionary kinship to animal opsins and fungus-bacterial opsins
Koji Ohnishi, Yuka Ishimoto, Yuji Murayama, Naotaka Furuichi

O-11. The Freshwater Ocean of Europa and Implications for the Origin of Life
Kevin P. Hand, Aaron Goldman, Christopher F. Chyba

O-12. Radio telescope FAST – a sensitive tool for SETI
Rendong Nan

O-13. Chemistry of Meridiani Planum, Mars, with Implications for Biological Activities and Abiotic Processes
Benton C. Clark, Andrew H. Knoll and the Athena Science Team

O-14. The historical significance of Herrera's theory on the origins of life
Erwin Silva, L. Perezgasga, A. Negrón-Mendoza and A. Lazcano

P-1. Irradiation of CN-containing compounds in frozen state and their correlation with cometary ices
M. Colín-García, A. Negrón-Mendoza, S. Ramos- Bernal

P-2. Abstraction of hydrogen from organic matter, caused by ionizing radiation in outer space
Zbigniew Pawel Zagorski

P-4. High-molecular-weight complex organics: Three dimensional imaging and pyrolysis experiment of simulated product via interstellar gas mixture irradiated with 3 MeV proton beam
Yoshinori Takano, Taiki Tsuboi, Takeo Kaneko, Katsumi Marumo and Kensei Kobayashi

P-9. Stability of bioorganic molecules in Martian environment: Key factor for further evolution processes
N. B. Gontareva, E. A. Kuzicheva

P-10. Phosphorus Oxychloride Assisted Peptide Formation for L-Proline
Qian-Yi Zhang and Kui Lu

P-11. Synthesis of Homo L-methionine oligopeptide mediated by phosphorus oxychloride
Xinling Wang, Qianyi Zhang, Yong Man, Shuxia Cao, Kui Lu

P-12. High-dose gamma-irradiation of fullerene c60: implications for interstellar fullerenes
Guadalupe Albarrán, Vladimir A. Basiuk, Elena V. Basiuk and José Manuel Saniger

P-13. An action of mineral surfaces in photochemical abiogenic synthesis of nucleotides
Michael B. Simakov and Eugenia A. Kuzicheva

P-14. Density Functional Theory Study of $(HCN)_n$ Clusters up to $n = 10$
Martine Adrian-Scotto, Dan Vasilescu

P-16. Thermal synthesis of possible prebiotic organic compounds from calcium-coordinated amino acids
Stefan Fox and Henry Strasdeit

P-17. Thermal transformation of metal-ion- and silicate-bound amino acids as a possible source of prebiotic molecules
Henry Strasdeit, Stefan Fox and Dmytro Denysenko

P-18. Intercalates of sheet silicates with amino acids as possible intermediates in prebiotic chemistry
Dmytro Denysenko and Henry Strasdeit

P-19. The stacking interaction energies of sequences of pyrimidine and purine polyribonucleotides
Nigel Aylward and N. Bofinger

P-23. Synthesis of pyrimidic nucleotides under potentially prebiotic conditions
Fabien F. Buchet John D. Sutherland

P-24. Synthesis of cyanobutadiyne
Yann Trolez and Jean-Claude Guillemin

P-26. Role of clays as protecting agents in prebiotic chemistry
A. Negrón-Mendoza, A. Guzmán, F.G. Mosquiera and S. Ramos-Bernal

P-27. Theoretical Studies on N-Phosphoryl Amino Acids for the Origin of Biomolecules
Yufen Zhao, Xiaohong Liu, Ming Sun, Changmei Cheng, Yanmei Li, Bo Tan and Zhongzhou Chen

P-28. Theoretical Study on Aggregates of Seryl-Histidine and Histidyl-Serine Dipeptide with 5′-TpTpdC-3′
Xiaohong Liu, Ming Sun, Changmei Cheng and Yufen Zhao

P-32. Stable at high temperature: homogeneous stacking aggregates of adenine, adenosine and cytidine in water, observed by luminescence
V.L. Rapoport, V.M. Malkin, S.V. Zorina, S.M. Komarov and V.V. Goriuchko

P-34. Purification and Formation of L-Tryptophan Homo-oligo Peptide as Activated by Phosphorus Oxychloride
Yong Man, Xin-Ling Wang, Ying-Yan Yao, Shu-Xia Cao and Kui Lu

P-35. An amino-acid based protometabolic system: the Primary Pump scenario. Implications on the emergence of homochirality
Laurent Boiteau, Grégoire Danger, Robert Pascal, Jacques Taillades, Auguste Commeyras

P-37. Evolutionary track of the genetic codon covered by the term degeneracy
Jingping Xiao

P-38. Nitrogen Fixation in Aqueous Solution Induced by Ion Implantation: Implications for primordial Amino Acid Synthesis
Wei Wang, Huaibin Shi, Xiangqin Wang, Shangbing Wang and Zengliang Yu

P-39. Potentially Prebiotic Chemistry of Acyl Phosphates
Andy Pratt

P-40. HPLC-ESI-Ms/Ms to Identify the Sequence of Dinucleotides Formed by N-Phosphoryl Alanine and Four Nucleosides
Shuxia Cao, Yanchun Guo, Xinchen Liao, Jianchen Zhang and Yufen Zhao

P-44. Structural and Chiral Selection by Phosphorus Participation
Yong Ju, Jianjun Hu, Yi Chen and Yufen Zhao

P-45. A novel rearrangement reaction of N-phosphoryl amino acid methyl esters in ESI-MS
Yi Chen and Zhao Yufen

P-49. Formation of Biologically Important Molecules on a Mineral Surface
V.A. Otroshchenko and N.V. Vasilyeva

P-50. Thermal Polyaspartic Acid Microspheres
Peter R. Bahn and Aristotel Pappelis

P-52. Molecular Modeling and Peptide Dendrimer of Ser-His and Related Dipeptides, the Possible Smallest Protease and Nuclease in the Prebiotic Synthesis
Yuan Ma, Jun He, Ming Sun and Yufen Zhao

P-55. Possibility of discrimination between optical isomers of amino acids by serpentine treated with some acids
Hideo Hashizume

P-57. Asymmetric Photolysis of Thin Solid Film of Aromatic Amino Acid with Circularly Polarized Light
Jun-ichi Takahashi

P-58. Stable Non-Racemic States in Far-From-Equilibrium Systems as Origin of Homochirality
Raphael Plasson, Kouichi Asakura and Dilip K. Kondepudi

P-59. Chiral Symmetry Breaking in Growth Front of Conglomerate Crystal Phase
Kouichi Asakura, Raphael Plasoon, Dilip K. Kondepudi

P-64. Recent Progress in Biological Chirality
G. Palyi, C. Zucchi and L. Caglioti

P-66. The Origin of Homochirality Explored by a New Theory Model
Daxiong Han, Weizhu Chen and Yufen Zhao

P-67. A Raman Spectroscopic Temperature Study of $-NH_3^+$, $-CO_2^-$, αC-H Motion related to the Hydrogen Bonding Dynamics of D- and L-alanine
Yan Gong and Wen-Qing Wang

P-68. The Natural Earth's Orbital Chirality Force Field and Its Role in the Origin of Life and Chemical Evolution
Yujian He, Fei Qi and Shengchu Qi

P-74. Oligonucleotides from Montmorillonite catalysis; Analysis and Modelling
Michael F. Aldersley, James P. Ferris, Wenhua Huang, Prakash C. Joshi and Dmitri Zagorevski

P-77. Genetic Encoding of 4-, 5- and 6-Fluorotryptophans: Role of Oligogenic Barriers
Flora W.K. Mat, Hong Xue and J. Tze-Fei Wong

P-79. Motif shuffling in RNA molecules? Structural constraints in the acquisition of function
Susanna C. Manrubia and Carlos Briones

P-81. Interaction experiments between RNA molecules and phosphate minerals
Kosuke Okihara and Satoru Nakashima

P-82. Exploratory Studies to Investigate a Linked Prebiotic Origin of RNA and Coded Peptides
Michael Crowe

P-83. The non-enzymatic template-directed ligation of oligonucleotides
A.V. Lutay, E.L. Chernolovskaya, M.A. Zenkova and V.V. Vlassov

P-87. N-Carboxyanhydrides in a prebiotic aminoacylation of nucleotides, and progress towards a potential prebiotic RNA-Coded Peptide synthesis
Alastair L. Parkes and John D. Sutherland

P-88. Prebiotic Evolution of Riboglycopeptides: Bridging the Entropy Gap at the Dawn of Life on Earth
Louis N. Irwin and Dirk Schulze-Makuch

P-92. Abiogenic Pteridins and Flavins as Photosensitizers for Peptide Formation and the ADP to ATP Phosphorylation
Taisiya A. Telegina, Michael P. Kolesnikov and Mikhail S. Kritsky

P-94. Microbial activity in zeolites deduced from mineral inclusions
Magnus Ivarsson

P-96. Study of the Osmotic Balance Problem in a Minimal Self-Maintaining Cell Model
Felix Olasagasti, Alvaro Moreno, Juli Peret, Federico Morán and Felix Olasagasti

P-97. A Model for Compartmentalization of Primitive Cell
Hai-Yan Wang, Yan-Mei Li, Yi Xiao and Yu-Fen Zhao

P-99 A Hypothesis of Origin of the Backbone of Nucleic Acid – Efficient Synthesis of 3′, 5′- Dithio-2′-Deoxypurinenucleosides
Hongchao Zheng, Changmei Cheng, Hua Wang, Shanshan Xu and Yufen Zhao

P-100. A Hypothesis of Origin of the Backbone of Nucleic Acid – Efficient Synthesis of 3′,5′-Dithio-2-dexoypyrimidine Nucleosides
Hua Wang, Changmei Cheng, Hongchao Zheng, Xiaohong Liu, Chang Fang, Shanshan Xu and Yufen Zhao

P-101. A vital way of life: apoptosis, inducted by nitrogen heterocycles synthesized in human leukemia K562 cells and its mechanism
Guoyu Ding, Ting Yang, Yuyang Jiang, Hua Fu and Yufen Zhao

P-107. Chemical Turing Machines – A Road Map for the Small Molecule World
Robert Vergenz

P-109. Differences in substrate specificity of C5-substituted uridine derivatives by DNA polymerases from hyper thermophilic bacteria, archaea and virus
H. Sawai, K. Kuwahara, A. Nakamura, T. Ohbayashi, Y. Takahata and H. Ozaki

P-111. Biochemical Evidence Vs. Metabolic Inference Form Complete Genomes: Lessons From The Arnon Cycle, An Autotrophic Carbon Dioxide Fixation Pathway
J. Peretó and J. Castresana

P-112. Comparative Analysis of Prokaryotic Genomes Sizes and the Gene Complement of a Minimal Dna/Rna/Protein Cell
Sara Islas, Arturo Becerra and Antonio Lazcano

P-113. Low Complexity Sequences in Lentivirus
A.M. Velasco, A. Becerra and A. Lazcano

P-114. Comparative analysis of methodologies for the detection of horizontally transferred genes: a reassessment of first-order Markov models
Diego Q. Cortez, Antonio Lazcano and Arturo Becerra

P-119. Multiple Proteobacterial Origins for Eukaryotic Thiolases
J. Peret, Purificacin López-García and David Moreira

P-121. Horizontal Gene Transfer: Retrospection and Beyond
Janet Siefert

P-122. IR and Raman microspectroscopy for the characterization of ancient life
Motoko Igisu, Satoru Nakashima, Yuichiro Ueno, Stanley M. Awramik and Shigenori Maruyama

P-126. Spectroscopic Analysis of the Thermal Alteration of Petrified Organic Matter
Andrew D. Czaja

P-129. Vendian (Ediacaran) Biota from the Lesser Himalaya, India and Southern China with Special Reference to Early Evolution of Life on Earth
Vinod C. Tewari

P-130. Origin and early evolution of small animal phyla: Priapulida
Huang Diying, Chen Junyuan and Vannier Jean

P-132. Linking Molecular Taxonomy with Environmental Geochemsitry in Environments Relevant to Astrobiology: The Anaerobic Oxidation of Methane in Cold Seeps & deeply Buried Marine Sediments
Christopher H. House

P-137. Martian meteorological measurements using ground-based telescopes
Andrew Simpson, Jeremy Bailey and Malcolm Walter

P-139. Sub-vent biosphere: Phosphatase activities in 308 deep-sea hydrothermal systems at Suiyo seamount, Izu-Bonin Arc, Western Pacific Ocean
Yoshinori Takano, Kensei Kobayashi, Yae Edazawa, Tetsuro Urabe and Katsumi Marumo

P-140. Algae colonization and succession in desert soil
Chunxiang Hu and Yongding Liu

P-141. Studies on the adaptation mechanism of desert algae to UV-B irradiance
Gaohong Wang, Lanzhou Chen, Chunxiang Hu, genbao Li and Yongding Liu

P-142. Study on Novel Peptide Formation process in origin of life under Microwave Irradiation
Rong Hu, Jingping Tian and Ying Wu Yin

P-150. NaCl enhanced oligomerization of O-phospho-L-serine
Yan Qin, Liu Yi-Nan and Wang Kong-Jiang ser

P-151. Na^+ enhanced oligomerization of L-glutamic acid
Ma Yan-Lin, Xin Liang and Wang Kong-Jiang

P-152. Alkanes to Diamonds: A Speculation about Titan
Peter Bahn, Steven Pravdo, Mark Rudis and Aristotel Pappelis

P-154. Plausible Metabolic Pathways and Energy Cycling on Titan
Dirk Schulze-Makuch and David H. Grinspoon

P-155. Possible sites for abiogenic and biogenic activity on Titan
Michael B. Simakov

P-156. Methanogens: A Model for Life on Mars
Timothy Kral

P-161. Microbial origin of life on Europa
Gunther Kletetschka, Stephanie A. Getty, Malcolm Shields, Jun Li, Vilem Mikula and Peter Wasilewski

P-162. Titan may hold clues to origin of life
He Youqiu, Geng Rongxia, Ming Lang and Zhou Mingming

P-164. Labortory Simulation of Photochemistry on Titan and Comparison with Available Huygens Data
J.P. Ferris, B.N. Tran, V. Vuitton and J. Joseph

P-170. Sensitivity effects of chemical kinetic uncertainties on photochemical modeling results: Application to Titan's atmosphere
Eric Hébrard, Michel Dobrijevic, Yves Bénilan and François Raulin

P-175. Electric activity on Titan before and after Cassini-Huygens arrival
Sandra I. Ramirez

P-176. The Origin of Life in the Nahua Culture
N. Valderrama-Negrón, S. Ramos-Amézquita, S. Ramos-Bernal and A. Negrón-Mendoza

P-179. Early Ideas Supporting Symbiogenesis and Against Cell Theory from Spanish-Speaking Scientists
Ulises Iturbe and Antonio Lazcano

P-180. Mechanism of amphioxus gastrulating cell movements: Forces that drive the most primitive form of chordate gastrulation
Yu Dan and Zhang Peijun

P-181. Synchronous Origination of Codon Strand and Coded Peptide: An Orchestration
Jing-Ping Xiao and Yu-Fen Zhao

P-182. Stability of Organic Compounds in High-Temperature and High-Pressure Environments Simulating Submarine Hydrothermal Systems
Hironari Kurihara, Suguru Yabashi, Tsukasa Horiuchi, Md. Nazrul Islam, Takeo Kaneko, Yoshinori Takano, Katsumi Marumo and Kensei Kobayashi

P-183. Biofilms on Biotic Surfaces: A Link in the Carbon Cycle on Early Earth
Susan Leschine and Almaris Alonso

EDITORIAL NOTE

This issue of Origins of Life and Evolution of Biospheres presents the abstracts of all papers and posters presented at ISSOL 2005, the 14th International Conference on the Origin of Life, held in Beijing, from June 19–24, 2005. This first ISSOL conference to be held in China was a great success, both scientifically and socially. Many members of the Society were afforded their first opportunity to visit the Peoples Republic, meet many colleagues there and visit some of the spectacular cultural monuments of China's long and fascinating history. I wish to thank Professor Yufen Zhao and all of her students and associates whose tireless efforts succeeded in a very successful conference.

Alan Schwartz

Commentary by the Conference Chairperson

It was our great pleasure and honor to organize the 14th International Conference on the Origin of Life (ISSOL'05) on June 19–24, 2005 in Beijing, China. We had more than 300 participants covering 34 countries. The theme of this conference was designed to cover eleven subject areas, of which we had 63 lectures including 4 impressive public lectures by Professors, Eigen, Miller, Bei and Chen, a splendid plenary lecture by Professor Joyce and 181 poster presentations. I thank the ISSOL, International Society for the Study of the Origin of Life, for sponsoring the meeting, and thank the organizations of the People's Republic of China and the private individuals who gave the conference generous assistance and funding. I hope that ISSOL'05 offered all participants an enrichment of understanding on important aspects of the origin of life, and a furthering of international collaboration on research. I would also like to present our thanks to Professor Alan Schwartz and all the staff of the journal of Origins of Life and Evolution of Biospheres, for their assistance to publish a special issue in the journal for this conference.

Conference Chairperson
Yufen Zhao

PUBLIC LECTURE: WHAT IS LIFE – NOW?

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An old question is revisited on the basis of novel thoughts and recent experimental evidence. A general physical theory is emerging that is able to answer key questions regarding:

- the transition from non-life to life,
- the solution of the problem of exponential complexity within polynomial time, and
- a closed mathematical representation of typically biological phenomena.

Experiments with RNA/protein systems as well as with viruses have been performed, that allow for a quantitative testing of the theory. Practical applications concern a new "Evolutionary Biotechnology" that involves selection and high throughput screening on a nanoscale, using automated and computerized equipment. Suggestions for new antiviral strategies have emerged that were successfully tested. The new development can be summarized by the slogan: "Darwin is dead – long live Darwin".

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PLENARY LECTURE: EVOLUTION IN AN RNA WORLD

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It is believed that an RNA-based genetic system, usually referred to as the "RNA world" preceded the DNA and protein-based genetic system that has existed on Earth for the past 3.5 billion years. Questions concerning how the RNA world arose and the degree of complexity it attained can be addressed through laboratory experiments in prebiotic chemistry and RNA biochemistry. In the realm of prebiotic chemistry, one seeks to explain how the chemical components of RNA (ribose, phosphate, and the nucleotide bases) arose and assembled to form polynucleotides in the presence of a complex mixture of closely-related compounds. Ribose, for example, would have been accompanied by many other sugars, and is more reactive and degrades more rapidly than these other sugars. Taking advantage of the greater reactivity of ribose, we found that it reacts especially rapidly with cyanamide to form a stable bicyclic adduct. This product crystallizes spontaneously in aqueous solution, whereas other sugar-cyanamides present in the same mixture do not (Springsteen and Joyce, 2004). The ribose-cyanamide crystals give the same diffraction pattern when derived from D-ribose, L-ribose, or a racemic mixture of D- and L-ribose. The crystals derived from racemic ribose contain a mosaic of pure-D and pure-L domains. Ribose-cyanamide in turn reacts with cyanoacetylene to form cytosine alpha-nucleoside in nearly quantitative yield. This reaction takes place either with ribose-cyanamide in solution or with ribose-cyanamide crystals, employing an aqueous solution of 50 mM cyanoacetylene over a broad range of pH and temperature. The much greater efficiency of this reaction compared to previous reports (Sanchez and Orgel, 1970) is due to the finding that higher concentrations of cyanoacetylene (as employed previously) are deleterious because they promote a side reaction of cyanoacetylene with cytosine nucleoside. Efforts to convert cytosine alpha-nucleoside to the beta-nucleoside under plausible prebiotic conditions have thus far been unsuccessful. Central to the operation of the RNA world is the ability of RNA to catalyze the replication of RNA, thereby enabling RNA-based evolution. Through methods of test-tube evolution, we have developed RNA enzymes that catalyze the template-directed joining of RNA. We evolved one such enzyme that contains only three of the four subunits of RNA (A, U, and G, but lacking C) (Rogers and Joyce, 2001). It subsequently was evolved to produce a more reactive variant that contains all four subunits, as well as a less reactive variant that contains only two subunits (2-amino-A and U) (Reader and Joyce, 2002). Most recently, the four-subunit variant was evolved to contain deoxynucleotides rather than ribonucleotides. This demonstrates how catalytic function can be retained during the conversion between an RNA and RNA-like (in this case DNA) molecule. The four-subunit ligase described above was used to construct a self-replicating ribozyme that catalyzes the ligation of two RNA substrates to form additional copies of itself (Paul and Joyce, 2002). This in turn was used to construct a pair of cross-replicating ribozymes that catalyze each other's synthesis from a total of four component substrates (Kim and Joyce, 2004). The rate of formation of the two ribozymes increases progressively over the course of the reaction, consistent with the overall autocatalytic behavior of the system. The system is not capable of undergoing Darwinian evolution, however, because there is no possibility for heritable mutations in the successive assembly of replicating molecules.

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I-1. EARTH'S PRIMITIVE ENVIRONMENT AND EXOGENOUS SOURCES OF INGREDIENTS FOR PREBIOTIC CHEMICAL EVOLUTION

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On the basis of our current understanding, it is likely that a combination of exogenous and endogenous sources provided the first building blocks necessary for life to arise on Earth. While identification of the dominant component remains elusive because of the many unknowns regarding this earliest period in our planet's history, it is important to consider the relative contribution of the most likely sources. Here, I will focus on extraterrestrial sources (carbonaceous meteorites, comets, and dust) and the viability of their delivery to Earth. The terrestrial planets and moons are marked with impact craters dating back to the early history of the solar system, when bombardment of their surfaces by comets and asteroids, as well as the more passive rain of interplanetary dust, was most intense. Meteorites provide our best samples of extraterrestrial organic material that has survived planetary impact. Recent space mission events have reinforced the notion that organic matter can survive impact delivery. For example, worms, C. elegans, were found thriving in canisters recovered from the space shuttle Columbia debris. Additionally, "fragile" sample plates from the Genesis Mission's payload were recovered intact after it crashed into the Utah desert. Comets and asteroids impact Earth at significantly higher speeds than these man-made objects experienced, resulting in substantially greater temperatures, pressures, and residual velocities. Recent numerical simulations and experimental studies provide insight into the fate of exogenous material delivered to the early Earth. All suggest that a higher fraction of organic material may have survived impacts than was considered previously. Shock experiments also reveal that simple organic compounds can polymerize as a result of impact processing. These results will be discussed in the context of thermodynamic reaction pathways.

I-2. ORGANIC MATTER IN SPACE

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Organic chemistry appears to be a nearly ubiquitous feature of our universe. The principal elements that are essential for terrestrial life (hydrogen, carbon, oxygen, nitrogen, sulfur, and phosphorus) take part in a complex chemistry in the dense interstellar clouds where new stars are forming. More than 100 molecular species, most of them organic and with molecular weights up to twice that of glycine, have been securely identified in these gas clouds. The low temperature kinetics in these regions leads to very large isotopic fractionation, particularly for hydrogen. There is strong evidence for significantly heavier organic molecules, particularly polycyclic aromatics, although precise identification of individual species has not yet been obtained. Moreover, observations suggest that a similar organic chemistry operates in other galaxies throughout the universe, and has done so back to times not long after the Big Bang. In our solar system cometary volatile compositions bear striking similarities to those of interstellar clouds, in both the relative abundances of molecular constituents and in the isotopic fractionation of hydrogen, raising the question of the extent to which comets may preserve interstellar organics. Comets, in turn, have supplied the Earth with volatiles, including complex organics, which conceivably played a role in the origin of life.

I-4. A HOT HADEAN FOR BIOGENESIS?

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The case for a hyperthermophilic Last Common Ancestor (LCA) of life and of biogenesis itself has been strengthened by recent research (discussed in Schwartzman and Lineweaver, 2004). A hyperthermophilic LCA is not of course inconsistent with biogenesis at lower temperatures if the two events were separated by a near sterilizing event leaving only hyperthermophilic survivors. These events could have included big impacts and large degassing pulses from the mantle. However, if no such event big enough to wipe out lower temperature procaryotes occurred since Hadean biogenesis, a possibility consistent with Ryder's (2002) reinterpretation of the early lunar impact record, then biogenesis was likewise hyperthermophilic and Hadean climatic temperatures were plausibly very warm. The apparent absence of deeply-rooted mesophiles/psychrophiles on molecular phylogenetic trees is consistent with a hot Hadean climate although a thermophilic Archean climate may have wiped out Hadean lower temperature organisms if they existed. But even thermophilic Archean temperatures near sea level could have been compatible with lower temperature environments on high mountains. Additional evidence for hyperthermophilic biogenesis includes new experiments demonstrating RNA stability at hyperthermophilic temperatures in saline solutions, plausible arguments for highly saline Hadean oceans (Knauth, 2005) and the high thermostability of ferredoxin. Hadean biogenesis is supported by some derivations of emergence times from molecular phylogeny (Battistuzzi et al., 2004). In addition to our previous demonstration of the strong anti-correlation of rRNA phylogenetic distance of (hyper)thermophilic prokaryotes and their maximum temperature of growth (Tmax), we observe an analogous correlation of Tmax in the tRNA tree, where phylogenetic distance is better quantified (Xue et al., 2003). Drawing on a plausible scenario of hydrothermal biogenesis near the seafloor (Russell and Hall, 1997; Martin and Russell, 2003), we propose that Bacterial and Archaeal protocells emerged simultaneously in the thermal gradient between a hydrothermal source on the seafloor and the ambient climatic temperature, between at least 120 and 80–100 deg C, in Hadean time. The Tmax of living Archaea and Bacteria presently known are 121 and 95 deg C respectively. A climatic temperature close to 80 deg in the late Hadean/early Archean is consistent with paleotemperatures derived from oxygen isotopes in marine cherts. Simultaneous emergence of multiple protocells, each at its upper temperature limit, implies that the age of emergence of primitive hyperthermophiles should have been the same. If possible variable mutation rate for each lineage can be inferred in the RNA tree, then this prediction can be tested.

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I-5. ROLES OF EXTRATERRESTRIAL COMPLEX ORGANICS IN CHEMICAL EVOLUTION TOWARD ORIGINS OF LIFE

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Earlier stages of chemical evolution process have been discussed basically in the context of the reactions of small molecules such as HCN and HCHO. Free amino acids, free nucleic acid bases, and free sugars should be formed at first in the conventional scenario. Then it is hypothesized that biological monomers were condensed together to form biological oligomers, which are peptides and oligonucleotides. It is claimed, however, that formation of these oligomers under prebiotic conditions is quite difficult. In addition, chemical fossils of these reactions before the origin of life are hardly found in the Earth since they are fragile. We are able to find the "fossils of chemical evolution" in extraterrestrial bodies. A wide variety of organic compounds have been detected in meteorites, comets and Titan, the largest satellite of Saturn. Major part of organics in carbonaceous chondrites is complex organics though some biological monomers like amino acids have been identified in extracts from them (Shimoyama, 1997). Mass spectra of dusts of Comet Halley suggested that the comet has quite complex organics (Kissel and Krueger, 1987). Titan has haze in its atmosphere. Laboratory experiments simulating reactions in Titan atmosphere suggested that the haze is composed of very complicated organic compounds that are often referred to as Tholin (Thompson et al., 1991). It is plausible that complex organics are delivered to the primitive Earth by comets and meteorites, and that they were possible sources of the terrestrial biosphere. It has been hypothesized that cometary and meteoritic organic compounds were first formed in interstellar dust particles (ISDs). Amino acid precursors have been reported to form in simulated ISD environments by proton (Kasamatsu et al., 1997) or UV (Caro et al., 2002) of simulated ISD ice mantles. Here we discuss nature of bioorganic compounds formed in simulated ISD environments. Carbon monoxide, methanol, ammonia and water were among possible interstellar media. When a mixture of methanol, ammonia and water was irradiated with gamma rays or heavy ions at 77 K or 293 K, amino acids were detected in the hydrolysate. The G-value (energy yield) of glycine was ca. 0.01, which was independent from the temperature or the phase (solid or liquid). These results suggest that amino acid precursors can be formed in ISD environments quite effectively even if the materials were frozen in low temperature. Amino acids were hardly found in the products before hydrolysis: Instead, complex organic compounds whose molecular weight was ca. 2000 were found. These results suggest that not free amino acid monomers but amino acid precursors with complex structure are abiotically formed in molecular clouds. We also examined stability of amino acids and related compounds. A mixture of carbon monoxide, ammonia and water was irradiated with high-energy protons. The resulting products were found to be complex amino acid precursors. Then aqueous solution of free amino acids and that of complex amino acid precursors were irradiated with gamma rays or heavy ions. Recovery of amino acids in the amino acid precursors was much higher than free amino acids against radiation. Stability of the complex amino acid precursors was also far more stable than amino acid monomers. According to these results, it is very likely that extraterrestrial complex organic compounds delivered to the Earth had important roles in generation of life on the Earth.

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I-6. THERMOLYSIS OF AMINO ACIDS IN THE GAS PHASE

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According to the detection of aminoacids or sugars in meteorites, molecules which led to life were brought on the Earth during the epoch of high meteoritic bombardment. (Cooper et al., 1995; Ehrenfreund et al., 2001) When meteorites entered into the primitive atmosphere, they were allowed to heat up to about 600 °C on average. So we wonder whether molecules could be formed by amino acids thermolysis. We report here the thermolysis in gas phase of sublimated samples of various aminoacids and the characterization of the low-boiling products. All thermolyses have been carried under vacuum at 400, 600 and 800 °C during less than 1s (flash thermolysis conditions). The low-boiling products were directly characterized by mass spectrometry in the gas phase or condensed on a cold finger with a solvent for analysis by NMR spectroscopy. Thus, we observed that ammonia, carbon monoxide, aldehydes or ketones have been formed in the thermolysis of amino acids with an alkyl side chain. $RCH(NH_2)CO_2H \rightarrow RC(H){=}O + CO + NH_3 + ?$ The formation of the corresponding imine has been demonstrated by Mass Spectrometry for several aminoacids and, pyrroline, for example, was identified in the thermolysis products of proline. Many other products like 2-pyrrolidinone, pyrrolinone, pyrrole, and styrene ... were also identified. The mixture of seach products in the Prebiotic Soup could have lead to the formation of many other compounds.

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I-7. PREBIOTIC OLIGOMERIZATION, PHOSPHORYLATION, AND CARBOXYLATION IN HYDROTHERMAL ENVIRONMENTS

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Constant circulation of seawater through hot vents in the ocean can support various synthetic reactions in prebiotic conditions. The major physical parameters characterizing synthetic reactions in hydrothermal environments include the cycle time of reaction fluids through hot vents, the residence time of reactants inside hot vents in each cycle, and the temperature gradient between the hot water in the vents and the cold surrounding water among others. Those parameters which could be optimum depend upon the type of synthetic reactions in focus. If the residence time in each cycle is too long, thermal decomposition would finally set the limit to which synthetic reactions could proceed. On the other hand, if the residence time is too short, the reactants could not acquire enough activation energy to form synthesized products.

We experimentally examined the optimum parameters specifying synthetic reactions proceeding in hydrothermal circulation of the reaction fluids with use of a flow reactor simulating the circulation. Oligomerization of amino acids (e.g., glycine, alanine, valine and aspartic acid) could proceed in the temperature gradient between 200 °C and 0 °C, while the workable temperature gradient for oligomerization of nucleotide (e.g., AMP) was 110/0 °C. Phosphorylation of nucleotide (e.g., from AMP to ATP) was observed to proceed in the gradient 100/0 °C. Carboxylation (e.g., from oxaloacetate to citrate) proceeded in the gradient 120/0 °C.

These results, when combined together, suggest that although hydrothermal environments in the ocean could have been versatile in facilitating various chemical syntheses of prebiotic significance, the likely sites of assembling those synthesized products for a functional organization might not have necessarily been restricted to near hydrothermal vents in one form or another.

I-8. STUDIES ON METAL – CYANOGEN COMPLEXES AS PREBIOTIC CATALYST

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We propose that transition metal ions present in the primeval seas could have formed a number of soluble and insoluble complexes with cyanide ions present there. Since most of the metal cyanogen complexes are insoluble in water, they might have settled at the shore or bottom of primeval seas.Thus, metal cyanogen complexes present on the primitive earth could have catalyzed a class of reactions in the course of chemical evolution. In order to test the above hypothesis a number metal cyanogen complexes of general formula $M'_x\ [M''(CN)_y]_z.nH_2O$ have been synthesized. Interaction of the metal cyanogen complexes thus synthesized was studied with several biologically important molecules of prebiotic relevance. Metal ferrocyanides, metal cobalticyanides and metal chromicyanides were found to possess high adsorption capacity towards amino acids and ribose nucleotides.Metal chromicyanides were able to catalyze the oxidation of hydroquinone to benzoquinone and NADPH to $NADP^+$. Copper chromicyanide was found to catalyze dimerization of cysteine to cystine as well as the conversion of fructose to pyruvaldehyde. The above results suggest that water insoluble metal cyanogen complexes might have concentrated the biomonomers from their dilute aqueous solutions through adsorption processes and subsequently catalyzed a class of reactions of prebiotic relevance.

I-10. AN UPDATED REVIEW OF HOMOCHIRALITY'S ORIGIN

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The origin of homochirality of virtually all of life's building blocks, the same handedness for example in all proteinogenic amino acids, is one of the most difficult-to-understand problems in the context of the origin and evolution of life itself. A number of different approaches to an explanation of this fact have been taken, which will be given in a brief summary here. One plausibly possibility for the origin of homochirality is its birth in space. It has been suggested that circularly polarized radiation may have favoured the construction or destruction of one enantiomer over the other by photochemical means. Recent experiments in our laboratory have shown that not only aqueous solutions of biomolecules are subject to this effect, but also solid state amino acids (1). Also, these experiments have shown that rather hard UV radiation ($\sim$160 nm) as it is present in space will lead to asymmetric photodecomposition of solid state amino acids. These results are in good agreement with the recently recorded solid-state CD-spectrum of the amino acid leucine. Furthermore a study of the Murchison meteorite has shown that the well documented effect of a significant enantiomeric excess of certain compounds is not limited to the proteinogenic amino acids and sugars, but is also observed in the case of the less familiar diaminocarboxilic acids, like diaminopropanoic, diaminobutanoic and diaminopentanoic acid (2). These molecules, which are thought to make up the monomers of a proposed archaic/prebiotic peptide nucleic acid (PNA) that may have served as a very early genetic material, have been identified on an extraterrestrial body for the first time.

(1) "Asymmetric VUV photodecomposition of the amino-acid D, L-leucine in the solid state" Uwe J. Meierhenrich et al., results in the process of being published
(2) "Identification of diamino acids in the Murchison meteorite" Meierhenrich et al., PNAS 25, Vol. 101, pp. 9182–9186, (2004).

I-11. AMINO ACID N-CARBOXYANHYDRIDES AS EARLY ENERGY CARRIERS – TOWARDS A CONTINUOUS SCENARIO FROM PREBIOTIC AMINO ACID CHEMISTRY TO THE EMERGENCE OF THE TRANSLATION APPARATUS

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Amino acid *N*-carboxyanhydrides (NCAs) are the only known peptide monomers capable of reaching significant polymerization degrees in aqueous solution Ferris et al., 1996, which suggests that they played a role in the prebiotic formation of uncoded peptides. This possibility is also supported by the reports of several plausible pathways for NCA formation during the last decade Commeyras et al., 2002. These compounds combine a high kinetic reactivity and a thermodynamically stabilized structure, properties that would be incompatible unless made possible by the cyclic arrangement. These very specific physicochemical properties, which have been deduced from a thermodynamic analysis, will be used to support NCA participation as a universal activated form of amino acids in primitive environments involving an atmosphere with a CO_2 content higher than present. It follows that NCAs could have been easily formed from many other activated amino acid derivatives in this context and, possibly, as transient intermediates in the reaction of poorly activated derivatives. Their energy content is easily exchangeable, which make them potent prebiotic energy carriers.

We anticipated that valuable chemistry would be achievable in the origin-of-life field if they were capable of interacting with inorganic phosphate and phosphate monoesters including nucleotides. In this way, a connection would be established between amino acid chemistry and two fundamental biochemical processes, namely, phosphorylation pathways and phosphoric acid mixed anhydride (adenylate) chemistry. Importantly, a scenario starting from the prebiotic chemistry of amino acids and leading to the emergence of the modern pathway of amino acid activation can be devised by means of this connection.

Evidences of the reaction of NCAs with inorganic Birnard Pascal, 2004 and organic phosphates will be presented. The process by which the chemical energy present in NCA is transferred to a phosphorylated intermediate simulates modern biological metabolic pathways. The possibility that amino acid chemistry has provided both phosphorylation pathways and nucleotide activation pathways will be discussed. It seems unlikely that an early connection of that kind could have been lost later, which challenges the occurrence of a *peptide-free* RNA world where living organisms used RNA for both catalysis and information storage.

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I-12. MINERAL CATALYSIS AND PREBIOTIC SYNTHESIS

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The montmorillonite-catalyzed synthesis of RNA oligomers from activated monomers has been described (Ferris and Ertem, 1993). The scope and selectivity of the synthesis will be discussed. Recent studies on the formation of RNA oligomers established that the sequences did not vary with chain length. The trimers formed from D, L-ImpA had a higher yield of homochiral products that would be expected if the products were formed by random synthesis. Only 11% of the trimers formed from ImpU were homochiral, a result that differs markedly from those formed from ImpA. We observed that mass spectral analysis provides a more sensitive detection of the RNA oligomers formed in these reactions than HPLC. Montmorillonite Catalysis of RNA Oligomer Formation in Aqueous Solution. A Model for the Prebiotic Formation of RNA, 1993, Ferris, J. P. and Ertem, G., *J. Am. Chem. Soc.*, **115**, 12270–12275.

I-13. BEYOND TNA

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After studying TNA as an informational base-pairing system work at the Scripps- and ETH-branch of the Eschenmoser research group has expanded beyond TNA towards informational oligomer systems not confined to sugar-backbones. The lecture will present some recent results: the chemistry of a family of allopurines that form C-nucleosides with relative ease and the base-pairing properties of a family of polypeptide backbone derived systems.

I-17. THE SIMPLEST CELLULAR LIFE

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The problem of the origin of life may be rephrased as "What was the simplest molecular entity capable of reproduction?" There is a widespread agreement that once self-copying of any kind took place, Darwinian selection and evolution could be initiated. Textbooks almost exclusively refer to one class of answers to the above question, invoking individual molecules, often templating biopolymers, such as RNA. The alternative "Lipid world" scenario (Segre et al., 2001) suggests the "pre-RNA" involvement of reproducing assemblies, (e.g. micelles), which contain only lipid-like amphiphilic monomers. These are suggested to have been the simplest, very primitive forms of cellular life. A conundrum then arises: how could non-covalent aggregates, made of molecules normally considered to be only involved in forming cellular partitions, store and propagate information? How could they do so without macromolecules with sequence-based templating? The Graded Autocatalysis Replication Domain (GARD) model (Segre and Lancet, 2000; Segre et al., 2000) provides a possible, though unorthodox solution. A crucial focus of this model is the notion of compositional information. It is proposed that in early prebiotic evolution, molecular assemblies could assume a distinct individuality via the counts of different organic compounds within them. We have demonstrated mathematically, and by computer simulations, that such compositions may encode Shannon information just like sequences. As for the chemical pathway that would copy this information, a useful relevant analogy is the propagation of epigenetic information in present-day cells. Prior to cell division, and in parallel with DNA replication, dividing cells must grow homeostatically, preserving the concentrations of thousands of components by de-novo metabolism-based synthesis. Only then may fission result in two identical progeny cells. Detailed computer simulations of GARD assemblies (Shenhav and Lancet, 2004) show that they are capable of an analogous homeostatic growth, by selective absorption of compounds from the environment. The specificity of molecular entry is governed by a network of mutually catalytic interactions, reminiscent of those invoked by pioneers in the field such as Dyson and Kauffman. The specific compositional states capable of homeostatic growth and information-preserving splits are called "composomes" (Segre et al., 2000). Their behavior is inferred from numerical solutions of differential equations governed by rigorous kinetic and thermodynamic rules. The parameter values for such equations, e.g. the distribution of catalytic potencies, are derived from real-world experiments in the realms of drug screening, combinatorial chemistry, membrane dynamics and micellar catalysis. GARD simulations show a rich dynamic behavior, whereby imperfect compositional propagation gives rise to mutation-like events. These, in turn, underlie transitions from one composome to another, in a simple evolutionary progression. In this respect, composomal amphiphilic assemblies may justly be regarded as primitive cells, capable of autopoietic reproduction and possessing life-like properties. The GARD model is highly flexible, and is currently being augmented to include the biosynthetic generation of simple peptide-like oligomers (Shenhav et al., 2005), with better mutual recognition and catalysis. A specific pathway is thought that will lead from such short oligomers to loger ones, capable of rudimentary templating and coding. A further expansion explores the analogy between the behavior of GARD assemblies and that of modern cells, as analyzed by the tools of Systems Biology. We argue that in fact very early in the evolution of life, molecular ensembles with high complexity may have arisen, which are best described and analyzed by the tools of Systems Biology. We show that modeled prebiotic mutually catalytic pathways have network attributes similar to those of present-day living cells. This includes network motifs and robustness attributes. We point out that early networks are weighted (graded), but that using a cutoff formalism one may probe their degree distribution and show that it approximates that of a random network. A question is then posed regarding the potential evolutionary mechanisms that may have led to the emergence of scale-free networks en-route to modern cells. Network analyses help understand how GARD dynamics could lead to the gradual appearance of larger and more complex cell-like systems.

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I-18. LOCATING THE ROOT OF LUCA THROUGH tRNA AND AMINOACYL-tRNA SYNTHETASE GENES

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Locating the root of life is a key step in approaching the origin of life and early biology, for knowledge of LUCA, or Last Universal Common Ancestor, defines how extant life began (Wong and Xue, 2002). Rootings using protein paralogs as mutual outgroups gave ambiguous results, and rRNAs are not useful because they lack paralogs. The coevolution theory of the genetic code suggests that the code actively expanded to add novel amino acids provided by evolving pathways of amino acid biosynthesis. Since tRNA gene duplications formed an important part of this expansion, homologies between tRNA genes could provide effective tools to search for LUCA (Wong, 1983, 2005). This expectation was verified when genetic distances between 'alloacceptor' tRNAs for dissimilar amino acids were estimated for 2878 tRNAs from 60 different genomes. Among 34 Bacteria, 18 Archaea and 8 Eukarya, the two hyperthermophilic Archaea *Methanopyrus kandleri* and *Aeropyrum pernix* yield the lowest alloacceptor distances. The results place LUCA between the branches leading to these two Archaea on the universal tRNA phylogenetic tree (Xue et al., 2003). Anticodon usages are also far more uniform, and the Crick wobble rules underdeveloped, in the Archaea compared to Bacteria and Eukarya, further supporting an archaeal root of life (Tong and Wong, 2004).

Analysis of ten pairs of potentially paralogous aminoacyl-tRNA synthetases indicates that highest homology between paralogs is displayed by *Methanopyrus kandleri*, followed by *Methanothermobacter thermoautotrophicum* and *Methanococcus jannaschii*. Therefore evidence from the synthetase genes and that from tRNA genes coincide exactly in establishing a *Methanopyrus*-proximal LUCA and its hyperthermophilic archaeal nature. Genetic code evolution thus helps to locate the root of life, and the finding of a single root in turn explains the universality of the code.

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I-21. EVOLUTIONARY GENOMICS APPROACH TO THE CORE OF MINIMAL BACTERIAL GENE SET

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Genome reduction is a process that takes place in many prokaryotes that are living together (i.e., symbionts and parasites) with eukaryotes the symbiotic association between insects and microorganisms has been extensively studied, particularly the symbiosis between aphids and their primary endosymbiont Buchnera aphidicola. On the bases of a comparative genomics study we have inferred the set of shared genes among five endosymbiotic bacteria from insects whose genomes have been sequenced (three B. aphidicola strains, Wigglesworthia glossinidia, and Blochmannia floridanus, primary endosymbionts of tse-tse flies and carpenter ant, respectively). This study was expanded by comparing such minimum set with the gene complement of Mycoplasma genitalium, an intracellular parasite.

Different experimental approaches (i.e., massive mutagenesis with transposons, antisense RNA or systematic inactivation of individual genes) have been applied to different microorganism, parasites and free living bacteria, to identify essential genes under defined culture conditions (M. genitalium, M. pneumoniae, Bacillus subtilis, Escherichia coli and Staphylococcus aureus). Combining the information derived from all these data, we reached a core of essential genes that was further analyzed to obtain a minimalist metabolic map. Finally, we propose a minimum set of 206 genes.

Our proposal is, obviously, hypothetical. To reinforce its likelihood, at least with respect to the preservation of such set of genes, several empirical approaches can be carried out. One of them consists on inspecting the presence of such core of genes in naturally reduced genomes that were not included in our previous studies. We particularly can take benefit of the sequence, already finished, of the smallest known bacterial genome, belonging to another Buchnera aphidicola strain from the aphid Cinara cedri. Although this study is still under way, we can advance that the hypothetical minimal gene set is mainly preserved.

I-22. WORKING TOWARDS THE “MINIMAL CELL”: A BOTTOM-UP PROPOSAL

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There are several different ways to approach the problem of assembling an artificial cell with just the necessary and sufficient ingredients so as to produce in the lab a system that shows the main properties and behaviour of a minimal living being. Although the growing community of scientists interested in this issue agrees that the level of complexity of the simplest living cells today is far too high for the task, there is little consensus on how to proceed (see the recent letter to Nature (Szathmáry, 2005, Nature 433, p. 469)). As expected at this, still precursory stage of the research, the focus strongly depends on the conception of life -of minimal life- dwelling in the mind of each researcher. Those who think that the major driving force of biological phenomena is Darwinian evolution tend to take up a top-down approach, which attempts to reduce the complexity of extant unicellular organisms (by various methods: knocking down secondary genes, stretching parasitic/symbiotic conditions, until they are no longer viable. Through the comparative analysis of a variety of such cases, the aim is to arrive at a common and indispensable genome core (nowadays thought to be around 200 genes, (Moya, 2004; Lazcano, 2004; Oral Comm. Towards the Minimal Cell, Erice Int. School on Complexity, Sicily, 7–10 Dec.)), from which it would be possible to infer the central features of a minimal cellular system capable of Darwinian evolution (i.e., a type of system that should resemble the cenancestor of all living organisms on Earth). When the background conception, instead, is rooted in the idea that minimal living systems form and behave according to a basic, characteristic type of chemical organization (generally coined by the term "metabolism", which would emerge -in its most rudimentary version- before any Darwinian evolutionary process could begin, the natural bias is to tackle the problem of the "minimal cell" from a bottom-up perspective. Researchers like Deamer et al. (2002), Astrobiology 2(4), p. 371] or Luisi et al. (2004), Artificial Life 10(3), p. 297] have been pioneers in this line of work, taking advantage of the self-organizing properties of lipids and amphiphilic molecules to obtain protocellular systems with very interesting properties (e.g., selective permeability, autocatalytic reproduction,?. Then, there is a good number of scientists developing a mixed approach (e.g., (Yomo (Matsuura et al.) 2002, PNAS 99 (11), p. 7514; Szostak (Chen et al.) 2004, Science 305, p. 1474)), in which already-made polymers (typically extracted from real living systems) are combined with self-assembled lipid vesicles, or other synthetic compartments, in order to analyse their interaction, mutual effects, or whether a particular (bio-)chemical reaction occurs under those bounded conditions. The present paper will try to throw some light into this multifarious research area, assessing the different lines of work, particularly with regard to their potential contribution to the problem of the origin of life. According to an alternative conception of minimal life and the process that leads to it (Ruiz-Mirazo et al., 2004, Origs. Life & Evol. Bios. 34, p. 323), I will explain why a strict bottom-up approach is the most adequate way to tackle the in vitro implementation of a minimal self-maintaining and self-producing cell, and why this should be the starting point for any process of origin of life. On these lines, a concrete model will be proposed, based on the interplay between fatty acid vesicles and small peptide chains (channel precursors). However, a single type of cellular system could never develop complete biological properties. The evolutionary capacity of living beings is the result of a historical-collective process in which many generations and diverse types of cellular systems have to take part. Thus, all the knowledge that we could gather from the top-down approaches would be relevant to guide the research beyond that initial stage of cellular proto-metabolisms. But will we ever be ready to bridge such a gap in a lab?

I-23. FUNCTIONAL PHYLOGENY: A CONSISTENT CLASSIFICATION OF ORGANISMS BASED ON TRANSLATION INHIBITION RESPONSE

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During the last two decades, the history of life has been reconstructed from the genetic information contained in extant organisms. The availability of many sequenced genomes has allowed the phylogenetic analysis of gene families and its comparison with traditional single-gene trees. However, the appearance of major discrepancies between both approaches questions whether horizontal gene transfer (HGT) has played a prominent role in shaping the topology of the universal tree. The constancy of the rate of the molecular clock in different genes and organisms has been also questioned, as well as the influences that population size and fixation of mutations with a selective effect have on the divergence of sequences.

Recent attempts at solving these controversies and reaching a consensus tree combine molecular data with additional phylogenetic markers. Among them, some phenotypic properties can be taken into account provided they correspond to universally distributed structures or functions, with clear genetic bases which are independent of environmental effects or growth conditions. Therefore, such features should be good candidates to test evolutionary hypotheses. Translation is a universal cellular function that involves a meaningful, highly conserved set of genes: both rRNA and r-protein operons have an undisputed phylogenetic value and rarely undergo HGT. Ribosomal function reflects the concerted expression of such a genetic network and consequently yields information about the evolutionary paths followed by the organisms. Also, it is possible to quantify the performance of the ribosomes by means of an optimized in vitro assay of protein synthesis inhibition.

We have developed a method to extract most of the information contained in the inhibition curves for thirty-three representative ribosomal systems belonging to the three major cellular lineages, probed against 38 antibiotics that inhibit specific steps of protein synthesis. Different definitions of distance between pairs of organisms have been explored, and the classical algorithm of bootstrap evaluation has been adapted to quantify the reliability of the reconstructions obtained. The analysis returns a consistent phylogeny, where archaea are systematically affiliated to eukarya, in agreement with recent reconstructions which used information-processing systems. Our results reveal the possibility of reconstructing evolutionary relationshsips from the quantification of functions that are subjected to selective processes. The integration of the information derived from relevant functional markers into current phylogenetic reconstructions might facilitate achieving a consensus Tree of Life.

I-24. THE LAST COMMON ANCESTOR: WHAT'S IN A NAME?

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We have analyzed twenty completely sequenced cellular genomes in order to characterize the most conserved protein-encoding ORFs (open reading frames). The resulting set is dominated by different putative ATPases, and by molecules involved in gene expression and RNA metabolism. Transcription and translation genes are as conserved as DEAD-type RNA helicase and enolase genes, which form part of the RNA degradosome. This suggests the early evolution of a control mechanism for gene expression at RNA level, and therefore supports the hypothesis that during early cellular evolution RNA molecules played a more prominent role. Conserved sequences related to metabolic pathways include ORFs encoding putative phosphoribosyl pyrophosphate synthase and thioredoxin, which participate in nucleotide biosynthesis. Although the information contained in the available databases corresponds only to a minor portion of biological diversity, the sequences reported here are likely to be part of an essential and highly conserved pool of proteins common domains to all organisms.

I-26. THE ROLE OF VIRUS IN THE ORIGIN OF DNA GENOME AND EARLY CELLULAR EVOLUTION

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For a long time, most evolutionists who used to consider viruses as by-products of cellular evolution neglected the problem of their origin and the importance of their role in early evolution. In particular, viruses were expelled from the universal tree of life because they lack ribosomes (hence rRNA). These views are rapidly changing as new knowledge about viral biodiversity has accumulated these recent years (Forterre, 2003; Raoult et al., 200X). Striking similarities were detected between viruses infecting cells from different domains (Archaea, Bacteria or Eukarya). These data now suggest that both RNA and DNA viruses predated the appearance of the LUCA (the Last Universal Cellular Ancestor). Viruses thus probably originated in the second age of the RNA world (after the invention of protein synthesis) and were present at the time of the RNA/DNA transition. They possibly evolved from primitive "cells" that were out-competed by the direct ancestors of LUCA (Forterre, 2005). In agreement with their antiquity, the diversity of viral proteins is astonishing: most of them have no homologous cellular proteins in database, and when these homologues exist they are often only very distantly related. It is also now clear that viruses have played and still play an important role in cellular genome evolution through lateral gene transfers. It has been widely assumed for a long time that viruses have picked up some cellular genes, but it is now more and more recognized that the reverse also occurred, i.e. some important cellular proteins could have a viral origin. For instance, it is now clearly established that the ancestral bacterial replication and transcription systems have been replaced by a new one of viral origin in the evolution from alpha-proteobacteria to mitochondria (Filee et al., 2003). I will discuss recent hypotheses suggesting that viruses have played critical roles in the origin of DNA genomes (Forterre, 2002; Bell, 2001). It has been postulated that DNA itself, as well as the eukaryotic nucleus, could have a viral origin. These hypotheses could solve some puzzling questions raised by comparative genomic analyses, such as the existence of non homologous DNA replication proteins in Bacteria, Archaea and Eukarya (Forterre et al., 2005). The viral origin of DNA implies that DNA and/or DNA replication mechanisms have been transferred from viruses to cells at early stages in cellular evolution. Several scenarios can be proposed depending of the number and timing of such transfer (Forterre et al., 2005). I will elaborate a recent hypothesis suggesting that three different transfers could be at the origin of the three cellular domains (Forterre, 2005).

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I-28. MEDIATION OF EARLY MICROBIAL EVOLUTION AND ECOLOGY BY CYANIDE INHIBITION?

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HCN has long been held as an important precursor molecule of life. It has been implicated in the prebiotic synthesis of important biomolecules like nucleic bases and amino acids. It is one of the principal initial products of a Miller-Urey spark discharge experiment and is formed in other similar prebiotic reactions using highly reduced atmospheres. It would also be formed in less reduced atmospheres containing CH_4 through a photochemical process (Zahnle, 1986). Presently, there is some uncertainty and changing views about the composition of the early atmosphere. Together, the early-reduced mantle, the importance of serpentinization, and newly-discovered inefficient hydrogen escape inherent to an anoxic atmosphere provide means by which the early environment may have had significant CH_4 and/or H_2 abundance. If both high CH_4 and H_2 concentrations lead to significant HCN concentrations, perhaps HCN production could have approached the limit imposed by the production of N atoms in the upper atmosphere. Almost paradoxically, cyanide is highly toxic to a diversity of metabolisms. Cyanide inhibition of O_2-dependent respiration is based on one molecule of cyanide binding to each copy of the enzyme cytochrome oxidase. Although the details appear to differ, other heme-containing enzymes, such as horseradish peroxidase, are also inhibited by binding of cyanide. Not surprisingly, cyanide also binds to other metalloenzymes including molyboenzymes such as nitrogenase, and enzymes containing zinc or copper, such as superoxide dismutase. The Ni-Fe-S containing enzyme carbon monoxide dehydrogenase (CODH) is also inhibited by cyanide (Ensign et al., 1989; Abbanat and Ferry, 1990; Smith et al., 1992; Anderson and Lindahl, 1994). Interestingly, the sensitivity of CODH to inhibition by cyanide varies, depending on the type of CODH and the particular reaction that it is catalyzing. Almost all known CODH enzymes are highly sensitive to cyanide, for example, when it is acting to oxidize CO to CO_2, 50% inhibition is achieved by 10 ?M cyanide. CODH is a key enzyme in methanogenesis. Because of the scarcity of oxidized inorganic substrates prior to the evolution of oxygenic photosynthesis, the most plausible microbial metabolisms to have been present in the last common ancestor of the Archaea are methanogenesis based on CO_2 and H_2, sulfur reduction using H_2, and possibly Fe-reduction (Vargas et al., 1998). The plausibility of sulfur-reduction as an early metabolism is bolstered by the fact that sulfur isotopes from Archean rocks definitively indicate through their mass-independent signatures that elemental sulfur was being deposited from the atmosphere and being reduced to sulfide (Farquhar et al., 2001; Pavlov et al., 2002; Ono et al., 2003). Recent genomic results suggest that the last common ancestor of the Archaea was not a methanogen and that methanogenesis arose later during subsequent microbial evolution (House et al., 2003). This leaves sulfur/Fe-reduction as the most geochemically plausible metabolisms for the base of the archaeal crown group. Phylogenetic results do not offer any suggestion as to why sulfur- reduction would arise before methanogenesis. The apparent delay in the early evolution of methanogens is hard to explain given that geochemically methanogenesis requires only hydrogen and carbon dioxide or simple organic compounds (methanol, methyl-amine, etc). Given the results of whole-genome tree building, the apparent sensitivity of methanogensis to cyanide inhibition, evidence for ancient atmospheric sulfur deposition, and the prospects of significant prebiotic cyanide, a novel hypothesis emerges: Did early Earth cyanide concentrations preclude methanogenesis, while allowing for the evolution of sulfur-reduction? Furthermore, considering that atmospheric CH_4 results in HCN production and that methanogensis is sensitive to cyanide, the following second question is apparent: In a world of global methanogenesis, would HCN moderate microbial ecology?

I-29. THREE-DIMENSIONAL OPTICAL AND MOLECULAR-STRUCTURAL IMAGERY OF PRECAMBRIAN MICROSCOPIC FOSSILS

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Throughout biologic history, microbe-level life has been ubiquitous, abundant, metabolically diverse, and for the earliest (Precambrian) seven-eighths of geological time, biotically predominant. Understanding of this earliest stage of biologic development has progressed markedly in past decades, but problems of interpreting the preserved fossil record still remain. Perhaps foremost among such problems is the difficulty of unambiguously distinguishing true microbial biologic remnants from nonbiologic (e.g., mineralic) look-alikes. This problem can be addressed by demonstrating in objects claimed to be microscopic fossils a one-to-one correlation, in three dimensions and at a micron scale, of preservable "biological morphology" with geochemically altered "biological chemistry." Two non-destructive, non-intrusive techniques, both new to paleobiology, meet this need: (1)

Confocal laser optical microscopy provides means to image in three dimensions the visible characteristics of organic-walled microscopic fossils *in situ*; and (2) Laser-Raman spectroscopic imagery provides means to map, in situ and in three dimensions, the distribution of the carbonaceous matter that comprises such fossils. Used in tandem, these techniques for the first time provide means to assess the optically discernable cellular morphology and chemical-structural composition of ancient fossil microbes, a major breakthrough in Precambrian paleobiology of obvious relevance to the deciphering of the earliest fossil evidences of life on Earth.

I-33. LITHOPANSPERMIA, A MODE OF NATURAL DISTRIBUTION OF LIFE IN THE SOLAR SYSTEM?

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The hypothesis of lithopanspermia suggests that the impact of a huge meteorite on a planet may expel microbe-bearing rocks and accelerate them to escape velocities, thereby providing a natural transport vehicle for microbes to travel between the terrestrial planets of our solar system. In order to survive such a scenario, endolithic microbial communities have to cope with three major steps: (i) escape from the planet, (ii) journey through space over extended time periods, and (iii) landing on another planet. We have provided experimental proof that, depending on the environmental conditions, resistant microorganisms may survive the first two steps of this scenario. The most plausible process capable of ejecting microbe-bearing surface material from a planet or moon into space is the hypervelocity impact of a large object, such as an asteroid or comet, under strong or moderate shock metamorphism of the ejected rock fragments. Although the shock pressure generally leads to localized melting in the ejected rocks, solid rock fragments from the uppermost layer of the target can be accelerated to very high velocities (e.g., >5 km/s) due to a spallation effect. Microorganisms, subjected to such a simulated meteorite impact, e.g., by use of shock recovery experiments with an explosive set-up, survived shock pressures in the range indicated by the Martian meteorites and which can be assumed to hold also for “Earth” meteorites. Once rocks have been ejected from the surface of their home planet, microbial passengers have to cope with an entirely new set of problems affecting their survival, namely exposure to the space environment. The responses of spores of Bacillus subtilis to parameters of space and potential protection mechanisms were studied during different space missions and at space simulation facilities in the laboratory. The following results were obtained: (i) Effects of space vacuum: although 70% of the spores survived extended periods of time (up to 6 years) in space vacuum, genetic changes occurred, such as increased mutation rates characterized by mutational hot spots, and an increased UV sensitivity probably caused by specific less repairable photoproducts in their DNA. (ii) Effects of solar UV radiation: inactivation of the spores by extraterrestrial solar UV radiation was three orders of magnitude more effective than by the UV on Earth; action spectroscopy showed the high effectiveness of UV-C radiation indicating the DNA as the sensitive target; shielding by a thin layer of meteorite dust provided substantial protection of the spores against UV radiation and nearly all spores survived 14 days in space within an "artificial meteorite" of 1 cm thickness; (iii) Effects of galactic cosmic radiation: damage by protons or heavy ions of cosmic radiation were not observed in space experiments unless the path of single heavy ions was traced back into the bacterial layer; from the data it was calculated that spores could escape a hit of a cosmic heavy ion (e.g. iron ion) for up to 1 Ma. It can be concluded that bacterial spores could survive a journey from one planet to another in our solar system for substantial periods of time if they are located inside a meteorite thus shielded against UV and cosmic radiation. More space experiments with different endolithic microorganisms in their natural habitat are under development using the space exposure facility EXPOSE of the European Space Agency ESA on board of the International Space Station ISS.

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I-34. SEARCHING FOR A SECOND GENESIS OF LIFE: WHY, WHERE, HOW

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In addition to its immense cultural and societal appeal, the discovery of a second genesis of life on another celestial body, thus demonstrating the ubiquity of life, would be strong support for the simplicity of the processes involved in the emergence of life. Although primitive life is expected to have been rather simple because it appeared when the Earth was under constant bombardment, such simple processes have not yet been reproduced in the laboratory. More than just a societal wish, the discovery of a second independent genesis of life on a celestial body is a scientific need for the origin of life studies, demonstrating that life is not a magic one-shot process but a rather common phenomenon, offering a real chance of being reproduced in a test tube. It is commonly agreed that terrestrial life arose in liquid water by the processing of organic molecules. Some organic molecules required for the appearance of life might have been produced in the primitive atmosphere or in hydrothermal systems (Holm and Charlou, 2001) but the largest fraction probably came from space, transported by micrometeorites. The chemical continuum running from the interstellar medium (ISM) to the terrestrial oceans via comets has been supported by experiments, i.e. laboratory simulation of ISM chemistry (Munoz Caro et al., 2002) and space experiments in Earth orbit (Boillot et al., 2002; Brack et al., 2002). As a consequence, any celestial body harboring permanent surficial oceans, and thus an atmosphere, acquires extraplanetary organics that are deccelerated by the atmosphere and that might eventually give rise to living entities, as in the scenario for early Mars. This would also be the case for a celestial body possessing a buried ocean with submarine volcanism, for example Europa. Saturn's moon Titan hosts liquid methane and very active organic chemical processes taking place in the atmosphere. This chemistry probably produces asymmetric hydrocarbons. More than 10 chiral hydrocarbons ranging from 3 to 7 carbon atoms can be foreseen with molecular weights lower than 100 Dalton. Racemic mixtures could conceivably spontaneously resolve in one-handed conglomerates or in open systems. At a later stage, these homochiral molecules might initiate an exotic carbon-based life in methane. On January 14, 2005, the Huygens probe penetrated the atmosphere and systematically analysed the organic chemistry in Titan's geofluid. For 150 minutes, in situ measurements were made of the organics present in the air, in the aerosols and at the surface. Unfortunately, no instrument was implemented to measure the handedness of the organic molecules.

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I-35. ASTROBIOLOGY AND THE EXPLORATION OF GUSEV CRATER BY THE MARS EXPLORATION ROVER SPIRIT

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We assess the availability of nutrient elements, energy and liquid water on the plains surrounding Columbia Memorial Station by evaluating data from Spirit in the context of previous Mars missions, Earth-based studies of martian meteorites and studies of microbial communities on Earth that represent potential analogs of martian biota. The compositions of Gusev basalts resemble those of olivine basalts beneath the seabed on Earth that deep drilling has shown to support life. Of particular relevance to biology, phosphate abundances are much greater in Gusev basalts ($0.84 + 0.07$ wt.% P_2O_5) than in oceanic basalts (typically 0.06 wt.%). Habitable environments must provide, at least intermittently, sources of energy to fuel metabolism and self-replication, and repair cellular constituents. Within Gusev crater, impacts and aeolian activity have reworked ancient basalts in a surface environment that has been dominated by dry and desiccating conditions for billions of years. In the absence of light, chemoautotrophic microorganisms can exploit oxidation-reduction reactions (e.g., of Fe^{2+}, Mn^{2+} and S species) to obtain energy. These reduced species and their oxidized alteration products have been documented in martian meteorites. On Earth, subsurface communities dominated by methanogenic archea obtain their energy and reducing power from H_2 and CO_2 generated by hydrothermal activity. The aqueous alteration of ultramafic rocks produces H_2, a near-universal source of energy and reducing power for microorganisms. Martian igneous rocks exhibit a broad range of silica and olivine abundances that broadly overlap compositions of mafic and ultramafic rocks on Earth, including rocks that have been shown to sustain subsurface microbial communities. Three Gusev basalts have olivine abundances that lie near middle of this range of abundances. Gusev basalts also contain magnetite and show evidence of at least limited chemical alteration. Although magnetite can occur solely from igneous processes, it also might indicate that olivine was altered to form serpentine, magnetite and H_2. The minimum water activity that is necessary to sustain microbial processes is $\sim$0.75 for haloarchea in NaCl brines and $\sim$0.61 for fungi in high sugar media (distilled water has an activity of 1.00). Evidence for the former presence of liquid water has emerged from analyses of materials in the basaltic plains. Laguna Hollow is a shallow impact crater that has been filled relatively recently with fine-grained deposits. A trench revealed a mixture of silicate and soluble salt constituents that are uniform with depth. Percolating water would have preferentially mobilized soluble salts and created abundance variations with depth. Habitable conditions very likely never developed within this fill since it and perhaps other such deposits were emplaced in Gusev. Spirit excavated two trenches ("Big Hole" and "The Boroughs") in

flat terrane that was remote from larger craters and thus developed over longer periods than soils in ejecta blankets and small impact-generated hollows. Abundances of S, Mg, Cl and Br varied with depth in these trenches, indicating that water probably percolated through these soils. Given the great age inferred for the Gusev plains landscape, these basalts might have formed 108 to109 years ago. Water might have weathered rock surfaces and deposited minerals in vugs and cracks. But the bulk elemental abundances of these rocks resemble those of unaltered olivine basalts. Thus water/rock values were low, fluid movements were minor, thus it seems unlikely that these rock interiors could have sustained life. A few rocks on the Gusev plains exhibited exfoliation and case hardening, features indicating extensive chemical alteration. The compositions of these rocks were not determined because they were found in images retrieved from Spirit after it had departed the area. The dry and cold climate of Mars is due in part to the planet's current obliquity of 25.19°. This is far from 41.80°, which the most probable value over the long term. Dramatic increases in summer insolation can create dynamical instabilities in the polar caps that can drive atmospheric humidity levels to as much as 50 times the present level. Quick disappearance of polar caps over some obliquity cycles can create surface ice in equatorial areas. During earlier periods when the obliquity of Mars was high, basal melting of snow/ice deposits might have recharged subsurface aquifers in Gusev crater. Also, transient increases in atmospheric density associated with large, sustained volcanic eruptions may have permitted liquid water to be stable near the surface. Aquifers that were periodically recharged might have sustained habitable conditions for geologically long periods of time. Because mafic and ultramafic terrains exhibit the potential to sustain chemosynthetic microorganisms in subsurface environments, these terrains merit closer scrutiny in future orbital and landed missions.

I-36. A NEW ASTROBIOLOGICAL VISION OF TITAN FROM THE CASSINI-HUYGENS DATA

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Titan, the largest satellite of Saturn and the only satellite in the solar system having a dense atmosphere, is one of the key planetary bodies for astrobiological studies, due to: the potential presence of a water ocean in its internal structure its many analogies with planet Earth, in spite of much lower temperatures the presence already well observed of an active organic chemistry, involving several of the key compounds of prebiotic chemistry.

Since the insertion of the Cassini spacecraft in the Saturn system, on July 1rst, 2004, the Cassini-Huygens NASA-ESA mission has already started to provide a tremendous amount of scientific data of fantastic interest, in particular from an astrobiological point of view. The 14th of January 2005, the Huygens probe entered the atmosphere of Titan. Thanks to its six scientific instruments, it was able to carry out a detailed in situ analysis of this environment during the 2.5 hours of descent, and more than one hour after it landed, safely, on Titan's surface.

All instruments have provided precious and numerous information on the atmosphere and surface of Titan.

DISR (Descent Imager/Spectral Radiometer): imaging in the visible and near IR, physical properties of clouds and aerosols, and surface.

HASI (Huygens Atmospheric Structure Instrument): pressure and temperature vertical profiles, electric charges measurement.

GCMS (Gas Chromatograph Mass Spectrometer): atmospheric gas phase composition, isotopic measurements, analysis of ACP samples, surface measurements.

ACP (Aerosol Collector & Pyrolyzer): collect and thermal analysis (up to pyrolysis temperatures) of atmospheric aerosols.

SSP (Surface Science Package): physical state and properties of Titan surface.

Some of the obtained – still very preliminary – data will be presented. The astrobiological consequences of these new data will be presented and discussed.

I-37. SOME PHILOSOPHICAL REMARKS CONCERNING THE ORIGIN OF LIFE

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Any origin of life research program will presuppose certain physical and chemical forms of order or organization. Order can be created either in the form of energetically conservative structures or in far from equilibrium (FFE) conditions (the so-called "dissipative structures"). Now, how to understand the enormous gap in terms of complexity between the physical or chemical systems and the biological world? Researchers have proposed two explanatory principles or mechanisms that would give account of the OL process: self-organization and self-replication. But there is not consensus concerning the role played by each neither of them, nor by their relations. Next I will present some considerations about this subject. (1) Self-organization. By SO we mean a FFE organization where local non-linear interactions between components generate a global (holistic) ordered dynamic structure, which is maintained through a certain number of constraints of which at least some of them are generated by the global dynamics. But for our purpose we have to consider a more elaborated form of SO that concerns recursive component production systems. A RCPS is a dissipative self-maintaining collection of elements that is established and that persists largely because of the rates of their combination. Certain autocatalytic systems fulfill this condition: self-maintenance is linked to the generation of a set of new components whose preservation is bounded to the global recursivity of their production relations. The system is self-maintaining because of the recursive and holistic form of its organization: the global dynamics is necessary for the maintenance of (many of) the reactions of the system and all the reactions are in turn necessary to the maintenance of the whole system. Obviously, this form of order requires a continuous flow of energy and is hence dissipative. However, the role played by most of these components is also related to their specific shape and composition (which in many cases, once created, is a conservative property). The production of new molecular variety in turn, can modify the whole organization, and this new organization can bring about new molecules, which may recursively produce new forms of organization. The generation of a wide variety of (increasingly complex) components that can act as selective constraints in the maintenance of the whole organization also increases its functional complexity. Accordingly, in a self-maintaining chemical organization there is an increase in complexity if it makes a contribution to the maintenance of the very organization. (2) Self-replication. By SR we mean the production of certain structures whose particular shape and material composition drives a recursive template-like process of replication. In SR the principle of order is the target structure of the replicating element. However, only SR of modular templates is interesting for OL. By this form of SR we mean a template of a complex modular structure whose replication is dependent of its particular shape and material composition, but not of the specific linear order of its modular sequence. The appearance of this form of SR before the existence of self-maintaining organizations is controversial (because such process seems to be aided by a set of other components) but what is clear is that, as a mechanism for increasing the complexity of prebiotic systems, modular SR requires (a population of) self-maintaining organizations. Now in this scenario, the appearance of self-replicating modular templates embedded in self-maintaining organizations constitutes a powerful mechanism for the (instructed) production of new functional components, because SR permits the exploration of a potentially huge sequence space that, thanks to the existence of a self-maintaining organization frame, can be matched with an also unlimited space of functions. As a consequence, self-replicating modular templates can take over the maintenance of the whole organization, leading to (a) a reliable reproduction of the whole organization in which they appeared; and (b) linking two organizational dimensions: the level of self-maintaining dissipative organizations and the level of selective survival at the historic and collective dimension. From here on a new powerful mechanism (Darwinian evolution) will also drive a new self-sustaining process, capable to an unlimited/open-ended increase of complexity. This process is based on a two dimensional organization: on the one hand, the individual capacity of self-maintenance and on the other, the historic-collective capacity to evolve.The invention of such organization occurred through a long-term process including different steps. During this process each new form of organization erases those previous forms of organization that brought them forth. Hence, the OL is a set of reversible, self-erasing increasingly complex organizational steps leading to a ratchet-like form of organization that is able to increase its complexity only by preserving its basic form. However, once the first form of living organization appeared, not only it will be preserved, but also becomes the condition of possibility for any further and more complex organizational steps. Therefore the invention of the basic living organization was qualitatively different from any other precedent invention in terms of long-term preservation, regardless the eventual increases of complexity. Last – but not least – such almost sudden and huge increase in functional complexity (complexity devoted to its own preservation and propagation) is what confers an intrinsic value on life.

I-38. CATHOLIC CRITICS OF EARLY SYNTHETIC BIOLOGY EXPERIMENTS: AGOSTINI GEMELLI, JAUME PUJIULA AND JEAN MAUMUS

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Historically different approaches of accepting evolutionism and facing the problem of the origin of life can be considered. As John Farley argued, cultural factors were significant in the diverse ways German, British or French reacted to the problem of life emergence in an evolutionary context. We could classify the positions taken by different authors on the causes of life origin in: (i) life is eternal, an inherent property of matter, and comes from the outer space (e.g. Arrhenius' panspermia), (ii) life emerged by natural physicochemical processes in a remote past (either by some special kind of spontaneous generation – Haeckel– or as the result of chemical evolution – Oparin) or (iii) supranatural forces created life. Catholic authors (notably Pasteur considering, in his opinon, the absurdity of a "Dieux inutile") claimed that God was an obligatory actor in the origin of life, even in an evolutionary general framework. In this work we review the writings of three scientists and Catholic priests at the beginning of 20th century, from three European Catholic countries (Italy, Spain and France), that passionately discussed and criticized early experiments on synthetic biology, specially the work of the French biophysicist Stéphane Leduc and the Mexican biologist Alfonso L. Herrera. Agostino Gemelli (Milano, 1878; Milano, 1959) did the doctoral studies under the supervision of Camilo Golgi and became a famous psychologist and the founder of the Catholic University in Milano. In "L'enigma della vita e i nuovi orizzonti della biologia" (Firenze, 1910), Gemelli argues at length against any materialistic approach to the study of life. Jaume Pujiula (Besalú, 1869; Barcelona, 1958) performed his doctoral research in Germany; he was a remarkable embryologist and author of many textbooks on biology. He collected several lectures given on evolution, all in all they were essentially an inflexible criticism against the Haeckelian views (monism): “conferencias biológicas. Estudios críticos sobre la teoría de la evolución” (Barcelona, 1910) and “La vida y su evolución filogenética” (Barcelona, 1914). Jean Maumus (Lassalles 1860; Paris, 1930) had a doctorate in medicine and another in science. He exercised the medical assistance at the Pasteur Hospital. Furthermore, he published several works on the impossibility of the spontaneous generation of microorganisms and a two-volume book on the structure, function and origin of cells: “La cellule. Son origine, sa vie, sa mort” (Paris, 1912, 1914). All three authors have in common the use of Pasteur’s experiments on spontaneous generation to argue against a natural origin of life, neither in extant laboratory conditions or a distant past. All three also center their strict censure and unappealable condemn on the works of Leduc on the synthesis of biological-like forms and Herrera’s plasmogeny, to conclude that in neither case they were chemically synthesizing artificial life forms but only mere structures with an apparent similitude to it. All of them adopted a vitalistic position considering that life has an essentially different nature compared to inert matter. Only a Divine action could explain the enigmatic origin of such an extremely complex and purposeful objects as living cells. Acknowledgements: This work is funded by MECD, Spain (BHA2003-04414-C03-02).

I-39. AN EPISTEMOLOGICAL SYNTHESIS CONCERNING THE STATUS OF PREBIOTIC EXPERIMENTS IN 20TH CENTURY STUDIES OF THE ORIGINS OF LIFE

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When considering the study of the origins of life, the middle of the XXth century is characterized by the beginning of prebiotic experiments. After a short historical examination of the main experiments, we will study several aspects of the epistemological status of this particular scientific approach. Firstly, we will concentrate on the historical aspect of the origins of life itself. The lack of paleontological records concerning the first stage of the origins of life gives prebiotic experiments a special role. If these experiments are a tool to be used for the study of the origins of life as a historical problem, then we have to understand their particular epistemological status. Secondly, it seems important to examine prebiotic experiments from an epistemological point of view, focusing on the evolution of reductionist ideas versus emergentist concepts. By connecting these two points we are finally able to characterise the specific epistemological status of studies on the origins of life.

O-1. THE REDUCTION OF NITROGEN TO AMMONIA BY FERROUS HYDROXIDE

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Because of the minor presence of reduced carbon and ammonia on present models of the primitive earth, the importance of reducing agents for carbon dioxide and nitrogen to supply the crucial ingredients for the chemical origin of life has become paramount. It is known that ferrous ion was prevalent in the early oceans and that it is a powerful reducing agent near neutral pH. Hydrogen is formed both thermally and photochemically under these conditions (Borowska and Mauzerall, Origins of Life, 17:251–259, 1987). We have been trying for some time to obtain quantitative evidence for the reduction of N_2 by $Fe(OH)_2$ but have been plagued by irreproducibility of results. Aside from the large number of sources of contamination by NH_3, we have found that the thermal reaction is more reproducible if the oxygen level is far below 1 ppm and/or a small amount of hydrogen is present. Whereas the H_2 formation does not require such strictly anaerobic conditions, the complex reactions leading to the formation of NH_3 seem to require an absolute minimum of O_2. It is quite possible that these conditions were met in the primitive oceans.

O-2. REMNANTS OF EARLY ARCHEAN (CIRCA 3.5 GA) SEAWATER IN BIF FROM CAOZHUANG FORMATION, QIAN'AN COUNTY, HEBEI PROVINCE, NORTH CHINA

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Fluid inclusions containing high-density CO_2 and saline water have been found in undeformed BIF from Caozhuang Formation at Qian'an County, Hebei Province, North China. In the silicate of BIF, there are several types of inclusions. One type is two-phase aqueous inclusions, and their sizes range from 3 to 18 μm. Their T_h (to liquid) are variable, in the 115 °C–326 °C. The NaCl equivalent salinity of aqueous inclusion are from 4.3 wt.% to 9.7 wt.%, and average salinity is 5.9%. (except one date of 1.22%). Another type is two-phase high-density CO_2-bearing inclusions at room temperature, containing relatively pure CO_2 component (T_m between -56.4 to -57.8 °C,and T_h between -13.9 °C to -20.7 °C), their sizes range from 6–10 μm. Even below -100 to -190 °C, a few inclusions are not frozen. This implies that the gases of some inclusions are very complex, including N_2 and/ or other gas, even perhaps long-chain hydrocarbon. There also are a lot of late, crossing-cutting, very small two-phase aqueous inclusions and a few monophase aqueous inclusions; no salinity or T_h date available for these inclusions due to their small size.

O-4. INVESTIGATION OF INTERACTIONS BETWEEN CYCLIC TRIRIBONUCLEOTIDES AND ALPHA-AMINO ACIDS

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Some studies carried out by the Ferris group (Ferris, J. P. et al.: 1999, Origins Life Evol. Biosphere 29, 563–591) showed that, under primitive earth reaction conditions, oligomerisation of activated 5′mononucleotides gives a high yield of cyclic triribonucleotides with a preference for 3′5′phosphate linkages. More recently, results obtained by our team (see A. Parkes’s work) on the reaction between 3′nucleotides and NCAs (amino acid N-carboxy anhydrides) have revealed that aminoacylation of the phosphate is followed by transfer of the aminoacyl-group to the 2′position giving a 2′aminoacyl-nucleotide. Considering these interesting results, we have investigated the synthesis of 3′5′phosphate linked cyclic trimers, of general structure CCN (C=cytidine, N=cytidine, uridine, adenine or guanine), and their possible reaction with different amino acids to give linear 2′aminoacyl-RNA trimers, considered as plausible prebiotic intermediates for coupled RNA and coded proteins synthesis (Borsenberger V. et al.: 2004; Chemistry & Biodiversity 1, 203–243). After a conventional solution-phase synthesis of the four 18-membered rings CCN trimers, we have followed, by NMR monitoring, their reaction with various amino acids and derivatives.

O-5. CHEMICAL CHAOS ON PRIMITIVE EARTH LEADING TO THE BIOLOGICAL EVOLUTION

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The origin of cellular life must have been a process of self-assembly on the basis of chemical chaos on the primitive earth, evolving farther and farther apart from the equilibrium. Ignorance of this dogma makes it impossible to integrate various theories and observations in this field to achieve a basic consensus. Therefore, we have tried to orchestrate several diversified theories and empirical works into two successive chemical chaotic phases:

(1) *The chaotic phases of prebiotic chemistry*. The new avenue of prebiotic chemistry for the study of the origin of life opened by Miller (1953) has led to an unexpected difficulty, namely all synthetic routes from prebiotic chemistry view are different from those from the compa- rative biochemistry view (Lazcano and Miller, 1999). Yet, this situation is not unexpected since the wide spectrum of compounds discovered by Miller was by no means a collection of products of linear reactions. Rather, the miracle he first discovered was the consequence of some kind of chemical chaos, mimicking the scenario on the primitive Earth. Furthermore, such non-contingence might have implied two discontinuous phases, existing in primitive air-water system, namely the **sink phase** of vectorial biochemical pathways arising from the **source phase** of random chemical reactions where racemates prevailed. Being not only the **substrate** of models of a few comparative chemistry, but also the **end product** of a model of prebiotic chemistry, **pyruvate** must have played a key role in channeling compounds from the source phase into the sink phase. If so, the metabolic pathways and the metabolite of biochirality might have coevolved, and the next phase would have thus started.

(2) *The chaotic phase of biochemistry*. Eigen et al. (1981) first describe the oscillating and chaotic nature of this phase with their Hypercycle Theory, suggesting the co-evolution of the RNA gene and encoded protein (enzyme). Zhao et al. (1996) demonstrated for the first time a model for the co-evolution of protein and nucleic acid with an self-assembly system of N-phosphoryl amino acids. their follow-up works further showed that this system could also constitute an in vitro oscillating and chaotic biochemical system, providing basis for genetic codons to come. In addition to protein and nucleic acid, this self-assemble system has produced or would be able to produce most elements or cofactors necessary for the emergence of the genetic codon, depending on the ingredients of reaction medium, enzymatic oligopeptides, and conjugates of amino acids and nucleotides etc, as many authors assumed. The possibility of co-evolution of codon strands (ORF) and coded polypeptide at the end of this phase has been discussed. (see another abstract: Synchronous Origination of Codon Strands and Coded Peptides).

O-7. RNA EVOLUTION BY RECOMBINATION AND SELECTION

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Ribo-organisms in an “RNA World” would have required the ability to evolve new RNA functions in response to changing environmental conditions. Theoretically it is possible that recombination of RNA fragments could have quickly led to the emergence of complicated new RNAs by rearrangement of RNA sequence found within a pre-existing RNA genome (Gilbert and Souza, 1999; Leman, 2003). This hypothesis is consistent with the finding that many natural and artificially selected ribozymes (catalytic RNAs) consist of modular structures. This modularity separates regions of sequence that are essential for function from flanking regions that are required to form a continuous strand of RNA sequence. Thus in many respects the motif elements of a ribozyme resemble the exon regions of an unspliced mRNA separated by the connecting and less important intron regions. Our recent findings suggest that nonhomologous recombination is a highly efficient way to define these intron-exon ribozyme motif boundaries (Wang and Unrau, 2005). In vitro selection from pools with long random sequences often results in motif elements interspersed within regions of extraneous linking sequences (Sabeti et al., 1997). Therefore, we deliberately constructed a population of RNA molecules consisting of randomly recombined fragments of a 271 nucleotide (nt) long pyrimidine synthase ribozyme, which was obtained from a previous in vitro selection (Unrau and Bartel, 1998). This recombined pool, which consists of approximately 10 to the power of 8 scrambled RNA variants, was then subjected to in vitro selection and quickly resulted in the isolation of a diverse size range of ribozyme variants that were as active as their much longer progenitor. The shortest ribozyme, only 81 nt long, consisted of four regions of sequence that was conserved by all of the truncated active variants and therefore clearly represents the core motif sequence. To further explore the mechanism of recombination in generating new functional ribozymes, we are using the same recombination methodology to construct a pool derived from several different ribozymes. We hope in the near future that we can isolate ribozymes from this population with activities Not found in any of the input sequences. This would provide the first clear evidence of the role that recombination might have played early in the evolution of RNA-based systems.

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O-8. THE ORIGIN AND EARLY EVOLUTION OF MEMBRANE PROTEINS

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Membrane proteins mediate functions that are essential to all cells. These functions include transport of ions, nutrients and waste products across cell walls, capture of energy and its transduction into the form usable in chemical reactions, transmission of environmental signals to the interior of the cell, cellular growth and cell volume regulation. In the absence of membrane proteins, ancestors of cell (protocells), would have had only very limited capabilities to communicate with their environment. Thus, it is not surprising that membrane proteins are quite common even in simplest prokaryotic cells. Considering that contemporary membrane channels are large and complex, both structurally and functionally, a question arises how their presumably much simpler ancestors could have emerged, perform functions and diversify in early protobiological evolution. Remarkably, despite their overall complexity, structural motifs in membrane proteins are quite simple, with a-helices being most common. This suggests that these proteins might have evolved from simple building blocks. To explain how these blocks could have organized into functional structures, we performed large-scale, accurate computer simulations of folding peptides at a water-membrane interface, their insertion into the membrane, self-assembly into higher-order structures and function. The results of these simulations, combined with analysis of structural and functional experimental data led to the first integrated view of the origin and early evolution of membrane proteins. We have shown that peptides with the amino acid sequence such that they can form a-helices, in which hydrophobic and hydrophilic residues are located at opposite faces readily fold at water-membrane interface. Such peptides are called amphiphatic and are quite common among small membrane proteins in contemporary cells. The match between the polarities of the peptide and its environment renders the amphiphatic helices particularly stable. The specific identity of amino acids appears to be less important. This is a desirable protobiological property because neither a precise protein synthesis mechanism nor the full suite of amino acids was required for the formation of amphiphatic helices. Considering that these helices had to fulfill only very modest sequence constraints, their presence in the protocellular environment should not have been rare. The peptides folded at the interface could have become inserted into the membrane such that they spanned the lipid bilayer. While the insertion of an a-helix into a membrane is unfavorable, stability can be regained by specific recognition and association of peptides into larger assemblies. Examples of such assemblies are associations of 4 to 7 a-helices

into ion-transporting channels. In contrast to folding and insertion, this process is strongly sequence-dependent. In fact, the ability to associate was probably one of the selection mechanisms operating on protocellular transmebrane peptides. We argue that the transport of solute species, especially ions, required an early evolution of efficient transport mechanisms, and that the emergence of simple ion channels was protobiologically plausible. We also argue that, despite their simple structure, such channels could possess properties that, at the first sight, appear to require markedly larger complexity. One example that will be discussed is a 25-amino acid fragment of the M2 protein of the influenza virus, which forms a tetrameric channel capable of efficient and selective transport of protons. Another example is a 16-residue peptaibol, antiamoebin, which is a simple structural analog to voltage-gated potassium channel, KvAP. Properties of these simple proteins can be subtly modulated by local modifications to the sequence rather than global changes in molecular architecture. This is a convenient evolutionary solution because it does not require imposing conditions on the whole amino acid sequence. In order to address the evolution and development of transmembrane ion channels, we identified protein domains that are commonly associated with ion channel proteins and are conserved throughout the three main domains of life. We argue that these domains have sufficiently universal architectures that they can readily adapt to the diverse functional demands arising during evolution. This work was supported by the NASA Exobiology Program.

O-9. NUCLEOTIDE-LIKE COENZYMES IN THE FORMATION OF PRIMITIVE METABOLIC SYSTEMS

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Nucleotides and structurally close coenzymes such as the derivatives of pteridine (pterins and folates), isoalloxasine (flavins) and nicotinamide (NAD and NADP) are inalienable components of organismic biocatalytic system of any cell and their absence makes impossible the functioning of basic segments of metabolism which include electron, hydrogen and group transfer reactions. In addition, some of these compounds (flavins and pterins) function in organisms as photosensor chromophores in several groups of photoreceptor proteins. According to results of chemical modeling of abiotic processes, including the research performed in our laboratory, we may believe that these compounds, first of all, their main functional unit–nitrogen -containing heterocycles? were available in prebiological era. In connection with the problem of reconstruction of primitive metabolic systems we carry out experimental study of abiogenesis of pterin and flavin coenzymes as well as their physicochemical, catalytic and, especially, photochemical properties. 1. We perform chemical modeling of abiogenic formation of coenzymes and their conjugates with amino acid and nucleotide polymers. The synthesis of covalent oligonucleotide-coenzyme conjugates and the analysis of their properties is of particular interest for understanding of the RNA origin and a manifestation of its catalytic functions at early stages of evolution. 2. The investigation of photochemical properties of pterin and flavin coenzymes has permitted us to use these compounds including the abiotically synthesized species, to construct efficient functional models of the systems capable to conserve photon energy in reduced metabolites as well as in the energy rich bonds of ATP. 3. The analysis of photochemical properties of coenzymes allows in some cases to answer the question: what properties of the molecule have influenced its selection to perform the function in modern organism. As an example, we will discuss what factors could favor a selection of 5,10-methenyltetrahydrofolate to play a role of light-harvesting antenna in molecules of photoenzyme DNA-photolyase and photoreceptor cryptochrome. Supported by The Program of the Presidium of Russian Academy of Sciences "The Emergence of Biosphere and its Evolution" and Russian Foundation for Basic Research Grant 04-04-49625.

O-10. ORIGIN AND EVOLUTION OF PHOTOSYNTHETIC REACTION CENTER II (PSII) SUBUNIT PROTEINS: EVOLUTIONARY KINSHIP TO ANIMAL OPSINS AND FUNGAL-BACTERIAL OPSINS

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Photosynthetic reaction centers I (PSII) proteins and II (PSII) proteins are key elements of contemporary photosynthetic systems not only in Cyanobacteria and plant chloroplasts, but also in photosynthetic rhodobacteria (Rhodobacter, Rhodopsedomonas, etc.). In order to find the origins of these elements, homologues of PSI and PSII subunits from green plants and those of rhodobacterial PSII proteins (PSII M and L subunits in Rhodobacter/Rhopseudomonas and PSII D1 and D2 subunits in Cyanobacteria/Chloroplasts) were searched for in protein and gene sequence Databases (SWISSPROT and GenBank) by using FASTA and BLAST algorithms. A cyanobacterial (Anabaena sp.) PSI subunit, PsaA (aa's 274–307), was found to be homologous to human green-sensitive opsin (aa's 262–304). FASTA search and further analyses revealed that fungal opsin (Leptospherus sp., aa's 54–271) is homologous to rhodobacterial (Chromatium vinosum) PSII subunit M, in showing a 16.8% aa identity with three core homology (43–57% aa matches) regions. Aa's 163 to 241 in human green sensitive opsin (GSO) shows a 22.9% aa identity and a 40.5% (= 85/210) base identity (matching probability by chance: Pnuc (85, 210) = 6.1×10^{-5}) with Chromatium PSII M, and moreover, shows a 17.9% aa identity

and a 37.1%(=83/234) base identity ($Pnuc(83, 234) = 2.3 \times 10^{-4}$) to the *E. coli* glycyl-tRNA synthetase (GlyRS) alpha subunit. These observations clearly elucidated that PSII M subunit is genuine homologue of animal opsins and fungus-bacterial opsins, and of eubacterial glycyl-tRNA synthetase alpha subunit. Since GlyRS alpha is known to be derived from a most ancient gene homologous to the tRNAGly-tRNACys-tRNALeu region of the Bacillus subtilus trnD tRNA gene cluster and to trnGCL tRNA clusters in wide-range eubacterial phyla (Ohnishi et al., 2002). In conclusion, not only PSII subunits (M and N subunits in photosynthetic rhodobacteria and D1 and D2 in Cyanobacteria/chloroplasts) but also animal opsins (including green-sensitive opsins) and fungus-bacterial opsins (including fungus opsins and archaebacterial rhodopsins) are concluded to have had derived from an ancient protein closely homologous to GlyRS-alpha.

O-11. THE FRESHWATER OCEAN OF EUROPA AND IMPLICATIONS FOR THE ORIGIN OF LIFE

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Recent work has shown that the hypersaline image of Europa's putative ocean may be incomplete [1]. The combination of empirical constraints from the Galileo spacecraft magnetometer, the Galileo gravity data, and data on $MgSO_4$ eutectics, permit dissolved salt concentration between 1–282 g $MgSO_4$ per kg H_2O. Empirically supported model allow for salt concentrations far below terrestrial ocean salt concentrations (~34 g per kg H_2O). Given these new constraints on salinity, we address the implications for habitability and the origin of life in a Europan ocean. Experimental investigations of the influence of ionic inorganic solutes on self-assembly of monocarboxylic acid vesicles, and the nonenzymatic, nontemplated polymerization of activated RNA monomers support the contention that life originated in a freshwater solution [6]. Concentrations as low as 25 mM NaCl (1.46 g per kg H_2O) were found to "substantially" reduce oligomerization, however these experiments have not yet been performed with $MgSO_4$. We also note that Mg^{2+} can serve as a catalyst for the activation of nucleotides and amino acids to form polymers [7], so there are different effects to be evaluated by experiment. With regard to vesicle formation, if the ratio of the cation to amphiphile, falls below ~1, then it becomes possible for the excess amphiphile to form membranes; above ~2 and the amphiphle precipitates and no membrane formation occurs. In other words, freshwater environments appear more conducive to membrane compartmentalization; potentially a critical step in the origin of life. Given these considerations for prebiotic chemistry, the upper limit of 282 g $MgSO_4$ per kg H_2O may pose problems for the origin of life. However, the currently available data for Europa allows for an aqueous environment compatible with conditions thought to be conducive to the origin of life on Earth. Our current knowledge of Europa does not eliminate the prospect for a second origin of life as we know it.

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O-12. RADIO TELESCOPE FAST – A SENSITIVE TOOL FOR SETI

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FAST, Five hundred meter Aperture Spherical Telescope, is the Chinese effort for the international project SKA, Square Kilometer Array. The innovative engineering concept and design pave a new road to realizing huge single dish in the most effective way. Three outstanding features of the telescope are the unique karst depressions as the sites, the active main reflector which corrects spherical aberration on the ground to achieve full polarization and wide band without involving complex feed system, and the light focus cabin driven by cables and servomechanism plus a parallel robot as secondary adjustable system to carry the most precise parts of the receivers. Feasibility study on the critical technologies of the FAST has been founded by the Chinese Academy of Sciences and S&T ministry of China. The project has successfully passed the research phase. The achievements and results from modeling are briefly summarized in this report. Being the most sensitive radio telescope, FAST will enable astronomers to jumpstart many of science goals, for example, the natural hydrogen line surveying in distant galaxies out to red-shift around 3, looking for the first star shining, detecting thousands of new pulsars, and etc. Extremely interesting and exotic objects may yet wait for discovery by the FAST. Among these subjects, the most striking one could be ‘the cradle of the life in the universe’. FAST will play pivotal role in bioastronomical studies. Joining ground DSN support, it is able to increase the tracking capability at low frequency which is critical during the turning and landing process of the spacecrafts of the planet exploration missions. As a ‘master’ of the VLBI network, FAST will increase the detection sensitivity by factor 10 at least as well as increase the angular resolution due to the large collecting area and the geographic location, which might enable the direct imaging the nearby extrasolar planetary systems. In its working frequency band, FAST can be aimed at those known planets outside the solar system to detect the line emission of various compounds such as methane (CH_4) which is being considered as potential biomarkers for surface life. An alternative approach is to search for the evidence of alien technology – Search for ExtraTerrestrial Intelligence (SETI). By virtue of the fact that radio emissions from the Earth make it detectable over interstellar space, a natural strategy is to search for the artificial signals. To meet extraterrestrial communicative society, radio wavelengths offer a number of advantages, especially, in the range 1.42 GHz hyperfine transitions of the neutral hydrogen and 1.65 GHz due to the OH radial which is referred to as the water-hole by SETI scientists. This window is precisely located at the center of the core band of the FAST on which multi-beam feeds and day-1 receivers are to be equipped at the frequencies. Being the most sensitive tool for SETI, radio telescope FAST will be able to search for “leakage” signals from other civilizations in a much larger volume than has been possible so far.

O-13. CHEMISTRY OF MERIDIANI PLANUM, MARS, WITH IMPLICATIONS FOR BIOLOGICAL ACTIVITIES AND ABIOTIC PROCESSES

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Detection of an infrared spectral signature of hematite in Meridiani Planum stimulated interest in exploring this region of Mars because this mineral is often formed under hydrous, or hydrothermal, conditions. The Opportunity rover of the Mars Exploration Rover (MER) missions has discovered layered sediments at Meridiani with clear indication of an aqueous history. Hematite-enriched concretionary spherules and a hematitic groundmass in the sediments are accompanied by an assemblage of additional Fe minerals, but dominated by various sulfate salts, aluminosilicates and additional siliceous components. Few, if any of the original igneous minerals appear to have remained unaltered during a series of aqueous-mediated processes. The presence of jarosite ($\sim$10% by wt), as well as models of mineralogical trends and compositional constraints, imply an acidic environment in the past, which may or may not persist to the present. Conditions of low pH have not generally been found favorable for abiotic organic synthesis, neither for a variety of pathways to monomer syntheses nor formation of polypeptides or polynucleotides. MER instruments were not intended to detect carbon-containing compounds via in situ sampling, but from spectral observations, carbonates are less than 5%, or absent in these chemical sediments. Although martian soils may contain carbonates up to 1–2%, the atmospheric CO_2 provides an assured carbon source available at a partial pressure commensurate with that on contemporaneous Earth. Outcrop sediment is a reservoir of H_2O, as hydrated salts, adsorption of H_2O molecules on high surface area material, and possibly also as chemically captured OH in clays and Fe oxyhydroxides (if present). Orbital observations confirm that Meridiani is high in H_2O content, at 7% by weight, for an equatorial region. All these forms of H_2O are, however, at water activities (aH_2O) which are unusable by all terrestrial organisms for which metabolism even under extreme desiccation is known. Aqueous infusions into the salt-rich Meridiani outcrop environments explored to date would produce hypersaline brines, unless the amount of water provided is greater than 2:1. An H_2O excess of 9:1 would be needed to achieve oceanic salinities (wt/wt). Martian brines will be dominated by sulfate anions, not the soluble chlorides which dominate the preponderance of ubiquitous salt concentrations on Earth. Although Cl concentrations are somewhat low (0.5 to 1% by wt), their importance to astrobiology will be highly significant if actually present as chlorites, chlorates, or perchlorates. These oxidized forms of Cl cannot be precluded by the MER data. Solar UV photochemical action on martian atmospheric constituents may have interacted with martian Cl to produces these forms which may, in turn, be responsible for a highly oxidizing regolith which adversely affects the survival of organic compounds. If pore ice is the source of H_2O, the environment will be highly osmotic, at an ionic strength sufficient to reduce a H_2O below extreme thresholds for survival or activity. Terrestrial halophiles may succumb or be insufficiently tolerant of SO_4^{2-} and Mg^{2+} concentrations to proliferate. From knowledge of martian trace element chemistries, other adverse solutes, including solubilized forms of Ni, Zn, Cr or As, may be present at levels toxic to many or most organisms. However, indications are that these environmental parameters are widespread on Mars. On the other hand, phosphates are in evidence, and nitrates may be present in soils, providing bioavailable sources of P and N. The ubiquitous presence of forms of S and Fe are favorable to several potential metabolic pathways for energy sources, and are also well-known for important catalytic properties. Putative martian organisms may have had ample opportunity to adapt to the progression of environments. Whether the current martian environment is truly oligotrophic, or organisms could have successfully adopted some style of resilient dormancy (spores, cysts, or other cryptobiotic forms) to survive antagonistic conditions during interludes between favorable changes in climate is an open issue. On balance, data from the Opportunity rover suggest that current environmental conditions in the Meridiani region present severe challenges for life. Several billion years ago, when Meridiani sediments accumulated, habitable environments may have existed regionally, if perhaps transiently. Pervasive acidity and oxidation at Meridiani would have posed a challenge for the origin of life. Future missions to detect metabolic or reproductive activity on Mars must account for those conditions to which indigenous biota could be attuned, as well as seek ancient environments more conducive to prebiotic evolution.

O-14. THE HISTORICAL SIGNIFICANCE OF HERRERA'S THEORY ON THE ORIGINS OF LIFE

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In the early 1930's, Alfonso Luis Herrera proposed his so-called sulfocyanic theory on the origin of life, an autotrophic proposal on the first living beings according to which NH_4SCN and H_2CO acted as raw materials for the synthesis of bio-organic compounds inside primordial photosynthetic protoplasmic structures. Since Herrera was convinced that the true nature of life was the so-called cellular plasma, he developed a theory based on the colloidal origin of living beings that he termed Plasmogenia. During his theoretical and experimental work, he highlighted the formation of chemical structures similar to cellular forms. These types of cellular forms were baptized with the name of "colpoids" and "sulphobes." Which believe presented cellular properties such as motility, osmosis, and growth. The abundance of sulfur in volcanic zones was an evidence that supported the sulfocianic theory of the origins of life. Based on this theory, he proposed that the "sulphobes" were generated starting off from sulfur-containing compounds. Ammonium thiocyanate turned out to be the best experimental model for in vitro life creation. To understand how life began, Herrera decided to use compounds such as ammonium thiocyanate and formaldehyde for the synthesis of organic molecules, following Pfluegerr's idea of the autotrophic origins of life. As an outcome of his studies he reported the presence of several structures similar to cells, starch, the synthesis of two amino acids, globules of red, green and yellow pigments as well as a proteinoid condensation product (Science, 1942).

P-1. IRRADIATION OF CN-CONTAINING COMPOUNDS IN FROZEN STATE AND THEIR CORRELATION WITH COMETARY ICES

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The study of extraterrestrial bodies has provided a profound insight on the formation and early history of the solar system. In this regard, many efforts have been put into gathering information from different sources; from grains in the interstellar medium to comets and planetary surface ices. Because these icy objects have been exposed to ionizing radiation and UV light at several stages of their evolution, they have been altered over time. These are very important issues because comets are thought to be carriers of material initially available in the early Earth. To this end, the organic inventory is of central importance concerning the origin of life. Among the organic inventory are the CN-containing compounds, and it is widely accepted that those compounds play a crucial role in primordial organic synthesis. This statement has been strongly substantiated by radio astronomical observations and an intense laboratory work related to prebiotic chemistry associated with cyanogen compounds. The aim of the present work is to study the chemical changes induced by ionizing radiation in several simple CN-containing molecules in frozen solutions. We studied the behavior of HCN, CH_3CN, CH_3CH_2CN and NH_4CN. These entire target compounds yield oligomers. For example, from the decomposed HCN molecules about 76% are converted into oligomeric material. The structure of these oligomers is different to those oligomers formed by thermal polymerization. Characterization of the structure of these oligomers is in process. The data obtained suggest that these are formed by polyamides and esters, and in turn, upon hydrolysis release compounds of biological significance like amino acids, purines and carboxylic acids. The oligomeric materials formed in a frozen system, present essentially the same characteristics that those formed in the liquid systems. The radiochemical yields of formation of these materials in ice were one or two orders of magnitude lower than in liquid solutions. This is, mainly due to the rigid structure of the ice and the limited mobility of the radicals at low temperature. The results found in this study underline the importance of radiation induced reactions as an energy source in extraterrestrial scenarios like comets or other icy objects.

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P-2. ABSTRACTION OF HYDROGEN FROM ORGANIC MATTER, CAUSED BY IONIZING RADIATION IN OUTER SPACE

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The idea of panspermia started a century ago, when Svante Arrhenius, the chemist, faced the question of origin of Life on Earth and has found difficulties to find an answer. As the best solution, he has invented the concept of extraterrestrial origin of Life and of transportation to the Earth from outer space, including even galaxies. The idea has attracted many followers and was a subject of extended interpretations. For instance, some preachers of panspermia have assumed the idea, that Life was always and everywhere present, from the beginning of the World, and it was the transportation between different places only, which mattered. As there are still no plausible theories and chemical experiments proposed to explain spontaneous formation of pure enantiomers, and preparations of minimal cell from ready, pure asymmetric blocks are at the very beginnings, there are numerable enthusiasts of panspermia. There are many variations of panspermia concept, but neither takes into account the ionizing radiation damage, which inactivates any life, even liofilized bacterial spores in vacuum, at temperatures close to absolute zero. The interaction of ionizing radiation, neither of primary quanta nor of particles is not influenced by the temperature of the material. The temperature can modify slightly secondary chemical reactions of intermediate products formed in ionization spurs. The main factor of biological inactivation by radiation seems to be an irreversible detachment of hydrogen from organic molecules. The fundamental assumption of any type of panspermia hypothesis is the transportation of live species in the space, not disturbed by ionizing radiation. Nowadays the average exposure to radiation in the space is known, as well as the shielding effect by the matter in which the object under consideration is transported. The intensity of exposure, multiplied by shielding factor and by the time of travel, yields the absorbed radiation dose. The absorbed energy initiates different chemical reactions leading to the inactivation of living processes, similar to used on Earth for sterilization operations. We have concentrated on measurements of radiation yields of hydrogen abstraction from biopolymers, in particular from the DNA. 10 MeV electrons from accelerators, applied in different dose rates are used to simulate the irradiation in space. Yields of hydrogen were measured by gas chromatography in the function of dose. The reaction of hydrogen abstraction is irreversible and results in killing of any form of life. Whereas the DNA in the living species, i.e. in aqueous system, when damaged slightly by ionizing radiation, can be repaired, the dry DNA in spores is effectively damaged by very first doses of radiation. The radiation induced removal of hydrogen is only slightly influenced by temperature (reaction of zero activation energy) and therefore the coldness of space does not function as the protection. The G values of hydrogen abstraction are given for typical biopolimers. Typically, GH2, i.e. the amount of H_2 molecules per 100 eV of absorbed energy, is e.g. from 0.10 for certain animal proteins to 0.37 for DNA. The maximum yield is 4.5 for non-biopolymers, in some polyolefins, when the reaction is connected to crosslinking. Similar radiation yields are observed for radiation induced deamination and decarboxylations, also catastrophic for living systems or for bio-building blocks. Detection of amino acids in meteorites, announced in some publications means that either the object stayed for a short time only in space or traveled in well shielded conditions. There is a need to support the real look on panspermia, especially concerning survival of living and prebiotic chemical structures in radiation fields of different LET values, well known to prevail in outer space. According to popular modern myth, mutants like Deinococcus radiodurans i.e. bacteria strains of increased radiation resistance, are fully radiation resistant and would travel without any harm through the radiation impregnated space. According to our experience, such strains, like observed in our Laboratory Micrococcus radiodurans (common even in the dirt of radiological installations in hospitals) has a typical survival curve, shifted only for 10–6 survival from usual 20 kGy to 40kGy. After collection of sufficient dose, it will be killed anyway. In conclusion, the probability of survival of spores in the living condition in space is very low. Actual enthusiasm toward panspermia is basing on insufficient knowledge of radiation chemistry and radiobiology. Dissemination of hard facts will help to establish the negligible probability of transfer of Life and slightly higher of building blocks of organics to Earth. It should promote concentration on looking for mechanisms of origin of Life here on Earth.

P-4. HIGH-MOLECULAR-WEIGHT COMPLEX ORGANICS: THREE DIMENSIONAL IMAGING AND PYROLYSIS EXPERIMENT OF SIMULATED PRODUCT VIA INTERSTELLAR GAS MIXTURE IRRADIATED WITH 3 MeV PROTON BEAM

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High molecular weight organic matter synthesized from mixtures of carbon monoxide, ammonia and water gases similar to those found in the interstellar medium were irradiated with a 3 MeV proton beam and analyzed by Curie point pyrolysis with detection by gas chromatograph and mass spectrometer (Pyr-GC-MS). A wide variety of organic compounds, not only a number of amide compounds, but also heterocyclic and polycyclic aromatic hydrocarbons (PAHs), were detected among the products of the pyrolysis. Detection of biologically interesting compounds such as glycolamide ($HOCH_2CONH_2$) is also cosmochemically interesting. The present data shows that primary and primitive organic matter serving as “precursors” to bioorganic compounds such as amino acids, nucleic acid bases, and sugar might have been formed in a gaseous mixture of similar composition to that of the interstellar dust environment. Consequently, the matrix of extraterrestrial organic compounds delivered by comets and meteorites may have played an important role in the early stages of chemical evolution on the primitive Earth. 2. Purpose of this study The idea that organic matter, including biologically important compounds such as amino acids and nucleic acid bases, was delivered to early Earth from extraterrestrial sources is strongly supported by the detection of a large variety of organic compounds in comets and carbonaceous chondrites from the interstellar medium. Cooper et al. have found a kind of sugar analog in the Murchison meteorite, which fell over the Australian town of Murchison in 1969, and in the Murray meteorite, which fell in Kentucky in 1950. Both of these carbon-rich meteorites are thought to be fragments of asteroids, rubble from the building of our Solar System. The Murchison meteorite has been particularly well studied, and the detection of amino acids, the molecular building blocks of proteins, helped to establish that these basic components of bioorganic molecules can be formed in extraterrestrial environments. In addition to the presence of fundamental organic materials, enantiomeric excesses of meteoritic amino acids; that is, biomolecular chirality also plays an important role in triggering stereochemical molecular evolution. Asymmetric photolysis of racemic mixtures of amino acids has been performed using a chiral source of circularly polarized light. The photostability of amino acids, and the survivability limits for extraterrestrial delivery have been experimentally reviewed. Greenberg et al. proposed a cyclic evolutional model of interstellar dust (ISD) where organic compounds are formed and transformed in ISD as they travel in molecular clouds and diffuse clouds and then are formed in comets where they are preserved in the proto-solar system. Representative carbon sources are carbon monoxide and the predominant nitrogen source is ammonia. Interstellar media are irradiated with galactic cosmic rays and secondary photons of ultraviolet radiation. However, little is known about the primary radiation products as they are complex organic molecules. Kobayashi et al. suggested that the primary products of proton irradiation obtained from mixtures simulating the primitive earth atmosphere (carbon monoxide, nitrogen, and water) were amino acid precursors (molecules which are converted to amino acids following hydrolysis) and not free amino acid analogs. It has been recognized that amino acid precursors and nucleic acid base precursors were formed in the irradiation experiments from interstellar gas mixture components. Recent experiments irradiating mixtures containing methanol by UV and quantitative discussion have also contributed significantly to the study of extraterrestrial organics. However, the matrix of the irradiation products has not been clarified yet. Here, we report the composition of high molecular organics synthesized from simulated interstellar media with high-energy proton irradiation. The pyrolysis experiment here revealed the primary composition of interstellar dust organics and elucidated their morphological aspects. The present results have significant implications regarding the extraterrestrial origins of amino acid precursors, such as meteoritic organic compounds and interstellar dust particles.

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P-9. STABILITY OF BIOORGANIC MOLECULES IN MARTIAN ENVIRONMENT: KEY FACTOR FOR FURTHER EVOLUTION PROCESSES

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Life has probably existed on earth for about 3.5 billion years and ever since people could wonder, they have tried to understand its origins. From the first signs of life it is thought that organisms as complex as bacteria had emerged within 0.5-1 billion years. But, this to some seems a rather short timescale for such an important step and suggest that a germ of life may have reached Earth from space. Organic molecules, such as amino acids, organic acids, and sugars have been observed in material from extraterrestrial sources in the solar system. The chemical evolution of life may have started in space as well. There are two ways for life to emerge – terrestrial and extraterrestrial – both are possible. We are not neglecting the endogenous origin of life but suggest also an extraterrestrial origin of organics. The question of possible ability for biomolecules to resist degradation on the Martian surface is of special importance in terms of planning of the forthcoming missions to this planet and the search for traces of life on and near its upper soil layer. Since the research task was to find out whether main organic substances (aminoacids and nucleosides) are able to survive and to form more complicated ones in the absence of water, our experimental dry films were exposed to the short ultraviolet radiation (254 nm) abundant on Mars at present time. The reaction must proceed under solvent-free conditions and incident ultraviolet radiation in a vacuum. Mineral beds (basalt and limonite) impregnated with biological molecules were used to approach the model of Martian surrounding. Structure and properties of experimental films were analyzed using confocal microscopy images with and without mineral beads. Experimental samples were placed into an isolated chamber containing two types of gases CO_2 and N_2 to figure out the more favorable environment for organic processes. Data obtained after applying mass spectrometry and chromatography techniques for samples analyzing revealed that the presence of basalt and limonite beds stabilized degradation processes occurring within the radiation period and and successfully shielded the monomeric products from decomposition by UV. Further calculation made to extrapolate experimental results to more extended time period showed that organic molecules could possibly survive long – duration exposure to

UVC radiation. These results coincide with our previous experiments representing the system where minerals of extraterrestrial origin such as meteorites Allende, Murchison and lunar soil were tested with respect to their influence over decay and biological synthesis in similar conditions. Hence it seems quite plausible that organic molecules are stable enough to survive in Martian conditions making the polymeric components of primitive life. Since organic molecules are much more resistant than bacteria in strong radiation conditions, future missions to explore exobiology sites of interest can be also targeted in order to reveal possible biomarkers such as aminoacids and nucleosides.

P-10. PHOSPHORUS OXYCHLORIDE ASSISTED PEPTIDE FORMATION FOR L-PROLINE

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Amino acids and phosphorus play vital roles in life science. Even though there are lots of papers about peptides synthesis related to the chemical evolution of life, there is no intensive investigation on the intrinsic relationship between the phosphorus and amino acids (Fu et al., 1999). In our previous work, we found that with the assistance of phosphorus oxychloride amino acids could be assembled into oligo-peptides (Lu, et al., 2002). In this paper, we used electrospray ionization mass spectrometry (ESI-MS) to investigate the reaction between phosphorus oxychloride and L-Proline. Quenching with water, the reaction mixtures yielded the corresponding peptides, with a series of mass peaks for the homo-oligo peptides of L-Proline as observed by ESI-MS. The peak at m/z 213, 310, 407, 504 were identified as oligopeptides of (Pro) n-OH with $n = 2, 3, 4, 5$, respectively. We found that the lengths of the peptides could be controlled by changing the reaction conditions. As the reaction time was prolonged and the polarity of reaction solvent was enhanced, the lengths of the peptides were increased. However, as the reaction temperature rose, there was side reaction happened vigorously. So we chose room temperature as the reaction temperature. It should be pointed out that only the α-amino acid could be activated by N-phosphorylation.

In conclusion, a simple and efficient method for the synthesis of homo-oligopeptides has been found. The presence of phosphorus could activate the amino acids. It might provide some information for the contribution of phosphorus to the origin of peptides.

Acknowledgements

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P-11. SYNTHESIS OF HOMO L-METHIONINE OLIGOPEPTIDE MEDIATED BY PHOSPHORUS OXYCHLORIDE

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As we know protein is composed of natural amino acids and it is the most important macro-molecule of the life system. However how the amino acids assembled into peptides and finally formed the protein in the origin of life has been a key problem. As the inorganic phosphorus compounds could exist on the primitive earth, these papers investigate the activation function of phosphorus reagents on the peptide formation. It was found that as the reaction time prolonged, polarity of solvent strengthened, and reaction temperature raisen, the peptide chain got longer. Equimolar $POCl_3$ and L-methionine were reacted in tetrahydrofuran, some short-chain polypeptides (Scheme 1) formed. The dipeptide ($M = 281$) and tripeptide ($M = 412$) were purified by HPLC. The structures of the products were characterized by 1H-NMR, 13C-NMR and ESI-MS. Scheme 1 showed the ESI-MS of L-methionine oligopeptide library.

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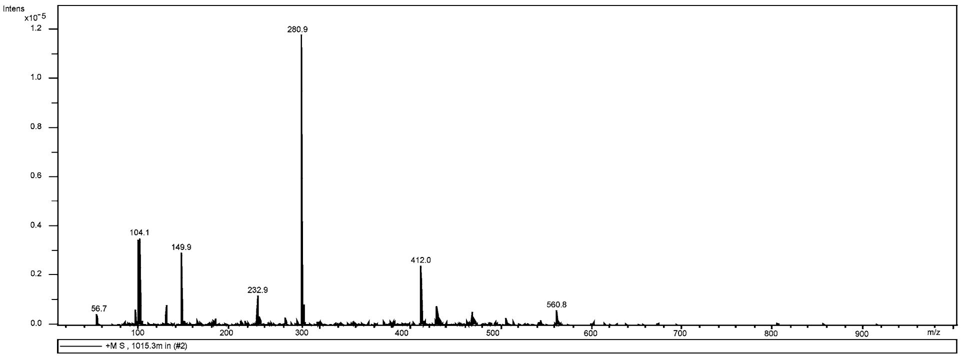

Scheme 1. ESI-MS of L-methionine oligopeptide library.

P-12. HIGH-DOSE GAMMA-IRRADIATION OF FULLERENE C60: IMPLICATIONS FOR INTERSTELLAR FULLERENES

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The widely-debated presence of fullerenes in the interstellar medium has not been supported directly and unambiguously by experimental data so far. Nevertheless, it is generally assumed that these large spherical carbon clusters can be generated within circumstellar envelopes of mass-losing carbon-rich stars. The detection of fullerenes in carbonaceous chondrites, in the geological strata of the Cretaceous-Tertiary and the Permian-Triassic boundary layers, associated with bolide impacts, can be considered as an indirect evidence of their formation in circumstellar envelopes. The presence of fullerene species in the extraterrestrial samples found on Earth implies that these compounds are able to survive very long passages through diverse space environments. The latter, especially those in close proximity to the stars where the fullerenes can be produced, are usually characterized by strong ionizing radiation. The most energetic known events in the Universe are supernovae and gamma ray bursts. Supernovae release 1043–1044J of energy in the form of photons, neutrinos, and kinetic energy imparted to debris from the explosion, about 1042J being in the form of gamma-radiation. Gamma ray bursts release the isotopic equivalent of about 1045–1047 ergs, with the peak energy of ca. 200 keV. Since due to a very low density of matter in the interstellar medium, attenuation of gamma-radiation is negligible, one can expect that gamma-rays (along with UV and proton radiation) decompose the newly formed fullerene molecules. Thus, a question arises whether fullerenes can survive in so harsh radiation environments. In other words, the existence of the large spherical carbon clusters must finally depend on competition between the rates of their formation and radiation decomposition. This relates both to the gas phase and to the condensed phase (interstellar grains and comets), due to the high penetrating ability of gamma-rays. Many aspects of fullerene chemistry are being extensively studied, however the lack of experimental data in the area under discussion is obvious. In the previous work we have begun to study decomposition of C60, the most common member of fullerene family, under prolonged gamma-irradiation. We exposed C60 to very high irradiation doses exceeding 6 MGy, and analyzed the irradiated samples by high-performance liquid chromatography (HPLC) and infrared (IR) spectroscopy. In the present work we continued our experiments, by exposing the dry and aqueous fullerene samples to gamma-rays at doses exceeding 50 MGy, with the total experiment duration of ca. 8 months. We found that the crystalline C60 fullerene is extremely resistant to prolonged gamma-irradiation. The doses exceeding 50 MGy, used in our experiments, are incomparably higher than those produced by gamma ray bursts (about 200 Gy every million years or so). Thus, the solid C60 can survive in all space environments, where it can form, incorporate into interstellar dust particles and subsequently into comets, and travel through the Universe. However, fullerenes might also exist in molecularly dispersed forms, e.g., in the gas phase or as solid solutions in the interstellar ices and cometary nuclei. How they would behave under the same radiation conditions is unclear so far and needs additional studies.

P-13. EFFECT OF MINERAL SURFACES IN PHOTOCHEMICAL ABIOGENIC SYNTHESIS OF NUCLEOTIDES

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Abiogenic photochemical synthesis of complex biochemical compounds on the surface of small bodies in our Solar system was examined. The hydrated minerals are found within a chondrite matrix of meteorites together with significant amounts of organic matter. Clays are likely to have formed when water was presented on parent meteoritic bodies. In order to verify the existence of a relationship between abiogenic synthesis of nucleotides and inorganic components of the meteorites we have investigated possible abiogenic reactions at the presence of different clay minerals (montmorillonite, kaolinite) and basaltic sample (Tjatja's volcanic ash) under action of open space energy sources for modeling of different exobiological environments on the surface of small space bodies. The abiogenic synthesis of natural adenine nucleotides from mixture of adenosine plus inorganic phosphate has been observed under an irradiation with VUV radiation at the presence of different mineral samples. The yields of the products (5′AMP, 2′AMP, 3′AMP, 2′cAMP and 3′cAMP) were depended from irradiation time and kind of used minerals. The discovery that meteoritic organic compounds may be trapped and protected within a clay mineral matrix has implications for our understanding of prebiotic molecular evolution in the early Solar system. Clay minerals may have concentrated organic compounds thereby promoting polymerization reactions also. An adsorption/binding of nucleic acids components by clay crystals could change in the electron distribution and/or the conformation of the molecules. The remnant water molecules in the clay sheets also could influence on the course of the reaction. Besides, an immobilization of phosphate on clay also could play an important role in our reaction. The influence of mineral substrates on the abiogenic synthesis may depend on the following mechanisms: (1) the protective function of the mineral, which prevents decay of both initial components and newly formed reaction products. The screening effect of clays has been studied earlier, and has been founded that the clays provided a significant protection against photolysis; (2) catalytic properties of the mineral in heterogeneous photochemical phosphorylation reactions; (3) the presence of residual water molecules, which can generate radicals under the influence of VUV radiation, in the interlayer space of clays; and (4) the dependence of the reactivity of both adenosine and inorganic phosphate molecules on their absorption by mineral substrates. The results obtained suggest that the action of the VUV-radiation on films of biologically significant compounds makes them more complicated and produces important natural compounds. One can assume that the abiogenic synthesis of relatively complex compounds can proceed under conditions of open space. Chondritic material would have been a common component of the inner Solar system shortly after its formation and the biologically useful products of clay mineral-organic matter interactions would have also widespread, and delivered to planetary surfaces through the accretion of carbonaceous asteroids.

P-14. DENSITY FUNCTIONAL THEORY STUDY OF $(HCN)_n$ CLUSTERS UP TO $n = 10$

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Hydrogen cyanide is an extraterrestrial material, and is also recognized today as a plausible prebiotic molecule. This polar triatomic compound, such as water but devoid of oxygen, is very particular in the sense that long linear chains exist in the crystalline forms. We have studied (HCN)n clusters, with $n = 1.10$ for the linear chains and the cyclic conformations for $n = 3$ and $n = 4$, with the help of DFT computations using the extended basis functions 6-311G++(3d, 3p). The vibrational spectra for infra red and Raman spectroscopy are discussed with respect to the existing experimental data. An interesting correlation between the dipole moment and the polarizability of the linear clusters was found, which induces a linear relation between the infra red intensity of C–H stretches and CN stretches and the Raman activity. The infrared spectra of cyclic $(HCN)_3$ and $(HCN)_4$ forms are discussed versus their corresponding spectra in linear forms. These results may be of interest for the data collected by probes such as Huygens for the Titan's atmosphere.

P-16. THERMAL SYNTHESIS OF POSSIBLE PREBIOTIC ORGANIC COMPOUNDS FROM CALCIUM-COORDINATED AMINO ACIDS

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It can be concluded from simulation experiments that abiotic syntheses of α-amino acids probably take place in dense interstellar clouds (Bernstein et al., 2002; Muñoz Caro *et al.*, 2002). During the formation of our solar system in such an interstellar environment, the amino acids were trapped in interplanetary dust particles, comets, meteorites and asteroids, which finally delivered them onto the early Earth. Today these amino acids are still found in carbonaceous chondrites such as the famous Murchison meteorite (Pizzarello, 2004).

Amino acids readily form complexes with metal ions, for example with Ca^{2+}, which frequently occurs in the Earth's crust. Two types of calcium compounds must be considered, namely $CaX_2 \cdot m\ Haa \cdot n\ H_2O$ and $Ca(aa)_2 \cdot n\ H_2O$ where X^- is, for example, chloride, Haa is a neutral amino acid, and aa^- is the amino acid anion. On the early Earth, aqueous solutions of Ca^{2+} and amino acids may have been evaporated to dryness on hot volcanic rocks or in "rock pools", which are small basins supplied with seawater by surf and tide in coastal regions. It is conceivable that the resulting solids were exposed to high temperatures from volcanism and impact of asteroids and meteorites. Coordination of the amino acids to metal ions is crucial for thermal transformations to occur, since most of the *free* amino acids usually sublime with only minor decomposition, except when in a more or less sealed compartment at ≥400 °C (Douda and Basiuk, 2000).

The crystalline compound $Ca(ala)_2 \cdot 3\ H_2O$ was synthesized by refluxing an aqueous solution /suspension of *rac*-alanine (Hala) and calcium hydroxide. A $CaCl_2$ complex of the neutral amino acid was obtained from a concentrated aqueous solution of *rac*-alanine and calcium chloride. In order to simulate thermal effects on the early Earth, samples of $Ca(ala)_2 \cdot 3\ H_2O$ were heated to temperatures between 280 and 450 °C in a quartz tube. The temperature choice was made on the basis of thermogravimetric measurements which showed two major steps of mass loss in the temperature range given. A constant flow of nitrogen gas simulated atmospheric movements and served to transport volatile compounds out of the reaction tube. $Ca(ala)_2 \cdot 3H_2O$ decomposed to give a large variety of organics. The non-volatile residue contained calcium carbonate and additional organic compounds. Some of the organic products are of potential interest as prebiotic molecules, for example several pyrrol derivatives.

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P-17. THERMAL TRANSFORMATION OF METAL-ION- AND SILICATE-BOUND AMINO ACIDS AS A POSSIBLE SOURCE OF PREBIOTIC MOLECULES

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The occurrence of amino acids in primitive meteorites strongly suggests that these compounds were also delivered to the early Earth. About 3.8 billion years ago, large amounts could have accumulated on the Earth's surface and in the oceans (Chyba and Sagan, 1992). α-Amino acids are known to form isolable complexes with virtually all metal ions. Coordination is especially strong for the amino acid anions H_2N–CRR′–COO$^-$. In these cases usually *O,N*-chelates are observed. Neutral amino acids ^+H_3N–CRR′–COO$^-$ can form complexes via coordination of the carboxylate group because of their zwitterionic character. It therefore seems save to assume that amino acids also formed metal complexes on the early Earth. The metal ions may have been present in solution or as interlayer cations in clay minerals such as montmorillonite. More generally, amino acids may also have been adsorbed onto other phyllosilicates (sheet silicates) such as serpentine which lacks interlayer metal ions. The metal-ion- and silicate-bound amino acids were almost certainly exposed to high temperatures from volcanism and episodical impacts of extraterrestrial objects. This is the starting point for our experimental studies (Strasdeit et al., 2001).

We report the large-scale (>10 g) preparation of amino acid /silicate intercalates and amino acid complexes such as $[Ca(ala)_2(H_2O)_3]$ (Hala = *rac*-alanine). Thermolysis experiments with these solids were conducted under a stream of nitrogen at a fixed temperature between 280 and 450 °C. For each compound, the temperature was chosen on the basis of thermogravimetric curves measured prior to the preparative scale thermolysis. A thermolysis apparatus is described that allows to collect several 100 mg of a mixture of organic products. These products are analysed by standard GC/MS and HPLC methods. The effect of the metal ions and silicates is twofold. First, they keep the amino acids from subliming without chemical reaction. Second, they probably determine the pathways of the thermal reactions, for example by Lewis acid catalysis.

The thermolyses not only yield simple decomposition products such as ammonia and carbon dioxide, but also a surprisingly high number of relatively complex organic compounds. For example, $[Ca(ala)_2(H_2O)_3]$ at 450 °C gives well over 200 organics which are volatile at the thermolysis temperature. Among them are at least 15 differently substituted pyrrols and the cyclic dipeptide of alanine. The non-volatile residue is mainly composed of calcium carbonate, but also contains a few percent of water-soluble organic compounds. Further products of potential prebiotic relevance and possible reaction pathways will be presented.

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P-18. INTERCALATES OF SHEET SILICATES WITH AMINO ACIDS AS POSSIBLE INTERMEDIATES IN PREBIOTIC CHEMISTRY

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It is generally assumed that clays and their main constituents, the sheet silicates, played a central role in prebiotic chemistry due to their specific properties and wide occurrence. This idea dates back to a lecture that was given by Bernal in 1947 and first published in 1949 (Bernal, 1949). Clays are readily formed either by weathering or by hydrothermal alteration of volcanic rock or other sheet silicates. Therefore, there is good reason to believe that clays were ubiquitous on the early Earth.

An interesting property of sheet silicates is "intercalation", which means the uptake of water and organic molecules into the interlayer spaces. There are also sheet silicates which are catalytically active, for example in the formation of RNA oligomers from activated monomers (Ferris, 1998). We are especially interested in the intercalation of α-amino acids which occurs, for example, with the sheet silicate montmorillonite $A_{0.33}\{Al_{1.67}Mg_{0.33}(OH)_2[Si_4O_{10}]\} \cdot x\ H_2O$ (Hedges and Hare, 1987). Intercalation of α-amino acids can proceed via different mechanisms. In the case of montmorillonite the two main mechanisms are exchange of interlayer cations ($A^+ = Na^+$, $\frac{1}{2}\,Ca^{2+}$ and others) by protonated α-amino acids and the substitution of intercalated water by neutral α-amino acids. Neutral α-amino acids ^+H_3N–CRR′–COO^- can coordinate to the interlayer cations. We suggest that such intercalates were formed on the early Earth where they were exposed to high temperatures. As sources of thermal transformation products they may have contributed to prebiotic chemical evolution.

Recently, we have started studying the thermal behaviour of such intercalates. The intercalates are readily prepared by treatment of fine powdered sheet silicates with aqueous solutions of α-amino acids. The amount of adsorbed amino acid was determined by elemental analysis. We used thermogravimetry (TG) and differential thermal analysis (DTA) to study the intercalates in the temperature range of 20 to 900 °C. Large differences were observed between Ca-montmorillonite and its intercalate with *rac*-alanine. For example, the amount of intercalated water in the last sample is strongly decreased (from 8% to 2%) which indicates that alanine has displaced most of the water. The thermal transformation of intercalated alanine occurs between 270 and 620 °C, while under the same conditions pure alanine sublimes in a narrow temperature range around 290 °C. On the basis of the TG and DTA results, preparative thermolysis experiments were conducted. GC/MS and

HPLC methods were applied to analyze the mixtures of organic products obtained. The results will be reported.

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P-19. THE STACKING INTERACTION ENERGIES OF SEQUENCES OF PYRIMIDINE AND PURINE POLYRIBONUCLEOTIDES

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Consistent relative stacking interaction energies have been calculated for triply ionised dinucleotide structures in the g-g- conformation. For the pyrimidine dinucleotides: UpUp, UpCp, CpUp and CpCp, the stacking energies were found to be 0.019, −0.031, 0.044, 0.028 ± 0.010, respectively. These values enable the preferred structures of sequences to be determined in the nearest neighbor Ising model of a polyribonucleotide. For instance, the lowest energy of a pyrimidine tetranucleotide is UpCpUpCp = −0.018 h, irrespective of the composition of the pyrimidine oligonucleotide. For the corresponding purine dinucleotides: ApAp, ApGp, GpAp and GpGp the stacking interaction energies were found to be 0.070, −0.053, 0.102, 0.079 ± 0.010 h, respectively. The lowest energy for a stacked purine tetranucleotide is ApGpApGp = −0.004 h, irrespective of the composition of the purine oligonucleotide. These values correlate qualitatively with the enthalpy changes for dangling 5′- unpaired nucleotides (D.H. Turner in "Nucleic acids: structures, properties and functions" university Science Books, 2000, 259–334), and are analogous to the (dG-dA)n · (dC-dT)n flanking regions of transcribing genes (T. Evans and A. Efstratiadis, J. Biol. Chem. 1985, **261**, 14771). These interactions have been shown to be feasible from the overall enthalpy changes in the ZKE approximation at the HF and MP2/6-31G* level.

Keywords: sequence stacking interaction energies, pyrimidine and purine dinucleotides

P-23. SYNTHESIS OF PYRIMIDIC NUCLEOTIDES UNDER POTENTIALLY PREBIOTIC CONDITIONS

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It has been suggested that pRNA could have preceeded RNA as an alternative genetic material early in chemical evolution. Previous work in the Manchester group has shown a prebiotically plausible synthesis of a furanosyl ribonucleotide from a sugar phosphate scaffold. More specifically, the conversion of D-arabinose-3′-phosphate to ß-D-ribocytidine-2′, 3′-cyclic phosphate via an amino- oxazoline, by successive reaction with cyanamide and cyanoacetylene, was demonstrated. Other work in Manchester has shown the abundant production (as part of a mixture) of xylose-2′, 4′-cylic phosphate by a predisposed intramolecular aldolisation of glyceraldehyde-2′- phosphoglycolaldehyde. Experiments have shown xylose-2-phosphate to be unreactive towards cyanamide due to the electron withdrawing effect of the phosphate on the open-chain aldehyde. We are now investigating this chemistry starting with xylose-4′-phosphate in the hope of forming a 1′3′amino-oxazoline. It is thought possible that this would then react with cyanoacetylene to give ß-D-pyranosylcytidine-3′4′cyclic phosphate, which could be a precursor of pRNA. My work has involved developing a synthesis of xylose-4-phosphate and subsequent 1H NMR studies of its reaction with cyanamide.

P-24. SYNTHESIS OF CYANOBUTADIYNE

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The cyanobutadiyne (HCC-CC-CN) has been detected in the interstellar medium, in comae and in numerous lab simulations of the atmospheres of Titan or the Primitive Earth. (de Vanssay et al., 1995) It is suspected to be a key-compound because, as the cyanoacetylene (HCC-CN), it may easily react with many nucleophiles and that could be the starting point of a rich organic chemistry in these media. Up to now, cyanobutadiyne has never been prepared in pure form but has only been detected in mixtures of molecules. The most important approaches were reported by Kroto, (Haas et al., 1994) Winnewisser (Alexander et al., 1976) and more recently Bizzocchi (Bizzocchi et al., 2004) In order to confirm (or to disprove) models which foresee the presence of cyanobutadiyne on Titan, it was necessary to have an authentic sample and to determine the physicochemical properties of this compound.

We report here the first preparation of a pure sample of cyanobutadiyne using a new reaction. The structure has been determined by 1H and 13C NMR spectroscopy and High Resolution Mass Spectrometry. An infrared spectrum of the pure compound recorded by the LISA (France) could allow to estimate the partial pressure of this molecule on Titan, provided it was detected on by the Cassini-Huygens probe. We also tried to precise how the cyanobutadiyne could be formed on Titan or in a similar environments. Given that on this Saturn's satellite the temperature is very low (Huygens recorded temperatures of about $-180\,^{\circ}$C on its surface), the light is the most abundant energy and therefore the cyanobutadiyne could be formed thanks to photochemical processes mainly. Thus, several compounds detected on Titan have been mixed in the gas phase and irradiated by UV lamps. The formation of cyanobutadiyne has been detected by 1H NMR spectroscopy in several cases as in the photolysis of acetylene with cyanoacetylene or dicyanoacetylene, and dicyanoacetylene with butadiyne. We then started the study of the reactivity of this molecule in the condensed and gas phase with other compounds detected on Titan or in the interstellar medium. As an example, the reaction with ammonia led to the corresponding enamine. $\text{HCC-CC-CN} + \text{NH}_3 \rightarrow \text{H}_2\text{N-CH=CH-CC-CN}$ Attempts to extend this new reaction to other nitriles interesting Space Sciences are currently under progress in our laboratory.

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P-26. ROLE OF CLAYS AS PROTECTING AGENTS IN PREBIOTIC CHEMISTRY

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Clay minerals might have had an important role in prebiotic synthesis as it has proposed by Bernal in a lecture in 1947. Clay minerals were necessary, (1) to concentrate the organic molecules present in a diluted ocean by adsorption on clay deposits, (2) Catalyze the polymerization of adsorbed organic compound, (3) Protect these organic molecules from destruction by ultraviolet light, (4) Induce the chirality in contemporary molecules. To this end, the investigation of the role of

clays in prebiotic organic synthesis ranges from mere adsorbents and catalysts to the controversial claim that clays were the first functional templates (Cairns-Smith, 1966). Prebiotic scenarios in nature can be found in mud beds, shores, hydrothermal vents at the sea bottom, and regions alternatively wet and dry as tidal estuaries. These environments stress the significance of multiphase systems in prebiotic processes. Adenine and other nitrogen bases are important compounds in biological systems. Purine bases are readily formed in prebiotic conditions. Its synthesis and stability in environmental conditions is of paramount importance in chemical evolution. There are several routes for the synthesis of adenine and other nitrogen bases simulating the primitive Earth (see Miller and Orgel, 1974). To explain why organic compounds endured in the primitive Earth there are several possible pathways: a) they were synthesized continuously and they reached steady state concentration. b) The compounds presented a long half-life in the environmental conditions of the primitive Earth. c) Solid surfaces protect the organic compound adsorbed in the clay, as it was postulated by Bernal. In spite of the importance of the presence of adenine and other nitrogen bases in the prebiotic environment, there are few papers that deal with the survival of this type of compounds. In particular, there are none about the study of the stability of adenine, xanthine and guanine in an aqueous medium, at high temperatures, or in the presence of high radiation fields. The attempt of this work is to show preliminary results about the studies of the stability of adenine and other nitrogen bases in a high to a high-energy radiation field.

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P-27. THEORETICAL STUDIES ON N-PHOSPHORYL AMINO ACIDS FOR THE ORIGIN OF BIOMOLECULES

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“Where there is life, there is phosphorus” (Todd, 1981). In this paper, theoretical studies of phosphoryl amino acids and their possible role for biomolecular origins are reviewed.

N-phosphoryl amino acids (PAA) are a unique chemical species with many chemical properties, including the ability to self-assemble into oligopeptides. In order to investigate the chemical characteristics, six intramolecular mixed carboxylic–phosphoric anhydrides (IMCPAs) as possible intermediates for the prebiotic synthesis of biopolymers have been discussed (Tan et al., 2004). The results of the theoretical study imply that it is possible for prebiotic proteins and nucleosides to be formed under mild conditions as observed in our study.

In order to understand the different reactivity of α-amino acid, β-amino acid and γ-amino acid, the penta-coordinate phosphorus intermediates were investigated by theoretical studies. The structures and relative potential energies of the intermediates were obtained by Gaussian98. The self-activation effects of phosphoryl group among α-Alanine, β-Alanine, and γ-amino butyric acid were studied by theoretical approach under B3LYP/6-31G** level (Jiang et al., 2003; Chen et al., 2001, 2002; Chen and Tan et al., 2001, 2003, 2004). The results showed that the structural differences among the α-, β-, and γ-amino acids could be distinguished by the formation of a penta-coordinate phosphorous IMPCA during phosphorylation on the amino group.

It was found that phosphoryl histidine and Ser-His dipeptide could cleave nucleic acids, proteins and esters in neutral condition (Li et al., 1995; 2000). In order to study the key features of DNA cleaving activity, molecular mechanic and docking techniques were used. Molecular interaction between seryl-histidine (or seryl-histidine related dipeptides) and DNA model molecule 5′-TpTpdC-3′ was studied by a molecular docking procedure (Sun and Chen et al., 2004; Sun and Ma et al., 2004; Sun et al., 2003; Liu et al., 2005). The key structural features of DNA cleaving activity study showed that a negative binding energy, a contactable O–P distance, and a multiple binding sites are all very important structure features.

After a long and systematic study on phosphorus chemistry, especially the function of phosphoryl amino acids and phosphoryl nucleosides, we proposed a hypothesis of “co-evolution of protein and nucleic acid” (Zhao and Cao, 1994, 1999; Zhou et al., 1996; Cheng et al., 2005). It was suggested that peptides and nucleic acids could be co-originated from phosphoryl amino acids. As volcanic activity on primitive earth was probably frequent, pyrophosphate and polyphosphate probably accumulated on the earth’s surface. They might have reacted with amino acids to form N-phosphoryl amino acids. The high energy of the P-N bond in phosphoryl amino acids could be transferred to peptide bonds and phosphodiester bonds through reaction with amino acids and nucleosides. Therefore, the reactions of N-phosphoryl amino acids could be considered as a model to study many processes of life origin, such as chiral origin and genetic code origin. This viewpoint has attracted popular attention (Landweber, 1999).

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P-28. THEORETICAL STUDY ON AGGREGATES OF SERYL-HISTIDINE AND HISTIDYL-SERINE DIPEPTIDE WITH 5′-TpTpdC-3′

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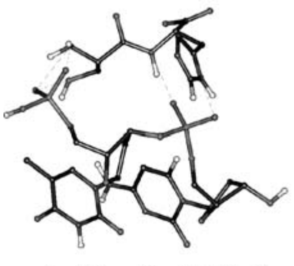
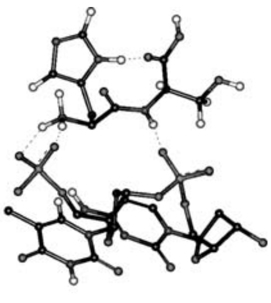
“Where there is life, there is phosphorus” (Todd, 1981). Many experiments have shown that phosphorus plays an important role in the formation of biomolecules such as amino acids, nucleosides, nucleotides, peptides, oligonucleotides and nucleic acids in prebiotic conditions. Phosphorus was even chosen as a standard of the existence of life in space (Weckwerth etal., 1995). As well known, the origin of life on the earth is one of the most difficult scientific puzzles (Joyce, 1989; Orgel, 1994), and the particular role of phosphorus has attracted much attention.

In our lab, it was found that Ser-His dipeptide could cleave nucleic acids in neutral condition (Li et al., 2000). Compared to short peptides, such as Lys-Trp-Lys and Lys-Tyr-Lys, which are able to cleave DNA strands (Ducker and Hart, 1982), Ser-His dipeptide is the smallest peptide able to cleave various natural substrates so far, and it is also the first reported DNA hydrolysis agent containing no metal ion. In this paper, aggregates of Seryl-histidine (Ser-His) and Histidyl-serine dipeptide (His-Ser) with DNA model compound 5′-TpTpdC-3′ are studied with DFT method. The molecular orbital energies, Mulliken charges and atomic orbital contribution to the frontier molecular orbital analysis show that Ser-His is more specific in recognizing DNA than His-Ser. This study verified the cleavage mechanism of DNA by Ser-His that the protonated amino group and imidazole group bind with the phosphodiester backbone by hydrogen bonds, then the hydroxyl group of Ser attacks phosphorus to hydrolyze the phosphodiester via a penta-coordinate phosphorus intermediate.



Ser-His···5′- pdTpdC -3′



His-Ser···5′- pdTpdC -3′

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P-32. STABLE AT HIGH TEMPERATURE: HOMOGENEOUS STACKING AGGREGATES OF ADENINE, ADENOSINE AND CYTIDINE IN WATER, OBSERVED BY LUMINESCENCE

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Unusually stable at high temperatures and relatively well luminescent stacking aggregates (dimers, trimers etc), with quantum yields of luminescence more than 0.01 were revealed in the homogeneous aqueous solutions of adenine, adenosine and cytidine (phosphate buffer, pH 7.0), with the concentrations 0.00003–0.01 M and in the water-salt solutions with (NaCl) up to 0.1 M for adenine. These stable stacking aggregates don't dissociated even at 85 °C, while usual stacking dimers in ApA, studied by absorption UV and CD spectroscopy, are one-half dissociated at 27 °C (Powell et al., 1972).

The luminescence spectra maxima of stable stacking aggregates of adenine and adenosine are shifted to long wave side in relation to the monomer spectra. For stacking dimers are founded the bands with maximums 400 and 435 nm, for the large aggregates (possibly, trimers and tetramers) – at 480 and 500 nm. In excitation spectra of stacked dimers is observed a strong exciton splitting 3500 cm^{-1}, because the interplane distance is very small – 3.0A (dipole-dipole interaction model). Earlier the stacking dimers with the same spectra of luminescence and its excitation were observed in works of our group for ApA at room temperature (water-salt solution) and at 77K (ethyleneglycol:water glass, 1:1, v) (Rapoport and Kononov, 1988; Kononov et al., 1993).

The study of the dependence of luminescence intensity of the adenine and adenosine aggregates bands on the temperature (18–85 °C) demonstrated their stability even at 85 °C. The fall of the intensity of aggregates luminescence with the temperature rise is the same as for monomers and may be explained by the temperature quenching only. Moreover, for adenosine it was observed that the warming up at 85 °C leads to a rise of aggregates concentration in the solution (approximately three times at 1.5 hours of warming up).

For the cytidine solutions the analogous results were obtained.

The stability of the revealed aggregates can be caused by small interplane distance (about 3.0 A). Furthermore, we have proposed the hypothesis that this unusually stability can be enforced by the water or/and salt bridges, bounding the nitrogen atoms of different molecules in aggregates. For adenine is possible the formation of three such bridges that may gives the rise of bound energy at about 1 eV.

The stability of the revealed stacking aggregates allows us to consider them as quasi-dinucleotides or the quasi-polymers (for the case of a large quantity of molecules in the aggregate) with the same information properties, as for oligonucleotide or RNA- molecule, i.e. as proto-RNA.

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P-34. PURIFICATION AND FORMATION OF L-TRYPTOPHAN HOMO-OLIGO PEPTIDE AS ACTIVATED BY PHOSPHORUS OXYCHLORIDE

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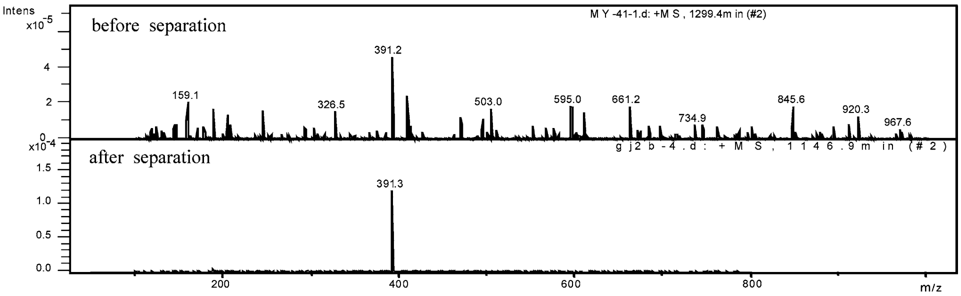
Peptide synthesis is an important issue in life chemistry. Among the methods for peptide synthesis, self-assembly of amino acid into peptide Lu et al., 2002; Zhou et al., 2002, abstracts intensive attention in recent years. In this paper it was found that L-tryptophane could be assembled into dipeptide to tetrapeptide as mediated by phosphorus oxychloride in THF. And the reaction was faster in THF than in acetonitrile. But there was no reaction in benzene. The length of formation peptides were increased if the reacting time was prolonged. Higher temperature could accelerate the reaction. Under the best condition, dipeptide Trp-Trp was prepared in 21% yield.

Reaction and separation: L-Trp and equimolar $POCl_3$ reacted in THF, 60 □, stirring for 15 minuts, quenched with H_2O, condensed below 40 □, separated by silica gel thin-layer chromatography, developing agent is the mixed solvents of $CHCl_3$, CH_3OH and H_2O(65:25:4, v/v), analyzed by electrospray ionization mass spectrometry. The mass spectrum of the sample before and after separation is shown as Scheme 1.



Scheme 1. Analysis by electrospray ionization mass spectrometry.

Acknowledgements

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P-35. AN AMINO-ACID BASED PROTOMETABOLIC SYSTEM: THE PRIMARY PUMP SCENARIO. IMPLICATIONS ON THE EMERGENCE OF HOMOCHIRALITY

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Prebiotic chemistry (as biochemistry) is not a static landscape, and chemical evolution towards the origin of life cannot just be straightforward organic synthesis. Besides understanding the emergence of biogenic molecular structures, prebiotic chemistry must understand the grow-up of interactions between those, which very probaly occurred in an open-flow environment and further lead to metabolisms.

Our working-group is currently investigating amino acid and peptide prebiotic chemistry. After having provided new insights on the Strecker synthesis of amino acids in a prebiotic scope (Taillades, 1998; Commeyras et al., 2005), then proposed a prebiotically relevant synthesis of amino acid *N*-carboxyanhydrides (NCA, the best-known polypeptide precursors) through nitrosation of *N*-carbamoylamino acids (CAA) (Taillades et al., 1999), we designed an original scenario (the *Primary Pump*) that would continuously activate amino acids and CAA into NCA, thus allowing peptide formation, accumulation and evolution (Commeyras, A. et al.: 2002, 2005). This scenario includes both chemical and physical steps: a cyclic reaction pathway involving (i) NCA formation, (ii) NCA condensation into peptides, then (iii) slow peptide hydrolysis and epimerisation, together with the recurrent alternation of dry and aqueous periods (what might have taken place on Hadean shores, where ebb/flow cycles) to ensure properly selective conditions to above reactions. The driving force is provided by the continuous income in activated species (NO_x, cyanate) as well as by phase changes (drying, then dissolution after watering), while slow, selective degradation of peptides would allow the growing peptide pool to evolve through chemical selection.

Being built on a cyclic scheme with continuous flow of energy and matter, the *Primary Pump* scenario is a model of protometabolism. While many of its chemical features are currently under investigation, we investigate the possible implications of this scenario in the prebiotic emergence of homochirality (an universal feature of biopolymers such as proteins or nucleic acids). The ability of the primary pump to drive the prebiotic pool towards homochirality (e.g. through the amplification of small enantiomeric excess) relies on the combined stereoselectivity at different stages:

- NCA coupling with AA or peptide;
- peptide bond hydrolysis;
- peptide residue epimerisation.

Computer-simulated kinetics showed that for some sets of the above stereoselectivity factors, the racemic state is unstable, the system being irreversibly driven towards homochirality although including no autocatalytic feature Plasson et al., 2004. We then started experimental investigation in order both to better understand the phenomenon, and to refine our theoretical model with more accurate kinetic parameters, focusing to the following topics:

- The stereoselectivity of NCA condensation – well-known with amino acids – had not yet been studied with α-alkyl amino acids, for which we suspect a higher stereoselectivity. These – non-epimerisable – compounds are delivered by meteorites as non racemic, thus possibly having been continuously seeding the prebiotic pool with enantiomeric excess.

- The epimerisation of peptide residues – especially *N*-terminal – appeared important in our numeric modellings for an effective deracemisation. Such epimerisation is subject to catalysis by e.g. aldehydes. We are also concerned by the epimerisation of monomeric compounds such as CAA.

We will present some highlights on these ongoing topics, some of which involve challenging analytical techniques.

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P-37. EVOLUTIONARY TRACK OF THE GENETIC CODON COVERED BY THE TERM DEGENERACY

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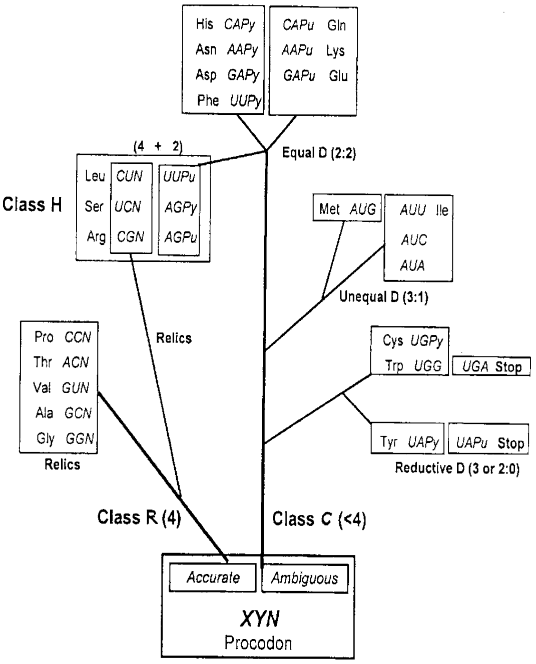
The term *Degeneracy* is unlikely appropriate to define the puzzling nature of the genetic codon that the codons per amino acid ranges from six to one but five. Rather, it covers the evolutionary track implied by such *polymorphism* of codon assignment, as seen in the dendrogram.

The structure of primitive codons (*Procodons*) has been inferred by several authors that it might have been triplets carrying two letter-codes, called *two-out-of-three* codon (XYN) (Lagerkvist, 1978; Jukes, 1983; Shen, 1987; Orgel, 1989; Ponnamperuma, 1996; Xiao, 2003), It is believed that some kind of interactions between amino acids and specific dimers of oligonucleotides would have shaped the code. Due to the different modes of interactions, three kinds of procodons have originated, resulting in the three classes in the current code. They were: (1) *Accurate procodon* (one code for one amino acid). It has still remained as relics in the code as the boxes of four synnonymous codes. Being relics of pro- codons, they are sort- ed into the *Class P (Procodon Class);* (2) *Ambiguous Pro-codon* (one codon for two amino acids), e.g., GAN for Asp & Glu. To eliminate ambiguity, the N has to be used for coding, forming two groups of *accurate codons* (XYPy; XYPu), equally distributed to each amino acid. These codons are included in the *Class C (Codon Class)* as branch *Equal D (2:2)*. In an unique case, the newly assigned third bases were *unequally* distributed, i.e. pro- codon AUN for both Ile and Met, of which 3 codons, (AU)U/C/A, have assigned to Ile, and only AUG to Met, as depicted in the *Class C,* branch *Unequal D (3:1)*. Besides, in case of the emergence of nonsense codons, *stop codons* occurred as the branch *Reductive D*; (3) *Heterologous Class* including the amino acid having *six (4+2)* codons from two different ori- gins, e.g. the six codons for Ser, of which (UC)U/C/A/G are *four* relic codons from *Class P*, and AGPy are *two* codons evolved from ambi- guouss procodons shared with Arg (AGPu), from *Class C, Equal D.*



P-38. NITROGEN FIXATION IN AQUEOUS SOLUTION INDUCED BY ION IMPLANTATION: IMPLICATIONS FOR PRIMORDIAL AMINO ACID SYNTHESIS

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The present experiments investigated amino acids synthesis in aqueous solution induced by ion implantation which was possible uniquitous on primitive Earth. When discharge was performed against ammonia water using a graphite rode as the anode under an nitrogen atmosphere, it shown that three kinds of amino acids were produced, i.e., glycine, serine and alannin. By introducing ion implantation into carboxylate solution, ammonia and amino acids were also formed via nitrogen deposition/fixation and participation of radicals. Therefore, we suggest that the impact of ions of original atmosphere components maybe played an important rol in the chemical origin and evolution of life.

P-39. POTENTIALLY PREBIOTIC CHEMISTRY OF ACYL PHOSPHATES

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Acyl phosphates are key biochemical intermediates. In extant metabolism they undergo reaction with thiols to generate thioesters and with phosphates to produce polyphosphates. Neither of these processes is efficient for simple acyl phosphates in aqueous solution. We report studies on the catalysis of reaction of acyl phosphates with nucleophiles mediated by spontaneous organisation of nucleophiles and acyl phosphates. One example of this is the ability of iron (II) minerals to mediate pyrophosphate formation. This process mimicks biochemical polyphosphate generation via substrate-level phosphorylation and, hence, demonstrates the potential prebiotic significance of these processes as sources of polyphosphates, especially in an iron-sulfur hotspring origins scenario (de Zwart et al.).

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P-40. HPLC-ESI-Ms/Ms TO IDENTIFY THE SEQUENCE OF DINUCLEOTIDES FORMED BY N-PHOSPHORYL ALANINE AND FOUR NUCLEOSIDES

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Which came first, nucleic acid or protein? This has long been a major question in origin of life studies. In previous work, it was found that N-(O, O-diisopropyl) phosphoryl amino acids (DIPP-aa) not only are capable of self-assembly into oligopeptides but also can act as the phosphoryl donor to phosphorylate nucleosides to nucleotides and oilgonucleotides (Zhou et al., 1996; Zhao et al., 2000). Therefore, the hypothesis was proposed that N-phosphoryl amino acids might be regarded as the common original seed for nucleic acids and prebiotic proteins (Zhao et al., 1994). However, how to identify the sequence of oligonucleotide in the reaction system has not been studied in detail. In this letter, HPLC-ESI-MS/MS was used to identify the sequence of dinucleotides formed by DIPP-Ala and four nucleosides in anhydrous pyridine. DIPP-Ala and four nucleosides, adenosine, guanosine, cytidine and uridine were stirred in anhydrous pyridine at constant temperature (37□) for two weeks. The reaction products were subjected to HPLC-ESI-MS. The results showed that mononucleotides and dinucleotides were observed. As shown in Figure 1, the characteristic fragmentation ion was used to identify the sequence of dinucleotides. Therefore, the sequence of dinucleotides was identified to be UpA and UpC but not ApU and CpU by HPLC-ESI-MS/MS.

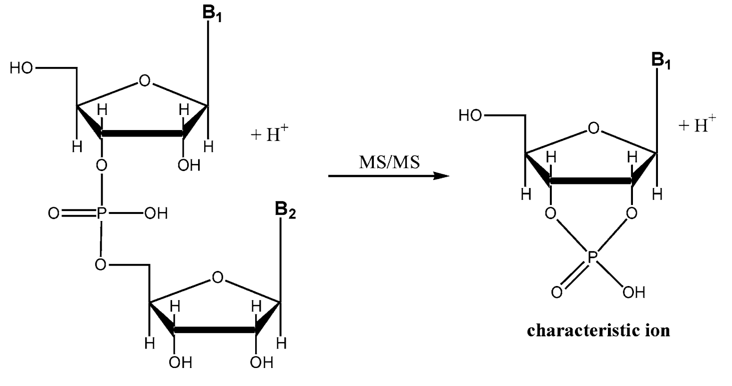

Figure 1. The characteristic fragmentation pathway of protonated dinucleotide.

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P-44. STRUCTURAL AND CHIRAL SELECTION BY PHOSPHORUS PARTICIPATION

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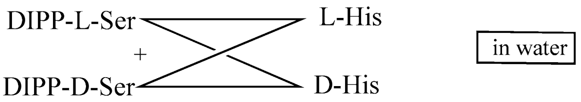
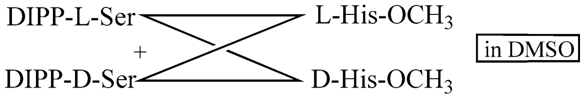
Phosphorus plays very important roles in life chemistry. In order to understand the structural and chirality selection, a series of biomimetic reactions were designed and investigated in this paper.

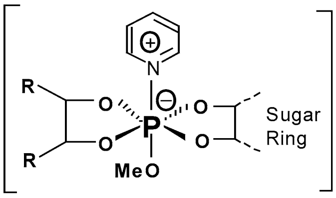
N- (O, O-diisopropyl) phosphoryl-L- (or D-) serine reacted with L- (or D-) histidine in aqueous solution, or with L- (or D-) histidine methyl ester in DMSO respectively. The reaction mixtures were analyzed by ion-pair reversed-phase HPLC with SDS as the ion-pairing reagent. It was found that dipeptide serylhistidine was formed in all these reaction systems. However, L-L and D-D type serylhistidine were yielded about four times more than that of the L-D and D-L type dipeptide.

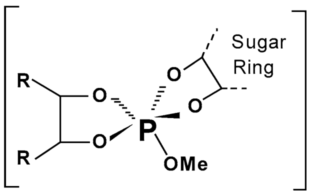




The interaction between N-phosphoryl amino acids and nucleosides in aqueous medium was studied and the products were analyzed on the basis of HPLC and LC-MS-MS techniques. The results demonstrated that peptides and oligonucleotides were simultaneously formed. Different selectivity was observed between various kinds of N-phosphoryl amino acids and different nucleosides.

In addition, various kinds of D-hexoses, D-pentose were related with penta-coordinate 1, 3, 2-dioxaphospholene respectively. It was showed that there were diversed, intermediate products formed.





The above results might give significant clue to phosphorus participation in the chemical evolution of biomolecules.

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P-45. A NOVEL REARRANGEMENT REACTION OF N-PHOSPHORYL AMINO ACID METHYL ESTERS IN ESI-MS

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N-phosphoryl amino acid showed various interesting bio-mimic reaction1. So it is significant to study them by elcctrospray ionization mass spectrometry (ESI-MSn) for further understanding their unique structures.

In this letter, N-phosphoryl amino acid esters were analyzed by ESI-MSn in positive mode. The results showed that a novel rearrangement reaction with a methoxyl group migration happened in the electrospray ionization multistage tandem mass spectrometry. A possible rearrangement mechanism was proposed that the methoxyl group migration could undergo a five-membered ring rearrangement reaction with the assistance of sodium ion2. So both the presence of metal ion and the position of phosphoryl group-methoxyl group play key roles in the rearrangement reaction3 (Figure 1).

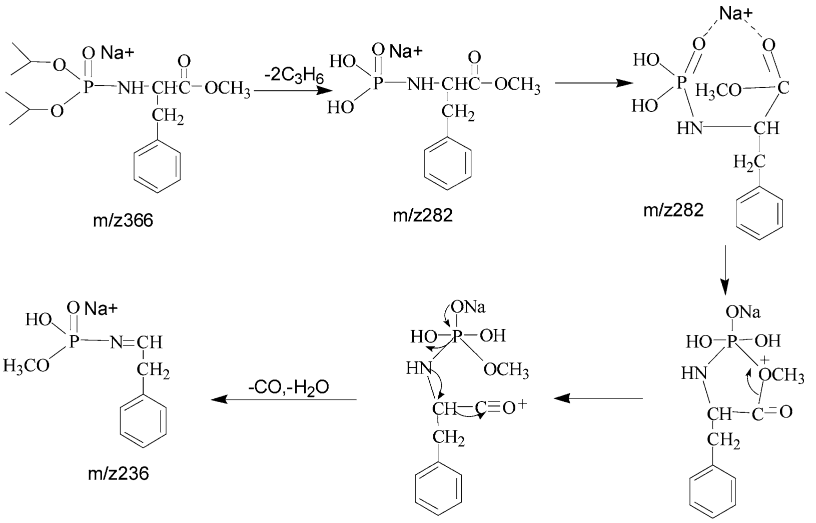

Figure 1. Possible rearrangement mechanism of N-DIPP-PheOMe.

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P-49. FORMATION OF BIOLOGICALLY IMPORTANT MOLECULES ON A MINERAL SURFACE

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There exist many reasons to believe that the synthesis of organic substances does take place in Interstellar Space, as it likely did on the Primitive Earth millions of years ago. Accordingly, a cosmic dust particle can be considered a logical place for the synthesis of organic species in open Interstellar Space. As the low temperature causes the accumulation of adsorbed molecules at particle surface, the concentration of adsorbed molecules can be even higher than the equilibrium concentration of adsorbed molecules at high pressure and high temperature in typical photocatalytic laboratory experiments. The effect of low reagent concentration on reaction rates can be also compensated by so called photoadsorption and photocatalytic "memory effect". Thus, pre-irradiated mineral particles will in methastable state for a very long time. The energy of excitation conserved in the solid particle can be realized for activation of chemical reaction at its surface at proper conditions. In this case the photo excitation of solid particle can be separated in time from the contact of molecules with particle surface. The post-sorption and post-catalytic effects can support the photocatalytic reaction in gas-dust cloud even in a case when dust particle transits from zone of irradiation (high radiation intensity, low molecule concentration) to zone of chemical reaction (low intensity of radiation, high molecule concentration). The photocatalytic reactions involving radical intermediates are known. The energy of activation of such reactions may be very small. In our work it is shown experimentally, that at adsorption of molecules adenosin 5′-monophosphate (AMP) on preliminary undergone UV to an irradiation a mineral surface (montmorillonite or SiO_2) after weak thermal influence on it more complex compounds, most likely oligonucleotides, are formed.In the control, i.e. over AMP adsorption on not irradiated surface, it does not occur. Thus, the mineral surface keeps "memory" of an irradiation which provides further formation of more complex molecules. Thus, "memory" is kept for a long time (at least, 7–10 days). Last circumstance testifies that at an irradiation, apparently, in structure of a mineral in result of the bonded water molecules' photolysis there is a formation of hydrogen peroxide which at corresponding contact to AMP molecules located side by side provides formation of internucleotide bonds. It proves to be true experiments in which the mineral surface preliminary was not irradiated, and was passed directly by peroxide of hydrogen, that also caused formation on the basis of adsorbed AMP more complex molecules as well as in case of a pre-irradiation. Preliminary comparison of results of the chromatographyanalysis of molecules again formed thus and standard oligonucleotide $(pA)_3$ has shown full agreement between the first peak chromatogramme and standard peak.(An important point is that both of these peaks are exposed by common ionic strength). This allows considering molecules formingthese fractions as three-nucleotides. So it can expect that first primitive oligonucleotides can be formedalready on the surface of the dust particles.

P-50. THERMAL POLYASPARTIC ACID MICROSPHERES

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In 1897 Schiff reported that aspartic acid polymerizes when heated to form thermal polyaspartic acid which is a branched polypeptide (*Berichte 30*, 2449). In 1958 Fox and Harada reported that a 2:2:1 mixture of aspartic acid, glutamic acid, and other amino acids copolymerize when heated to form branched thermal protein (*Science 128*, 1214). In 1959, Fox, Harada, and Kendrick reported that branched thermal

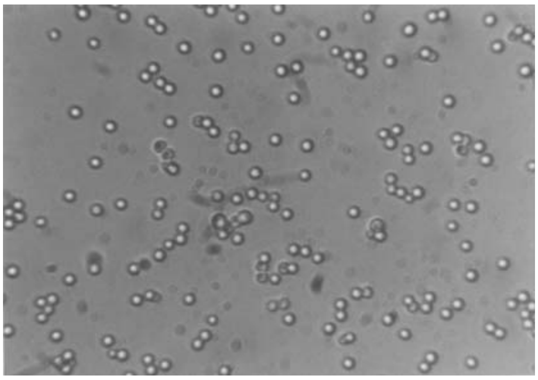

Figure 1.

protein when heated in boiling water and allowed to cool forms microspheres (*Science 129*, 1221). Apparently, the ability to form microspheres in water is not a property of modern biological proteins which are non-branched proteins. We report here that thermal polyaspartic acid alone also forms microspheres when heated in boiling water and allowed to cool. Shown below in Figure 1 are microspheres made by heating 10 mg of thermal polyaspartic acid (molecular weight range 10,000–20,000 Daltons) from Miles Laboratories in 1 ml of boiling water in a test tube and allowed to cool to room temperature .The microspheres are approximately 1 micron in diameter. Thermal polyaspartic acid microspheres constitute extremely simplified models of protocells.

P-52. MOLECULAR MODELING AND PEPTIDE DENDRIMER OF SER-HIS AND RELATED DIPEPTIDES, THE POSSIBLE SMALLEST PROTEASE AND NUCLEASE IN THE PREBIOTIC SYNTHESIS

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Previous studies in our laboratory have shown that dipeptide seryl-histidine (Ser-His) and related oligopeptides can cleave multiple categories of natural substrates, such as DNA, protein, and the ester *p*-nitrophenyl acetate (p-NPA), with the hydrolysis mechanism (Li et al., 2000). It has been proved that the hydroxyl functional group of serine serves as a nucleophile, and the imidazole functional group of histidine is the requisite group for cleavage (Wan et al., 2000; Chen et al., 2001). Our research demonstrated that the functional mechanism of Ser-His was similar to that of diverse enzymes, such as serine protease and elastase, in which the active sites

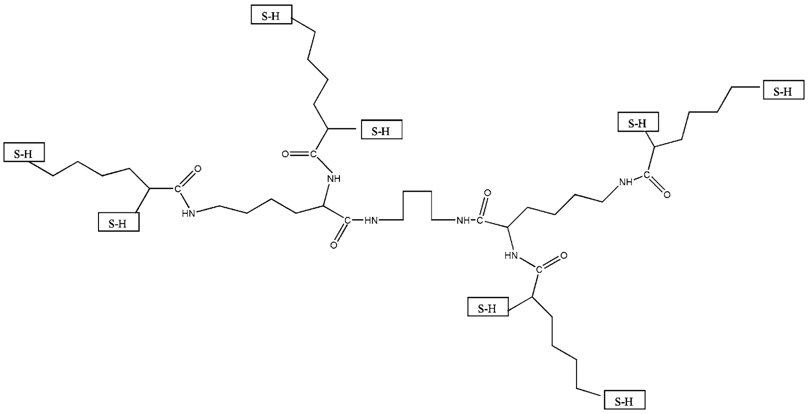

Figure 1. Ser-His attached peptide dendrimer.

are also mainly composed of serine and histidine. Ser-His, as an enzyme mimic, is attracting more and more attention for its special biological functions (Li et al. 2002; Madder et al., 2002; Brzyska et al., 2001; Reddy et al., 2004; Beloglazova et al., 2004).

Our recent investigation on DNA cleavage activity of Ser-His by molecular modeling method revealed that a negative binding energy, a contactable O-P distance, and a multiple binding sites are all very important structure features contributive to the cleavage function (Sun et al., 2004). We also decorated the Ser-His, Thr-His and Cys-His by planting them as the surface groups of a poly-lysine scaffolded peptide dendrimer (Figure 1). Electrophoresis result showed that even though these dendrimers showed extraordinary combinative inclination with DNA, its cleavage ability are not increased comparing with the monomer dipeptides under the same condition. This may be due to the enlarged size is disfavored to the combination of related residues in DNA and peptides.

The amenability of the dipeptide to variation through addition of amino acid residues, either internally or to the C-terminus while retaining its multiple cleavage activities, combined with its reactivity over wide ranges of pH and temperature, demonstrate the evolutionary capacity of the Ser/His dyad and evokes many questions about possible roles it may have played in molecular evolution and its potential role as a core for selection of oligopeptides with enhanced cleavage activities and target specificity (Li et al., 2000).

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P-55. POSSIBILITY OF DISCRIMINATION BETWEEN OPTICAL ISOMERS OF AMINO ACIDS BY SERPENTINE TREATED WITH SOME ACIDS

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Origin of chirality is one of the most important problems in a process of chemical evolution. Various predominant hypotheses about the chiral problem have been proposed. The selective discrimination by clay minerals is also offered in those hypotheses. Clay minerals have characteristics such as adsorption of organic matters and catalytic activity like polymerization. Therefore, it has been said that clay minerals might give some effects on chemical evolution. Selective adsorption of optical isomers by clay minerals had been performed, However it is difficult to discriminate between optical isomers by clay minerals, because most clay minerals do not have a chiral structure in the crystal structure. On the other hand, there is another hypothesis that the edge of a sheet silicate such as kaolinite may discriminate between optical isomers. For investigation into that, adsorption of racemic amino acids by fine particles of submicron meters of kaolinite was carried out. The fine particle of kaolinite tended to adsorb L-alanine and L-proline more than D-alanine and D-proline. Many edge pits on the surface of the kaolinite were observed by a TEM. It was predicted that the edge pit might affect L-amino acids preference of kaolinite. Chrysotile (Ch) and lizardite (Lz), which belong to serpentine ($Mg_3Si_2O_5(OH)_4$), have almost the same crystal structure as kaolinite ($Al_2Si_2O_5(OH)_4$). It is expected that serpentine discriminates between optical isomers as well as kaolinite. However, Ch and Lz hardly discriminated between optical isomers of amino acids. For that, Ch or Lz was treated with acids such as HCl, HNO_3 etc. to form the edge pit on its surface. The difference of adsorption of amino acids between serpentines before and after treating with acids is reported, here. And it is also reported whether it is possible to discriminate between optical isomers of amino acids by serpentines treated with acids. Ch and Lz were synthesized. MgO and SiO_2 ($Al(OH)_3$ were added in Lz synthesis) were mixed according to the stoichiometry of Ch and Lz. 5 gs of both the mixture and water were put in a reactive vessel. It was placed in an oven at 200 Centigrade for 4 weeks. The recovered sample was measured by XRD to confirm that serpentine was synthesized. Ch or Lz was soaked in 0.1 mol/l HCl or HNO_3 and shaken for 17 hours. After that, pH was adjust at 7 by 0.1 mol/l NaOH and Ch or Lz was washed 5 times by deionized water. Then, it was dried at 60 Centigrade in the oven. Racemic amino acids used were alanine (ala), valine (val), leucine (leu), isoleucine (ile), proline (pro), serine (ser), phenylalanine (phe), aspartic acid (asp) and glutaminc acid (glu). 200 mg of serpentine treated with acids was mixed with 7 ml of 5 mmol/l amino acid. The mixture was shaken for 65 hours. After that, pH was measured. Supernatant was separated from the mixture by centrifugation. Supernatant and starting solution were measured by a TOC. Adsorption was estimated by the carbon content in supernatant and starting solution. Further, supernatant was analyzed by an HPLC with a CD detector to find the selective adsorption. Adsorption of asp and glu by Ch and Lz treated with the acid was higher than that before the acid treatment except Lz treated with HCl. As adsorption of amino acids by Ch treated with HCl was compared with that with HNO3, adsorption of amino acids by both Ch treated with HCl and HNO_3 were almost the same except that of asp. The adsorption of asp by Ch treated with HNO_3 was much higher than that with HCl. In the case of Lz, adsorption of all amino acids used by Lz treated HCl was smaller than that before the treatment with acids. Adsorption of asp, glu, phe and ser by Lz treated with HNO_3 was higher than that before the treatment. Adsorption of other amino acids by both Lz before and after treatment with HNO_3 was almost the same. For the analysis of supernatant by the HPLC with the CD detector, D-asp, D-glu and D-phe in supernatant, which were made adsorption by Ch treated with HCl, tended to exist a little more in supernatant than L-asp, L-glu and L-phe. That means L-asp, L-glu and L-phe were a little more adsorbed by Ch treated with HCl than D-asp, D-glu and D-phe. On adsorption of other amino acids by Ch and Lz treated with HCl or HNO_3, the selective adsorption of optical isomers was not found clearly.

P-57. ASYMMETRIC PHOTOLYSIS OF THIN SOLID FILM OF AROMATIC AMINO ACID WITH CIRCULARLY POLARIZED LIGHT

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The origin of homochirality in terrestrial bioorganic compounds is one of the most mysterious issues in the study of the chemical evolution of life. Experiments on the emergence of enantiomeric excesses into solid-phase bioorganic molecules, not liquid-phase, are important for constructing models of solid-phase or surface-catalytic reactions on extraterrestrial-material surfaces, such as meteorites or interstellar dust. To clarify the emergence of enantiomeric excesses into a solid phase experimentally, we measured the optical anisotropy of amino acid films after the excitation by a physically asymmetric excitation source; left- and right-handed circularly polarized synchrotron radiation. As the sample of solid-phase bioorganic molecules, we formed thin solid films of phenylalanine, one of the aromatic amino acids, on silica substrate by deposition using a thermal-crucible?type vacuum evaporator (ANELVA VEP-38230) from crystal powder of L-, D-, and DL-phenylalanine. Thicknesses of the deposited films were measured with a quartz oscillator monitor during the deposition and calibrated by ellipsometry to the thickness of the same film sample deposited on silicon substrates. The thicknesses of the films used in this experiment were all 260 nm. To clarify the optical anisotropy of the films, we measured circular dichroism (CD) spectra of the deposited films using a spectropolarimeter (JASCO J-725). CD spectra of the deposited film from L-phenylalanine showed a positive peak at 226 and 188 nm and intense negative one at 204 nm. The deposited film from D-phenylalanine showed the exact same peak position but with the opposite sign, and the film from DL-phenylalanine presented no peaks in this region. For comparison, we also measured CD spectra of an aqueous solution of the crystal powder source (0.1 w%, cell length 0.1 mm). The CD spectra of the aqueous solution of L- (D-) phenylalanine showed a positive (negative) broad peak at 198–216 nm and a negative (positive) one at 190 nm, where the former is derived from carboxyl group and the latter from the aromatic six-member ring of phenylalanine. The CD spectra of the deposited film showed the same tendencies as those of the solution, but the CD- and photoabsorption-peak wavelength shifted in the longer wavelength direction. To introduce the asymmetry into the racemic film from DL- phenylalanine, we irradiated the film with left- and right-handed circularly polarized light separately. The circularly polarized light was introduced by synchrotron radiation from the normal conducting accelerator ring (NAR) of NTT∏s synchrotron radiation facilities. We used the bending-magnet white beam line, BL-6A, and the wavelength of the irradiated light is limited to the region longer than 180 nm by the light-extracting quartz window. Left- and right-handed circularly polarized light can be selected by changing the light-extracting angle to the plane of the electron orbital of the synchrotron ring. The CD spectra of the deposited film from DL-phenylalanine after irradiation of left-handed circularly polarized light showed a negative peak at 201 nm and no positive peaks. On the contrary, the film after irradiation of right-handed polarized light showed a positive peak at 201 nm and also no negative peaks. According to the CD spectra of D- or L-phenylalanine film, the 201-nm peak indicates that circularly polarized light in the 200-nm region selectively decomposed the six-member ring of DL-phenylalanine; left-handed circularly polarized light preferentially decomposed D-phenylalanine resulting in the appearance of the L-phenylalanine. In the case of right-handed circularly polarized light, the reverse occurred. Carboxyl-originated 226 nm peaks of both D- and L-phenylalanine film cannot be observed in the photodecomposed DL-phenylalanine film because of their weak photoabsorption. Further investigation of the mechanism of photochemical asymmetric reactions in solid-phase bioorganic molecules is necessary. In summary, we have observed asymmetric photolysis of aromatic amino acid in the solid phase. The emergence of enantiomeric excesses into bioorganic molecules in the solid phase by circularly polarized light is effective enough to demonstrate the origins of terrestrial homochirality via the solid-phase or surface-catalytic reactions on extraterrestrial materials.

P-58. STABLE NON-RACEMIC STATES IN FAR-FROM-EQUILIBRIUM SYSTEMS AS ORIGIN OF HOMOCHIRALITY

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The onset of homochirality is a key element in the understanding of the origin of life. This subject is particularly appealing, as part of the philosophical question of the meaning of symmetry in nature. How asymmetry could originate in an universe endowed with symmetrical laws, without contradicting the Curie's Principle (Curie, 1894). There are two possibilities to explain symmetry breaking: Explicit symmetry breaking, involving an asymmetry of the environment (e.g. presence of circularly polarized light) or of the fundamental laws (e.g. asymmetry of weak forces). These effects are however very weak, and won't be detailed here. Spontaneous symmetry breaking (SSB), where asymmetry emerge in a totally symmetric environment. Obtaining a SSB from a racemic system (symmetric state) to a homochiral system (asymmetric state) implies specific conditions. The racemic state is favored for entropic reasons, and is always the only stable state at equilibrium. As a direct consequence, the system must be out of equilibrium, implying the system to be non-isolated (i.e. a continuous matter or energy flux must exist to maintain a stable stationary non-equilibrium state). Moreover, in order to favor asymmetric states over symmetric states, each enantiomer must increase its own formation, either directly or indirectly. This means chiral autocatalysis is required in the reaction network. On top of that, the autocatalysis must be nonlinear to be effective (de Min et al., 1988; Saito and Hyuga, 2004; Kondepudi and Asakura, 2001). Such chiral autocatalysis can be embodied in real system either by a direct non-linear autocatalysis, or by an indirect network autocatalysis. Thus, such SSB will be characterized by the following facts: 1. The system should be far from thermodynamic equilibrium 2. Due to chiral autocatalysis, when sufficiently far from equilibrium, the symmetric state should become unstable, and the asymmetric should become stable. By symmetry, there will be two asymmetric states, each similarly dominated by one enantiomer. 3. Infinitesimal asymmetric perturbations can occur, allowing a transition from the unstable symmetric state to one of the stable asymmetric states. In these conditions, SSB occurs in a totally symmetric system, without infringing

Curie's principle. Firstly, the set of all asymmetric solutions preserves the symmetry of the kinetic rate equations. Secondly, considering the evolution of a given system, the cause of the asymmetry of the finale state originates in the asymmetry of an infinitesimal asymmetric fluctuation, further amplified by the process. Initial asymmetric perturbation is obviously present in any situation. The finite number N of molecules implies a statistical fluctuation of the enantiomeric excess, proportional to square-root of N, around the racemic state. Thus, an external asymmetric action is not required, as asymmetric perturbations are inherent to the system. In this scope, several chemical systems can be described, both theoretically and experimentally: Some crystallization system can generate homochiral crystals from a racemic liquid. Such reactions are based on direct non-linear autocatalytic mechanisms on the growth front of crystallization (Kondepudi and Asakura, 2001; Asakura et al., 2005). This system is fundamentally open, as the growth front is continuously fed with an incoming flow of liquid compounds, and generates a continuous outgoing flow of crystals. A theoretical reaction network, based on experimental works, is developed, showing how homochirality can emerge in a simple prebiotic system of amino acids and short peptides. It is based on an indirect network autocatalysis, generated by the embedding of stereoselective reactions in a totally recycled system of amino acid derivatives, maintained out of equilibrium by a continuous energy flow. The whole reaction network constitutes an early protometabolism pattern (Plasson et al., 2004). In that scope, very strict prebiotic conditions are necessary, requiring a far-from-equilibrium state. This can ensure the emergence of a stable non-racemic system.

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P-59. CHIRAL SYMMETRY BREAKING IN GROWTH FRONT OF CONGLOMERATE CRYSTAL PHASE

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In far-from-equilibrium open systems, self-organized states such as oscillations, propagating chemical waves, and spatial patterns, can be generated. In these cases, irreversible dissipative processes such as chemical reaction, diffusion, and heat conduction, cause fluctuations to grow and drive the system to organized states. Since the irreversible dissipative processes that wiped out the fluctuation in isolated system create and maintain the organized states in far-from-equilibrium open system, they are called dissipative structures (Kondepudi and Prigogine, 1998). Life itself is a dissipative structure and the self-organized complex behaviors are ubiquitous in living systems. Chiral molecules such as amino acids and sugars have a set of isomers called enantiomers that are mirror image with each other. The both enantiomers are identically produced if one synthesizes chiral molecules by regular chemical reaction. However, living systems on earth are dominated by left-handed amino acids and right-handed sugars. The phenomenon can be regarded as an example of self-organized state in far-from-equilibrium system. This asymmetric state is maintained in open living systems through the flow of matter and energy. Kondepudi and Nelson formulated a general theory of spontaneous chiral symmetry breaking in open chemical systems that have an inflow of reactants and an outflow of products (Kondepudi and Nelson, 1985; Kondepudi and Asakura, 2001). A real chemical reaction system in which chiral symmetry breaking occurs in accordance with the specific reaction steps in the Kondepudi-Nelson's model, however, has yet to be realized. Primary nucleation from supersaturated solution or supercooled melt is a slow process, while crystal growth and secondary nucleation proceed autocatalytically. From its supercooled molten phase, 1,1′-binaphthyl can crystallize as a conglomerate of R and S crystals. The crystal growth and secondary is thus chirally autocatalytic in this case. In addition, 1,1′-binaphthyl in its molten phase is always racemic due to its high racemization rate. We have analyzed the crystallization in which chiral asymmetry is spontaneously been generated (Kondepudi et al., 1999; Asakura et al., 2002, 2003, 2004, 2005). Our experiments have indicated that, under some conditions, the growth front of crystal phase of 1, 1′-binaphthyl shows many of the characteristics of an open system in which chiral symmetry is broken, i.e., the growing solid phase becomes predominantly R or S. Under appropriate conditions, distribution of enantiomeric excess (ee) of the crystal phase was bimodal at around 60%. In addition, the ee was mass independent showing that the growing front maintains a constant ee, which is a clear signature of open systems in steady state. Based on these experimental results, a kinetic model to explain the chiral symmetry breaking transition in the growth front of a conglomerate crystal phase of 1,1′-binaphthyl is formulated. The model is based on growth due to attachment of R or S growth units to a crystal surface in a supercooled melt. This model contains a chirally autocatalytic step, as in the Kondepudi-Nelson model, but does not contain a cross-inhibition between the enantiomers. An asymmetric and a symmetric steady-state solution which do not intersect were found in the model. Through linear stability analysis, the critical point for the strength of chiral autocatalysis, at which a symmetric solution becomes unstable and makes a transition to an asymmetric solution, is determined. The results of the computer simulation of the model were consistent with the linear stability analysis. In this paper, we summarize our research on the chiral symmetry breaking in the growth front of conglomerate crystal phase of 1,1′-binaphthyl as one of the examples of self-organized dissipative structure. Though the material itself does not related with any biomolecules, the concept introduced here is also applicable to other same crystallization system in which biomolecules are involved.

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P-64. RECENT PROGRESS IN BIOLOGICAL CHIRALITY

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Since the last ISSOL Conference in Oaxaca (2002) several important results have been achieved in the field of biological chirality. These results bring closer the solution of the origin of this interesting phenomenon, which apparently may have played a crucial role at the origin of life itself.

Without doubt, the most interesting result is the 2003 publication of the Soai-group (Tokyo), describing chiral autocatalysis without chiral additives. This result gives a strong argument for the "by-chance" origin of biological chirality and brings us considerably nearer to the solution of the origin. As it happens with important new findings, it opens also a lot of new questions, such are the identity of racemates or the possibility whether this by-chance phenomenon controls alone the origin of biological chirality, or it is (was) mixed with other influences, as (first of all) weak nuclear forces. The lecture will primarily discuss these open questions.

Another interesting approach to the biological chirality came from a group of Israel- and California-based scientists (Shinitzky, Deamer, et al) regarding observations about the different chemical identity of D- and L-amino acid "enantiomers". This again opens new questions and the lecture will concentrate upon these new perspectives.

Palaeontology brings one of the oldest messages about the early existence of biochirality in the form of macroscopic morphological chirality of some fossilized organisms. An exciting report (Soulie Marsche) decribes the change of the direction of morphological chirality at Charophytes, cca 250 Myears ago. This result and possible interpretation will be reported shortly.

Preparative coordination chemistry offers some new aspects to Wachtershauser's fundamental ideas about the role of transition metal catalysis around the origin of life. Recently some new results (by the Authors) about the transfer of chiral information within ligands of coordination compounds (Co) as well as the use of such effects in organic synthesis (Cr). These results will be summarized in the lecture and their significance for the origin of biological chirality will be discussed.

P-66. THE ORIGIN OF HOMOCHIRALITY EXPLORED BY A NEW THEORY MODEL

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The most important two questions facing the origin of life is the origin of genetic code and homochirality. In this paper, a theory model to expatiate the chiral selection mechanism for amino acids was built. Of course, the spontaneously interaction between the free amino acids and ribonucleotides occurs at a very low rate (Zaia, 2004). It was proposed before that the charged phosphate groups might serve as not only surface-bonding mediation, but also fulfilling the functions of connectors and activation (Arrhenius et al., 1997). Here in this letter, the free amino acids and ribonucleotides could be connected by the charged phosphodiester bonds. Accordingly, a structural model with amino acid side chain stereo specifically interacted with the bases of ribonucleotides was built. In order to clarify the chiral selection the 160 formation potentials with 20 amino acides, four ribonucleotides and two enantiomers were calculated. It was found that the selected rate of the L-amino acids is 59% by ribonucleotides and that of the D-amino acids is 40%. It is worth noting that the rate of L-amino acids selection is explicitly higher than that of D-amino acids for the earliest, or the oldest amino acids: Ala, Ser, Asp, Glu and Val (Di Giulio, 2004; Trifonov, 2000), except glycine which was no chiral center. The favorable selection for the L-amino acids is 90% and that of the D-amino acids is only 10%. Here, the formation potential mainly consists of hydrogen bonding, van de Waals, electrostatic, and so on. However, for the later or the younger amino acids, the L-enantiomers binding with ribonucleotides are not prior to D-enantiomers in term of the formation potential. It implies that the chiral selection of the later or younger amino acids had somehow already abandoned strict stereochemical/physicochemical determinism. It was rationalized that the oldest amino acids first appeared (the precursors), (Ala, Ser, Asp, Glu and Val, except for Gly), might be selected as L-enantiomers. While the other amino acids developed biosynthetically from these precursors.

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P-67. A RAMAN SPECTROSCOPIC TEMPERATURE STUDY OF -NH_3^+, -CO_2^-, αC–H MOTION RELATED TO THE HYDROGEN BONDING DYNAMICS OF D-AND L-ALANINE

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One of the greatest challenges in the field of life science is the origin of homocharlity in molecular biology. Parity violation leads to energy differences of enantiomers in $10^{-15} - 10^{-12}$ $Jmol^{-1}$ range. Different concepts for spectroscopic experiments on parity violation can be distinguished by the nature of the transition because of the corresponding transition energies $h\nu_L$ and $h\nu_D$ will be slightly different, such as NMR, IR or Raman spectroscopy. The temperature-dependent Raman spectra measurements of D- and L-alanine crystals have been performed by using a Jobin Yvon T64000 spectrometer. This study presents a new insight into the temperature dynamics difference between D- and L-alanine in three main aspects: First, we have found the difference of the lattice instability between D-and L-alanine single crystal in the range 170–250K. Second, the behavior of the modes at 1305 cm^{-1} corresponding to the αC–H bending of alanine molecule. An obvious difference in the full width of half-maximum intensity of 1305 cm^{-1}, which is characterized by a micro-transition $\sim$250 K of D-alanine and $\sim$170 K of L-alanine in the b(cc)b geometry. Third, the peak at 482 cm^{-1} (at 290 K) in the b(cc)b spectrum corresponds to the localized -NH_3^+ torsion of alanine molecule. Because each of the three protons in the -NH_3^+ group is coupled to a neighboring molecule by the N–H. . .O hydrogen bond, the torsional motion of this -NH_3^+ group is correlated with the dynamic behavior of hydrogen bonding. It is found some humps presented at both the low and the high-frequency sides and the spectral intensity distribution is asymmetrical. The features indicate that the -NH_3^+ torsion is anharmonic. Temperature-dependent Raman spectra show the crystal lattice distortion, -NH_3^+ torsion, -CO_2^- bending and the contribution of αC–H. . .O=C interaction which related to the E_{PV} energy as a function of the -CO_2^- and -NH_3^+ torsion angles. Observation of the behavior of dynamic hydrogen bonding between D- and L-alanine, which could be attributed to the parity-violating weak interactions. Because the molecular arrangement is restricted by the crystal lattice so the configuration transition of D- to L-alanine is impossible. According to our recent findings of the boson peak of D- and L-alanine at cryogenic temperature, we demonstrate an intrinsic nature of bifurcated amplification mechanism. The indirect universal systematic influence of the electroweak interactions on the prebiotic-biotic transition, through the parity-violating energy differences in enantiomer, may have specifical contribution to the terrestrial biomolecular homochirality.

P-68. THE NATURAL EARTH'S ORBITAL CHIRALITY FORCE FIELD AND ITS ROLE IN THE ORIGIN OF LIFE AND CHEMICAL EVOLUTION

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This presentation discussed the existence and roles of the natural Earth's orbital chirality (EOC) force field with both right-handed helical chirality and rhythms (Figure 1). All terrestrial living beings, including ourselves, are living in the natural EOC force field that is able to interact with the chiral molecules/particles to result in chiral effects. Our studies showed that the natural EOC force field might play an

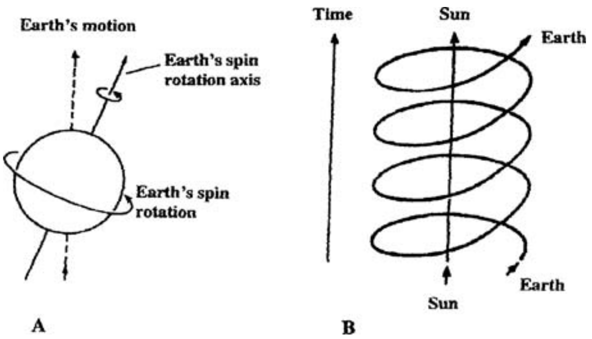

Figure 1. The natural right-handed helical Earth's Orbital Chirality (EOC) force field, it is produced by both the Earth's right-handed helical rotation around its spin rotation axis (A) and the Earth's helical revolution around the Sun (B).

important asymmetrical mechanic role in the origin of biomolecular homochirality, the unification of chiral asymmetries on different levels, and the origin of biological rhythms [Y.J. He *et al.*, *Medical Hypotheses* 1998, 51(2): 125–128; 2000, 54(5): 783–785; 2000, 55(3): 253–256]. According to the further theoretical and experimental studies [Y.J.He *et al.*, *Medical Hypotheses*, 2001, 56(4): 493–496], it was also suggested that 1) the natural EOC force field could serve as the driving force of biomolecular evolution via the chiral interactions; (2) the EOC force field could cause the origin of non-coding repetitive DNA sequences ("Junk DNA") to increase the genomes stability and complexity; (3) the EOC force field could increase the structural order of biological systems via the biomolecular EOC stabilization energy effects; (4) the biological information could be spontaneously produced by the chiral interactions of the protogenes with the EOC force field. In our recent unpublished work, it was demonstrated that there also was the "circadian rhythm" in the process of β-decay, it was suggested that the weak force that produces the symmetry violation in β-decay might originate from the natural EOC force field.

Thus, in our opinion, it was strongly believed that the natural EOC force field, as the source of the natural force with both right-handed helical chirality and rhythms, should play a key role in both the symmetry breaking (violation) and biological rhythms to result in the origin of life and chemical evolution on the Earth.

P-74. OLIGONUCLEOTIDES FROM MONTMORILLONITE CATALYSIS; ANALYSIS AND MODELLING

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The formation and analysis of oligonucleotides within the framework of an RNA world is one of the key areas within the Origin of Life. Activated nucleotides can be catalysed by minerals fo form long oligomers, with the goal being to determine if any of the longest oligomers exhibit biological activity.

Montmorillonite-catalyzed synthesis of oligonucleotides has been expanded to include new reagents and new analytical methods in an attempt to provide evidence of the longest oligomers which may be formed in these reactions.

The standard methodology has recently turned to using an alkali metal chloride solution buffered with MOBS at pH 8.00 with an activated nucleotide with a homoionic Montmorillonite.

$\mathrm{ImpA} \rightarrow (\mathrm{pA})_n$

$\mathrm{ImpU} \rightarrow (\mathrm{pU})_n$

(plus pyrophosphates and cyclic products)

Lithium, sodium and potassium chlorides all work efficiently and hplc traces are qualitatively identical, with oligomers up to the 10 or 11-mer being identified by hplc together with pyrophosphate containing long oligomers.

Samples have been subjected to MALDI-TOF mass spectrometry and oligomers up to $n = 35$ in the $(\mathrm{pA})_n$ series and 25 in the $(\mathrm{pU})_n$ series are readily detected; this analysis is ongoing.

Products containing $2'$-$5'$ linkages are unaffected at this linkage when hydrolyzed by RNase T2 digestion. Thus $2'$-$5'$ linked ApA and ApApA can be identified and the amounts compared with the theoretical hydrolysis products.

However, the presence of pyrophosphate-containing long oligomers (one pyrophosphate per oligomer chain) prevents a simple analysis of the enzyme hydrolysis products from any given oligomer fraction containing both the non-pyrophosphate and pyrophosphate containing compounds. Moreover, the number of isomers possible when $2'$-$5'$ and $3'$-$5'$ links are considered as well increases dramatically more rapidly with oligomer length than it does for the simpler oligomer.

Numerical analysis of the theoretical hydrolysis products available from materials has been compared with the experimental values obtained. With the Solver Macro in Excel, simultaneous agreement from 7-mer to 13-mer has been reached between these values and the numerical model

Reactions involving enantiomeric mixtures of reactants (ImpA (D and L), and ImpU (D and L) have been analysed and the numerical analysis has assisted in clarifying the chiral selectivity of the processes involved here.

Retro numerical analysis of trimers in terms of occurrence and percentage v selectivity for the products derived from ImpA and ImpU display surprising complementarities

The dimers and trimers obtained from the experiments involving D-L ImpA and D-L ImpU were modelled using Spartan'04. A molecular mechanics derived conformational analysis revealed that the dominant isomers obtained from the clay catalysed reactions are not the most thermodynamically stable products neither in cyclic nor linear cases.

P-77. GENETIC ENCODING OF 4-, 5- AND 6-FLUOROTRYPTOPHANS: ROLE OF OLIGOGENIC BARRIERS

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The universal genetic code encoding twenty canonical amino acids has remained invariant over possibly the past two billion years other than limited changes in codon assignments in some genomes. This had raised the question of whether the code is in fact frozen and immutable. The basic mutability of the code was first proven when mutants of Bacillus subtilis were isolated which could encode 4-fluoroTrp in replacement of Trp, or even completely rejecting Trp itself as incompetent analogue, in the ensemble of encoded amino acids capable of supporting indefinite cell growth (JT Wong, Proc. Natl. Acad. Sci. USA 80, 6303–06, 1983). In the present study, the LC33 mutant of B. subtilis Trp-auxotroph QB928 has been further mutated to enable the encoding of 5-fluoroTrp and 6-fluoroTrp for indefinite growth. Mutants unable to grow on Trp also could be readily back mutated to regain this capacity. Withdraw of individual amino acids, nucleosides and other growth factors showed that most withdrawals did not prevent LC33 growth on 4-fluoroTrp. These observations, along with similar observations on 5-fluoroTrp or 6-fluoroTrp supported growth, suggest that the barrier against the admission of novel amino acid analogues into the genetically encoded amino acid ensemble is controlled by only a small number of proteins where the function of the analogue is particularly inadequate. The mutation of the genetic code to admit an amino acid analogue even as toxic as 5-fluoroTrp may thus require overcoming the functional bias of only a small number of proteins. Therefore a continued opening of the genetic code to a wide range of amino acid analogues for indefinite growth and protein engineering appears feasible through the mutational removal of such oligogenic barriers to evolution and change. This study was supported by the Research Grants Council of Hong Kong.

P-79. MOTIF SHUFFLING IN RNA MOLECULES: STRUCTURAL CONSTRAINTS IN THE ACQUISITION OF FUNCTION

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In the early stages of biochemical evolution, molecular size was strongly constrained by the accuracy in replication. In an environment where proof-reading mechanisms were initially absent, information had to be stored in short macromolecules (i.e., short RNA or RNA-like chains). In that scenario, it is likely that each molecule performed a single, simple function, and participated in a network of chemical reactions. The appearance of such networks (hypercycles among them) represented a way to increase the information encoded in primeval genetic systems. The initial repertoire of small functional and structural (molecular) variants was formed by the basic motifs which, once replication fidelity increased, could combine to produce larger, multifunctional molecules. At that subsequent stage, evolutionary processes additional to the accumulation of advantageous mutations, such as the shuffling of molecular modules or motifs, were probably acting. In this framework, we analyze the combination of different RNA modules in order to quantify the likeliness that two sequences could combine and give rise to a molecule endowed with their two original, independent functions, represented as two different secondary structures. To this end we consider two sets of molecules where different RNA sequences (covering a broad spectrum of folding abilities and thermodynamic landscapes) can fold into a given secondary structure each. The first set has as a minimum free energy configuration a hammerhead structure, known to catalyze self-cleavage reactions. The second set of sequences is characterized by a terminal hairpin structure, which can perform both RNase and RNA ligase activities. We systematically analyze all possible positions where sequences in the first set could be inserted in sequences in the second set and vice versa, and estimate the probability that the resulting molecule conserves the two original structures as independent motifs. These results might have implications for the increase of functional complexity in the first macromolecules that combined genotype and phenotype, in the context of the RNA world hypothesis.

P-81. INTERACTION EXPERIMENTS BETWEEN RNA MOLECULES AND PHOSPHATE MINERALS

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Transmission of genetic information is an essential factor for life, and it is presumed that RNA played a primary role in the first primitive life. Howaver, little is known about formation processes of RNA in the chemical evolution. RNA is made of nucleosides (composed of sugars and bases) and phosphoric acids bound by phosphodiester linkages between sugar parts of nucleosides and phosphoric acids. It has been suggested that the linkage can be formed through surfaces of phosphate minerals. To examine this possibility, it is necessary to study interactions between precursors of RNA and phosphate minerals. In this study, hydrothermal experiments were conducted using adenosine as a nucleoside and hydroxylapatite(HAP) as a phosphate mineral. Another series of experiments between HAP and ribose which is a sugar composing RNA was also conducted. First, adenosine solutions were heated with and without HAP at 140 °C for 1 × 10 days. UV-visible spectroscopy and ATR-IR spectroscopy were used for analyzing product solutions. UV-visible spectra of product solutions were different from that of the starting adenosine solution. And, the spectral shapes of product solutions changed with heating time. The absorbance at 260nm decreased with time. And this decrease rate was increased by HAP. ATR-IR spectra of product solutions with HAP indicated absorption peaks by phosphoric acids dissolved from HAP. Peak heights of these dissolved phosphates decreased from 6 days heating. Next, adenosine solutions with and without HAP were heated at 120 °C for 1 × 10 days. UV-visible spectra of product solutions changed, and these changes depended on the presence or absence of HAP. ATR-IR spectra of product solutions with HAP indicated absorption peaks by phosphoric acids dissolved from HAP. Based on these experimental results of adenosine-HAP systems heated at 120 °C or 140 °C, a possibility was suggested that the part of ribose(sugar part of adenosine) caused the change of heated adenosine and the interaction between adenosine and HAP. Therefore, heating experiments using ribose solutions with and without HAP at 120 °C for 1 × 3 days were conducted. As a result, film-like products were formed on the surface of product solutions. And the color of product solutions depended on the presence or absence of HAP. UV-visible and ATR-IR spectra of product solutions indicated that substance C=O containing substances were produced in solutions. There production rate was increased by HAP. To produce RNA, it is necessary that the phosphoric acid and the ribose part of adenosine binds together without decomposition of adenosine. The present experimental results suggested this possibility during the interaction between adenosine and HAP, although further detailed systematic studies are needed.

P-82. EXPLORATORY STUDIES TO INVESTIGATE A LINKED PREBIOTIC ORIGIN OF RNA AND CODED PEPTIDES

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The lack of a prebiotically plausible synthesis of ribonucleotides has previously been seen as a major difficulty associated with the RNA world hypothesis. Work in the Manchester group has previously shown the conversion of D-arabinose-3-phosphate into D-ribocytidine-2′3′cyclic phosphate under potentially prebiotic conditions. The sugar phosphate was observed to react with cyanamide to give a furanosyl amino-oxazoline, which, upon reaction with cyanoacetylene, gave the desired ribonucleotide. In this process a β-configured furanose product is produced from a starting material which exists predominantly in pyranose forms. In addition, the C(2′) configuration is inverted and the phosphate is activated. My work has focused on a more detailed study of this pyrimidine base-assembly process on simple sugars, exploring the sequential reaction of cyanamide and cyanoacetylene with all the aldopentoses. Work has also been directed towards the activation of phosphate mono and diesters under conditions compatible with those needed for pyrimidine nucleotide assembly. Activation of phosphate monoesters by cyanamide, and inorganic phosphate by cyanoacetylene, have both previously been reported (Orgel and Ferris respectively). We have found that cyanoacetylene is extremely efficient at activating phosphate monoesters towards nucleophilic attack by appropriately positioned hydroxyl groups in the presence of water. The phosphate diesters produced however, appear to be inert towards further reaction with cyanoacetylene, suggesting a situation whereby the nucleobase building blocks could be used to both activate phosphate monoesters and perhaps aid oligomerisation of the nucleotides in a template-directed synthesis of longer RNA molecules.

P-83. THE NON-ENZYMATIC TEMPLATE-DIRECTED LIGATION OF OLIGONUCLEOTIDES

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RNA-ligation could be a powerful driving force for increasing complexity in the RNA-world. One possibility of non-enzymatic ligation of RNA-fragments is provided by reactions of oligonucleotides with 2′3′cyclophosphate end group that are generated in reversible transesterification reaction of RNA molecules. We investigated nonenzymatic, template-directed ligation of oligonucleotides with 2′3′cyclophosphate residue and 5′OH-DNA ligator, hybridized to the DNA template. The complex was incubated at 37 °C for 3 days in 50 mM buffer (Tris or cacodylate), containing 200 mM NaCl and 5 mM salts of different metals. The maximal ligation yield was observed at pH 8.8; some metal ions catalyzed the reaction. In the presence of Mg^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} and Pb^{2+} ions, the ligation yields reached 5% in cacodylate buffer (pH 6.0–7.2) and more than 10% in Tris buffer (pH 7.2–8.8), respectively. The obtained results demonstrate that hybridization assisted ligation of oligonucleotides, produced by RNA cleavage, can occur non-enzymatically with reasonable yield. This reaction could provide a mechanism of shuffling of RNA fragments needed for increasing complexity of RNA molecules in the molecular ensembles developing at the early steps of the RNA world evolution.

P-87. N-CARBOXYANHYDRIDES IN A PREBIOTIC AMINOACYLATION OF NUCLEOTIDES, AND PROGRESS TOWARDS A POTENTIAL PREBIOTIC RNA-CODED PEPTIDE SYNTHESIS

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The modern mechanism of peptide synthesis involves coded attachment of amino acids to RNA. For this modern process to have evolved via a stepwise pathway, a coded interaction between RNA and aminoacids is likely to have been present at an early stage. In order to explain this proposed link, Sutherland has developed a theory involving interaction between amino acids and triribonucleotides giving rise to a simplified genetic code (Borsenberger et al., 2004). There is much evidence for the prebiotic viability of short chain ribonucleotides, particularly cyclic triribonucleotides (Kawamura and Ferris, 1999). A mechanism has been proposed for the coded interaction of such cyclic triribonucleotides with aminoacids to afford aminoacylated RNA molecules capable of oligomerisation, with concomitant coded peptide synthesis. In the RNA-world hypothesis, the evolution of a coded peptide synthesis requires the initial formation of aminoacylated RNA molecules. In modern biochemistry enzyme catalysis is required for this reaction. However, in the absence of such catalysis (i.e. in an RNA-world), a robust prebiotic aminoacylation reaction is required. Amino acid N-carboxyanhydrides (NCAs) have been shown to be prebiotically plausible compounds (Commeyras et al., 2002; Lemma et al., 2004). Recent work in Montpellier has revealed that these activated amino acid species are reactive towards phosphate dianions, resulting in transient formation of mixed anhydrides (Biron and Pascal, 2004). We aimed to exploit this reactivity to test whether NCAs could be used to aminoacylate nucleotide monomers. This would also enable us to investigate a potential 3′phosphate to 2′hydroxyl aminoacyl transfer reaction required by Sutherland's current RNA/Coded Peptides hypothesis. The results of these investigations will be presented.

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P-88. PREBIOTIC EVOLUTION OF RIBOGLYCOPEPTIDES: BRIDGING THE ENTROPY GAP AT THE DAWN OF LIFE ON EARTH

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Membrane-bounded, energy-metabolizing, self-perpetuat ing cellular life, even in its simplest form, requires so much more information than a random set of organic monomers of equivalent mass, that the probability of its spontaneous emergence is astronomically low. The transition from a chemically rich but informationally low microenvironment to the high information content of the simplest living cell is one of the persistent barriers to envisioning the origin of life. The barrier is lessened, however, if the informational increment between prebiotic and biotic chemistry is minimized. Accordingly, we propose that there existed a rich repertoire of prebiotic molecules, including protomacromolecules, that persisted over a long period without precise replication, prior to the onset of life. We designate these molecules, which we envision as precursors to the RNA World, as riboglycopeptides (RGPs). The term riboglycopeptide derives from the fact that the mixture was constituted of a complex set of nitrogen bases, amino acids, and sugars, arrayed in various combinations. The following scenario traces the ascent of RGPs from simple precursors, assuming a water solution interface with a solid substrate, wherein the solutes were subjected to periodic cycles of dessication and rehydration, as would occur in transient tide pools subject to solar drying followed by reflooding: (1) Monomeric organic compounds, such as simple carbohydrates, amino acids, and nitrogen bases, are delivered to Earth by meteorites or formed by prebiotic chemical reactions driven by robust energy gradients during the terminal phase of the Great Bombardment. Many form high-energy bonds with phosphorus, given the abundance of energy and mineral phosphate (e.g. in the form of apatite). (2) Lacking consumer organisms or biocatabolic reactions, the early Earth accumulates these organic monomers to sizeable concentrations in primordial seas. (3) Along coastlines, recurrent dessication/rehydration cycles in shallow reservoirs such as ephemeral tide pools promote polymerization by dehydration condensation reactions. Since all monomers would be capable of forming bonds through condensation reactions, the combinatorial possibilities initially are vast and virtually random, forming many permutations of bases + amino acids, bases + sugars, sugars + amino acids, or all three. (4) Each dessication destroys many protopolymers, but some are more stable than others and survive to the next influx of monomers with the next flooding by sea water. (5) A succession of reconstitution and destruction cycles brings about continual change in the composition of local reservoirs, but integrated over a vast number of parallel reservoirs across the planet and extending through long periods of time, a progressive increase in complexity of constituents fills each pool. The contents are not the same across pools, but certain molecular motifs gradually emerge with higher frequency because of greater stability and/or favorable thermodynamic characteristics. (6) Increased heterogeneity of reservoir contents enables a more complicated web of interactions. With high-energy phosphate bonds readily available, endergonic as well as exergonic reactions occur. As polymers elongate, they acquire limited catalytic and autocatalytic functions, by virtue of assuming secondary and tertiary conformations. This in turn sustains an increasingly complex set of intermediary metabolic reactions. While overall average complexity of the protobiomolecular pool would progressively increase under the scenario above, it would initially remain well below that of a living cell, primarily because directed replication would be absent. However, while such a system would not replicate with the accuracy of a true biological system, it would approximate replication of the overall capabilities of the system because of residual constituents carried over through each dessication/rehydration cycle, and the bias that the residual contents would exert toward the reconstituted contents of the succeeding reservoir. We hypothesize that the RGP World persisted for a long time prior to the advent of true replication in the RNA World. During this period, an increasingly complex mix of RGPs and smaller metabolites would have persisted, never replicating in exact composition or function, but reconstituting overall system capabilities in a sustained way. This provided the time and opportunity for a true and accurate replicative system to evolve, as the bioinformatic content of the RGP World gradually approached that of the RNA World. The transition from protolife to life thus was seamless and imprecise. Once fully established, however, life would have lost all traces of its abiotic predecessors.

P-92. ABIOGENIC PTERIDINS AND FLAVINS AS PHOTOSENSITIZERS FOR PEPTIDE FORMATION AND THE ADP TO ATP PHOSPHORYLATION

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In modern organisms the derivatives of chemically and, especially, photochemically active pyrasine structure, flavins and pterins, when bound to apoprotein act as cofactors for enzymes catalyzing electron and group transfer and as photosensors. These molecules are available from abiotic processes. According to our results, besides the known abiogenic formation of these compounds in process of amino acids thermocondensation to proteinoids, pteridines are formed after UV-irradiation of an aqueous solution containing acetaldehyde and ammonium salts. Adsorption of these products on silica gel brought to a formation of organomineral matrix. This matrix was put into a quartz column through which a flow of aqueous 103 M alanine solution was passing and the whole system was subjected to UV-irradiation at 254 nm. The formation of tetraalanine was demonstrated in this experiment, whereas the passing of alanine solution through a column containing the pigment-free silica gel has brought only to a formation of dipeptide in trace quantities. The experiments to demonstrate photophosphorylation of ADP to ATP by orthophosphate were performed with proteinoid microspheres containing abiogenic pteridine and flavin pigments endogenously present in amino acid thermocondensation products. To increase the content of flavin and pteridine molecules in proteinoids, they were prepared by using of a dry mixture of glutamic acid, glycine and lysine in the ratio (8:3:1) incubated at 185 °C for 6 hrs. The pigment-containing proteinoid microspheres were obtained by treating of dry proteinoid material with boiling water, and to increase the microspheres stability orthosilicon acid was added to the suspension. The system to study photophosphorylation, in addition to pigment-containing proteinoid microspheres, contained 30 mol K_2HPO_4, 10 mol ADP and 0.05 M Tris-HCl buffer solution (pH 7.8 to 8.2) to final volume of 3.0 ml and was subjected to UV-irradiation (365 nm). In some experiments the incubation mixture also contained H_2O_2 and Cu^{2+} ions to generate after irradiation OH radical. The ATP formation was measured by luminometric luciferin-luciferase assay and additionally confirmed by the results of HPLC analysis. The formation of ATP was demonstrated in these experiments with a yield (calculated to initial ADP) up to 30%. In the analysis of mechanisms of the photocondensation and photophosporylation processes the main emphasis is made on the role of quinonoid pyrasine structure in pteridine and flavin photosensitizers as well on a possible participation of reactive oxygen species and peroxides in reactions.Supported by The Program of the Presidium of Russian Academy of Sciences[1] 25 “The Emergence of Biosphere and its Evolution” (Subprogram[1] 1) and Russian Foundation for Basic Research Grant 04-04-49625-à.

P-94. MICROBIAL ACTIVITY IN ZEOLITES DEDUCED FROM MINERAL INCLUSIONS

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Textures on mineral surfaces of phillipsites and associated chemical enrichments as a result of microbial activity have been found in samples collected during ODP Leg 197 at Emperor Seamounts at a depth of 824–936 meters below seafloor. The textures consist of cavities on the mineral surfaces, 1–5 μm in size, with a dark appearance as well as brighter globules, 1–5 μm in size, that appear to occupy some of the cavities. The cavities display a chemical enrichment in Fe but also in Ti and Mn. Both textural features show slight element enrichment of Mg as well as depletion in Na and K. The globules are interpreted either as precipitations by attached microbes or actual fossilized microbes. The enrichment in Fe indicates that Fe-oxidizing bacteria, e.g. Gallionella spp, have been responsible for the mineral dissolution, and observations of bacteria filaments of iron-oxidizing bacteria in associated volcanic glass support this. However, the variety in textural sizes and chemical enrichments implies that several different species may have been involved. Since the chemical composition of the enrichments corresponds more to microbial activity in basalts and volcanic glass than to zeolites, it is evident that the microbes have been providing elements from elsewhere. Microscopy and ESEM studies have shown that the phillipsites contain a large amount of inclusions of Fe-oxyhydroxides and altered basalt, possibly due to rapid growth rates. It is also possible that the phillipsites contain inclusions of Mn-oxides and Ti-rich minerals since such phases are abundant in these environments. Concentration of the microbial textures to these mineral inclusions indicates that the microbes used these inclusions to provide for the essential elements. This indicates that microbial activity and alteration of the oceanic crust not only are restricted to basalts and volcanic glass but also occur in a later stage in association with secondary minerals. Obviously microbes may survive and exist in a subsurface biosphere over an extended period of time. The study also shows that microbial activity in minerals increases the rate and speed of alteration in comparison to inorganic weathering and alteration, something that probably may affect the composition of hydrothermal fluids, seawater composition and mobilization of elements. But more important, this is of great significance considering the role zeolites may have played for the early life on Earth. Zeolites have been suggested, due to their ability to adsorb organic molecules, to act as ion-exchangers and molecular sieves as well as due to their characteristic internal structure, to have served as protected micro-environments where prebiotic reactions could occur and proto-organisms evolve. The observation of microbes using mineral inclusions within zeolites adds a completely new dimension to the idea. Zeolites may have acted both as micro-environments and as supplies of essential nutrients.

P-96. STUDY OF THE OSMOTIC BALANCE PROBLEM IN A MINIMAL SELF-MAINTAINING CELL MODEL

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Primitive cells that had to struggle that had to struggle for self-maintenance on a preiotic scenario had to deal with a number of difficulties, not always easy to solve.

Unbalanced osmotic pressure would lead any system composed of semi-permeable membranes to its detruction by osmolysis or plasmolysis. In order to avwid such unbalanced osmotic pressure, cellular systems had to develop an energetically active mechanis that would allow them to pump model. The model contains the following elements: structural membrane elements (*Lm*), transdrcers (*T*), molecules which combine enzyme-like molecules through the membrane (*E*), energy-rich molecules (*A*), precursors of each type of molecule (*l, t, e* and *a*, respectively) and an ionic substance (x). The energetic and kinetic conditions for the system to be energetically and osmotically coherent are presented. These conditions must lie on the set of kinetic parameters that allow the existence of kinetically stable steady states. Thus, this model provides insight about the need for energetic and osmotic balances to be mechanistically coupled in primitive celluar systems. The quantitative relations that the system could be osmotically balanced during the transition between different stationary states will be slso discussed.

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P-97. A MODEL FOR COMPARTMENTALIZATION OF A PRIMITIVE CELL

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It has been previously found that N-(O,O-dialkyl) phosphoryl amino acids could oligomerize into peptides in aqueous solution (Zhao et al., 1995) and incubation of N-phosphoryl amino acid with nulcleoside could lead to simultaneous formation of peptides and nucleotides (Zhou et al., 1996). Therefore, Zhao et al proposed the interaction of N-phosphoryl amino acids with nucleosides as a model for co-evolution of proteins and nucleic acids (Zhao and Cao, 1994). However, our recent work indicates that the supramolecular structure of vesicles from amphiphilic N-phosphoryl amino acid could block the interaction of N-phosphoryl amino acid with nucleosides effectively, which could be regarded as an experimental evidence of the compartmentalization of the primitive cell from the surroundings. An synthesized lipid N-(O,O-dihexadecyl) phosphoryl amino acids could self-assembly into stable unilamellar vesicles under appropriate conditions. The incubation of the vesicular suspensions could lead to the formation of dipeptide, which was confirmed by ESI-MS. It is considered that the suitable orientation and packing of amphiphilic molecules at the vesicle/water interface together with certain conformational freedom in the vesicular bilayer are favorable for the condensation in ordered systems as vesicles. However, The incubation of the vesicular dispersions entrapping nucleoside did not result in the formation of oligonucleotide through the interaction of phosphoryl alanine and nucleoside, as in the case of the bulk system in the aqueous or organic solutions. The effective compartmentalization is believed to be due to the separation of the two species in different phases – inner aqueous phases and lipid bilayers of the vesicles. The observations showed that amphiphilic N-phosphoryl amino acid could be a model for the evolution of cell membranes besides its significance as the model of the evolution of biopolymolecules.

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P-99 A HYPOTHESIS OF ORIGIN OF THE BACKBONE OF NUCLEIC ACID – EFFICIENT SYNTHESIS OF 3′, 5′-DITHIO-2′-DEOXYPURINENUCLEOSIDES

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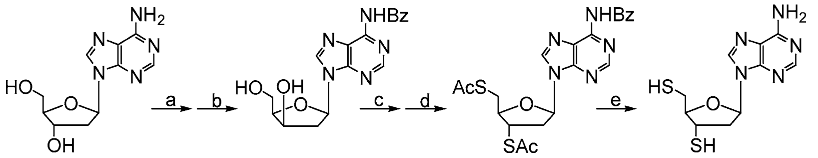
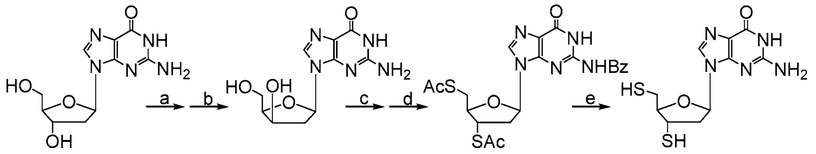
As well known, the formation of nucleic acids with phosphodiester backbone is very difficult under simulated prebiotic conditions. Our recent research shows that the reactions of 3′, 5′-Dithio-2′-Deoxynucleosides with HCHO can easily afford a novel nucleic acid with -S-CH_2-S- linkages under mild conditions. Thus, we propose a



Scheme 1. Reaction conditions: a) (1) BzCl, C_5H_5N; (2) Me_3SiCl, BzCl, MeOH, NH_3, 80%; b) (1) $(CF_3SO_2)_2O$, C_5H_5N, CH_2Cl_2, H_2O; (2) MeOH, MeONa, 70%; c) MsCl, C_5H_5N, 91%; d) AcSK, Dioxane, N_2, 60 °C, 36 h, 77%; e) EtSH, EtSNa, N_2, 85%.



Scheme 2. Reaction conditions: a) (1) Bu_2SnO, DMF, MeOH; (2) TsCl, Et_3N; (3) Ac_2O, C_5H_5N; (4) MeOH, NH_3, 70%; b) Et_3LiBH, DMSO, OH^- ion exchange resin, 92%; c) (1) Me_3SiCl, BzCl, MeOH, NH_3; (2) MsCl, C_5H_5N, 83%; d) AcSK, Dioxane, N_2, 60 °C, 42h, 75%; e) EtSH, EtSNa, N_2, 88%.

novel hypothesis about the origin of nucleic acids, which employs 3′, 5′-Dithio-2′-Deoxy- nucleosides as monomers to build up -S-CH_2-S- as the primitive backbone of the nucleic acids. In this symposium, we would like to report an efficient synthesis of 3′, 5′-Dithio-2′-Deoxyadenosine and 3′, 5′-Dithio-2′-Deoxyguanosine.

All compounds have been identified by MS and ^1H NMR spectra.

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P-100. A HYPOTHESIS OF ORIGIN OF THE BACKBONE OF NUCLEIC ACID — EFFICIENT SYNTHESIS OF 3′, 5′-DITHIO-2-DEXOYPYRIMIDINE NUCLEOSIDES

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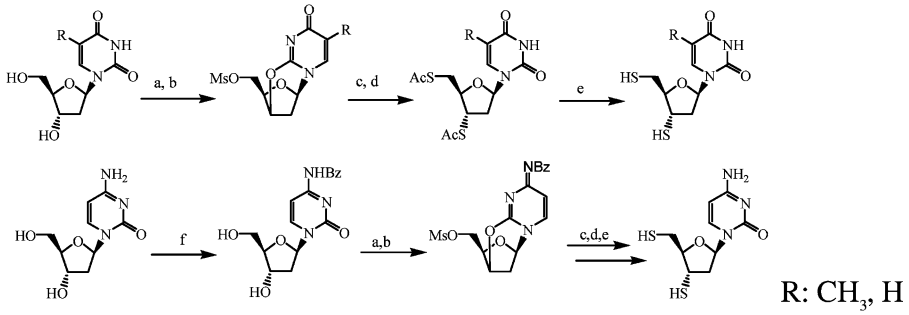
The origin of nucleic acid has puzzled people for many decades. The key problems lying unsolved are how nucleosides to react with phosphorus reagents and form the long nucleic acid strand in the diluted water solution. In our recent research, we found that the 3′,5′-Dithiothymidine can easily form the disulfide linkage between the monomers in a very diluted water solution at room temperature under neutral pH condition. 3′,5′-Dithiothymidine also can form long nucleic acid in the presence of formaldehyde in dithioformacetal backbone. We believe that such kind of nucleic acid provide a clue to explore the origin of the nucleic acid. In this report, the method to efficiently synthesize 3′, 5′-dithiopyrimidine nucleoside was described. The detailed procedure was presented as followed.



Scheme 1. Synthetic Route for $3',5'$-Dithionucleosides. (a) MsCl, Pyridine; b)DBU, CH$_3$CN, 50 °C; c)AcSH, reflux, N$_2$; d) AcSK, Dioxane, N$_2$, 50 °C; e) EtSNa, EtSH, N$_2$, rt; f) Me$_3$SiCl, Pyridine, BzCl, 0 °C.

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P-101. A VITAL WAY OF LIFE: APOPTOSIS, INDUCTED BY NITROGEN HETEROCYCLES SYNTHESIZED IN HUMAN LEUKEMIA K562 CELLS AND ITS MECHANISM

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Apoptosis is a vital way of life, involved in embryonic development and diseases (Danial et al., 2004). Medium-sized heterocycles are very important compounds as biologically active natural products and drug candidates. Twelve nitrogen heterocycles are synthesized in our lab, the one of which with a ring of 12 atoms is the best inhibitor with IC50 78.5 μM, assessed by MTT assay. Apoptosis was investigated in terms of nuclear morphology and phosphatidylserine externalization. Cell cycle analysis was performed via PI staining and flow cytometry (FCM). Dramatic activation of caspase-3 was observed. Caspase-8 and Caspase-9 are to be detected to determine its mechanism (Lawen et al., 2003).

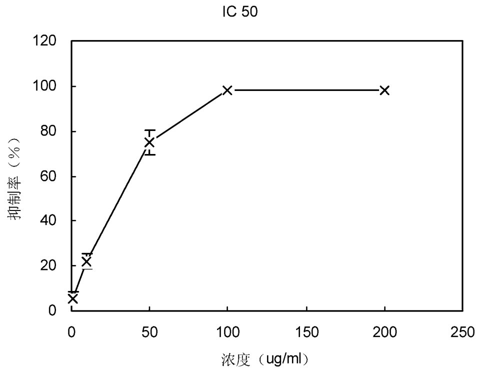

Figure 1. The IC50 of the nitrogen heterocycle with a ring of 12 atoms, detected by MTT assay.

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Danial, N.N. and Korsmeyer, S.J.: 2004, *Cell* **1**(116), 205–219.

P-107. CHEMICAL TURING MACHINES – A ROAD MAP FOR THE SMALL MOLECULE WORLD

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Any theory of the origin of life by chemical evolution must at some point account for the origin of genetic information. A process is suggested for uncovering and testing specific mechanisms for the origin of genetic information within a small molecule world hypothesis. A small molecule world hypothesis may be defined as a specific set of coupled chemical reactions with reactants including building blocks such as amino acids or nitrogenous bases, which, perhaps after protracted chemical evolution, leads to formation, among other species, of nucleic acids (in an RNA-first hypothesis) or proteins (in a protein-first hypothesis) or both. Such an hypothesis must account for many interlocking functions. If a small molecule world hypothesis includes a component of chemical evolution (natural selection with modification), the important question of the origin of genetic information must then be located precisely within this stage of any overarching theory. Good reasons for seeking the origin of genetic information at this stage are discussed in detail. A reasonable working hypothesis is that an amount of information sufficient to account for the origin of genetic information is demonstrably stored within the laws of chemistry that govern the reactive and non-reactive interactions of sets of small molecules. A Turing machine is the simplest logical form of a computer. The simplest physical forms necessary to perform the logical functions of a Turing machine are not well studied. Identifying appropriate sets of molecules and their corresponding small molecule worlds as capable of chemical evolution requires no more and no less than demonstrating an isomorphism between the chemical laws governing the interactions within a set of molecules and the set of operations and initial data that defines a universal Turing machine in both logical and physical senses. Examples from modern biochemistry and from an hypothetical primordial subset of the amino acids will be used to explore the forms such an isomorphism might take.

P-109. DIFFERENCES IN SUBSTRATE SPECIFICITY OF C5-SUBSTITUTED URIDINE DERIVATIVES BY DNA POLYMERASES FROM HYPER-THERMOPHILIC BACTERIA, ARCHAEA AND VIRUS

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The RNA world hypothesis postulates that RNA played the roles of information carrier and catalysts in an early stage of origins of life, and that the DNA-RNA-protein world developed in the later stage from the ancestral RNA-based system. Pyrimidine bases of RNA are uridine (U) and cytosine (C), on the other hand, thymidien (T) and C are used for DNA. The C-5 position of C and U is un-substituted, whereas the C5 of T is substituted with a methyl group. Miller et al. hypothesized that the C-5 position of U was reacted with formaldehyde giving 5-hydroxymethyl U, followed by reaction with various nucleophiles forming various C5-substituted U. They also suggest that the C5-substituted U could play important roles in the transition sate from RNA world to DNA world. It is also believed that the last common ancestor life was originated in the hydrothermal environment, and that hyper-thermophilic bacteria and archaea are old-type lives which are close to the last common ancestor. Thus, we examined whether DNA polymerases from hyper-thermophilic bacteria, archaea and virus can accept dUTP or other various C5-substituted dUTPs as a substrate, giving the corresponding DNA by PCR. We found that substrate specificity of dUTP and several C5-substituted dUTPs for the DNA polymerases differs greatly depending on the type of the C5-substituent group and on the kinds of DNA polymerases from different families, A-family DNA polymerases from hyper thermophilic bacteria, B-family and D-family polymerases from hyper-thermophilic archaea. Significance of the difference in the substrate specificity of the DNA polymerases between bacteria and archaea for the evolution of genetic system will be described briefly.

P-111. BIOCHEMICAL EVIDENCE VS. METABOLIC INFERENCE FROM COMPLETE GENOMES: LESSONS FROM THE ARNON CYCLE, AN AUTOTROPHIC CARBON DIOXIDE FIXATION PATHWAY

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Carbon dioxide fixation shows a wide phylogenetic distribution. The entirely different biochemical strategies used for CO_2 assimilation indicate that autotrophy is a polyphyletic trait evolved independently in many distant prokaryotic groups. Thus the Calvin-Benson cycle or reductive pentose-phosphate pathway, that makes use of Rubisco, is prents in cyanobacteria and some phototrophic proteobacteria, as well as in some Gram-negative chemolithotrophs. Besides this well-known autotrophic pathway, the only on present in autogrophic eukaryotes, microorganisms can slao fix carbon by way of different routes: the reductive citric acid (Arnon) cylcle, the net acety-CoA synthsis (Wood pathway), and other less common routes, like the hydroxypropionate pathway. These pathways are well distributed in both Bacteria and Archaea domains.

Besides the classical version of the Arnon cycle that makes use of ATP: citrate lyase to regenerate oxaloacetate, originally described in the green-sulfur bacteria Chlorobium limicola, there is another enzymetic path using citrate lyse, a completerly different, nonhomologous protein. The analysis of the complete genomes of six diverse autotrophic (phototrophic and chemolithotrophic) prokaryotes shows that this second solution appears to be more common than the canonical on. In fact the presence of a complete Arnon cycle has been in many occasions overlooked in the inferred metabolic maps of sequenced organisms. In addition, based on phylogenetic analysis we propose a solution for the missing steps in the Arnon cycle of the hyperthermophile Aqufex aeolicus and show that the metabolic virtuosity of the non-sulfur alpha-proteobacteria Rhodopseudomonas palustris is still higher than expected.

Its is worth remarking that the presence of the genes coding for an autotrophic pathway is necessary condition by but not sufficient to claim that it is fully functional ina a cell. Thus all enzymes participating in the Arnon cycle can have other metabolic functions (e.g. amino acid fermentations or acetyl-CoA synthesis from carbon skeletons). This happens for example in Halobacterium sp. and Haloarcula marismoruui. Our observations on the Arnon cycle together with recently published evidences on metabolic functions for Rubisco other than the autotrophic one, and the presence of Rubisco-like proteins in heterotrophic microorganisms like Bacillus subtilis, point out to a necessary revision of the "key-enzyme" concept in the light of the evolution by molecular tinkering: to become autotrophic it is necessary the complete set of enzymatic activities that may belong to diverse heterotrophic pathways, and a source of reducing power strong enough (e.g. reduced ferredoxin), either of photosynthetic or chemolithotrophic origin.

Acknowledgements

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P-112. COMPARATIVE ANALYSIS OF PROKARYOTIC GENOME SIZES AND THE GENE COMPLEMENT OF A MINIMAL DNA/RNA/PROTEIN CELL

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We will discuss from the comparative genomics perspective, the genome sizes of minimal DNA/RNA/protein cells. Analysis of published DNA content values determined for 681 different prokaryotic species by pulsed field gel electrophoresis has lead to a more precise definition of the genome size ranges of free-living and host-associated organisms. DNA content is not an indicator of phylogenetic position. However, the smallest genomes in our sample do not have a random distribution in rRNA-based evolutionary trees, and are found mostly in (a) the basal branches of the tree where thermophiles are located; and (b) in derived clades, such as those of Gram positive parasitic bacteria like mycoplasma. The range of genome size in our sample covers from 448 Mb (Buchnera spCCE) up to 12,200 Mb (Sorangium cellulosum Soce56). While the smallest-known genome size for an endosymbiont is only 448 Mb, no free-living prokaryote has been described to have genomes <1450 Mb. Estimates of the size of minimal gene complements can provide important insights on the primary biological functions required for a sustainable, reproducing cell nowadays and throughout evolutionary times, but definitions of minimal cells are dependent on specific environments. The analysis of small genomes allows the detection of a set of highly conserved genes whose presence is consistent with the idea that extant cells were preceded by RNA/protein ones.

P-113. LOW COMPLEXITY SEQUENCES IN LENTIVIRUS

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In spite of the high frequency of low complexity sequences (LCS) in the three cellular lineages (Bacteria, Archaea and Eucarya), the role that they may play in the architecture and function of cellular genomes has not been analyzed in detail. Much less is known about viral LCSs. In this work we present the results of a gene search using the completely sequenced genomes of lentivirus available in public databases. Analysis of the products of the genes of each the major groups of lentivirus, we found that a significant fraction of them present a LCS region. The highest number of LCSs was found in the polypeptidic product of the env gene, while in gag and pol there are only two regions with LCS. It is important to note that in the accesory genes which are characteristic of this group of retrovirus, one or two regions present LCS. The characteristics of a previously unknown highly conserved region of LCS has been found in then product of gene rev will be discussed.

P-114. COMPARATIVE ANALYSIS OF METHODOLOGIES FOR THE DETECTION OF HORIZONTALLY TRANSFERRED GENES: A REASSESSMENT OF FIRST-ORDER MARKOV MODELS

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Detection of horizontal gene transfer events has been transformed into an increasingly important issue in recent years. Several different methods have been developed, but with few exceptions they have been employed without experimental controls that could evaluate their accuracy. A simple theoretical analysis based on the in silico artificial addition of known foreign genes from different prokaryotic groups into the genomes of Escherichia coli strains K12 MG1655 and O157 EDL933 will be present. Using this dataset as a control, we have tested the efficiency of four methodologies commonly employed to detect HTG, which are based on (a) the codon adaptation index (CAI); (b) the third codon position GC percentage (GC3); (c) a distributional profile (DP) approach made by a gene search in the closely-related phylogenetic genomes; and (d) a first-order Markov model (MM). All methods exhibit severe limitations although, as shown here, the MM is a better approximation when it is applied using the enterobacterial conserved genes to calculate the Markov genome index media and standard deviations (Sd). The application of the MM to detect recently transferred genes in the genomes of E. coli strains K12 MG1655 and O157 EDL933 and Salmonella typhimurium, shows that these organisms have received a rather significant amount of HTG, a number of which appears to be involved in the direct interaction of the organisms with their environment.

P-119. MULTIPLE PROTEOBACTERIAL ORIGINS FOR EUKARYOTIC THIOLASES

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Thiolase is a key enzymatic activity present in the three domains of life. There are two main classes of thiolases: (i)acy-CoA;acetyl-CoA C-acyltransferase (EC2.3.1.16), also known as 3-oxoacyl-CoA thiolase or thiolase I, and (ii) acetyl-CoA: acetyl-CoA C-acetyltransferase (EC 2.3.1.9), also known as acetoacetyl-coA thiolase or thiolase II. Both classes of thiolases share significant sequence similarity, a common crystallographic fold, and possibly the same reaction mechanism with an acetylated cysteine as covalent intermediate. Altogether, this indicates that both anabolic and catabolic thiolases share a common evolutionary origin. Eukaryotic thiolases are located in three different compartments (peroxisome, mitochondrion and cytosol) that can display catabolic or anabolic functions.

Taking advantage of the increasing number of complete genome sequences it is now possible to carry out comparative phylogenetic analyses of the available genes in order to elucidate the distribution and evolutionary origin of the thiolase isoenzymes form the different eukaryotic cell compartments. The analysis of eukaryotic sequences showed that thiolase I and II form six well-defined phylogenetic clusters, one of them highly divergent, that in general cooresponds to isoenzymes with a concrete cell compartment location. But we also observed remarkable exceptions indication that, during eukaryotic evolution, some thiolase genes duplicated, gaining or losing diverse targeting sequences, which resulted in changes in their subcellular location, and even in functional shifts between anabolic and catabolic modes of action. In summary, we propose that there is no direct relationship between the phylogenetic origin of this metabolic enzyme, its final metabolic function and the cell compartment where it acts.

In order to study the remote origins of the eukaryotic thiolase family we analysed a set of the diverse eukaryotic sequences together with a representative sample of prokaryotic thiolases. All eukaryotic thiolase groups emerged close to proteobacterial sequences. Metazoan cytosolic thiolase II was related to alpha-proteobacterial sequences, suggesting a mitochondrial origin. Umexpectedly, cytosolic thiolases from green plants and fungi as well as at least one member of all eukaryotic peroxisomal and mitochondrial thiolases.had delta-rroteo bacteria as closest relatives. Our analysis suggests that these eukaryotic peroxisomal and mitochondrial thiolases may have been acquired from delta-proteobacteria prior to the ancestor of all known eukaryotes.

Acknowledgements

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P-121. HORIZONTAL GENE TRANSFER: RETROSPECTION AND BEYOND

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The process of microbial genome evolution is a fundamental question in biology. In the last 5 decades genomic analysis has forced a paradigm shift for the role of vertical transmission of genetic material and genome evolution. So much so, that the evidence of horizontally transferred genes has threatened to undermine the ribosomal RNA tree as a molecular chronometer. For such an important phenomenon as horizontal gene transfer (HGT) to be at work in the evolution of prokaryotic genomes, it is remarkable how little we actually know about how, when and why the process is likely to occur. Standard protocols for assessing HGT in genomes have produced mixed results. We report 2 specific studies for HGT in whole genome analysis. One combines the use of whole genome analysis and information from geology to trace the history of nitrogen fixation in bacteria. The other evaluates the use of "signature genes" for phylogenetic reconstructions of specific bacterial lineages. This retrospective look at past HGT events provides some insight into the process of HGT. However, the future for progress in understanding the dimensions of the process of HGT in genome evolution will require integration of bioinformatics with tools that allow us to evaluate HGT in real time and real places. Initial prospects will be discussed.

P-122. IR AND RAMAN MICROSPECTROSCOPY FOR THE CHARACTERIZATION OF ANCIENT LIFE

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Spectroscopic analyses by using IR and laser Raman microspectroscopy have been conducted on microfossils in order to find molecular traces of ancient life. Microfossils in $\sim$850 Million year ago (Ma) old black chert collected from the Bitter Springs Formation, Central Australia, are well preserved, are morphologically diverse, and have inner structures that resemble cell walls and/or membranes. Micro-Raman spectroscopy on carbonaceous brown to amber portions of microfossils showed disordered peak (D peak, 1340 cm-1) and ordered peak (O peak, 1600 cm-1) of graphite, indicating their kerogen-like structure. IR micro-mapping results revealed that the distributions of peak heights at 2920 cm-1 (aliphatic CH2) and around 1365 cm-1 (possibly C-N) are quite similar to those of microfossils. These results indicate that IR and Raman microspectroscopy can be used for characterization of ancient microfossils.

P-126. SPECTROSCOPIC ANALYSIS OF THE THERMAL ALTERATION OF PETRIFIED ORGANIC MATTER

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Raman spectroscopy is a technique that has received much attention recently in the astrobiological and paleobiological communities. It is a technique for non-destructively analyzing carbonaceous matter in situ and therefore lends itself to the examination of delicate and precious samples, such as those of organisms from ancient Earth or of extraterrestrial origin that may be discovered and returned to Earth in the future. This study, one that examines the thermal alteration of the chemistry of petrified organic matter, helps to refine our understanding of fossilization and to better understand those more delicate and precious specimens. Using Raman spectroscopy, as well as other spectroscopic techniques, the organic chemical makeup of a fossil fern species, Dennstaedtiopsis aerenchymata, from two distinct localities, both of Eocene age, has been analyzed and the sequence of chemical steps that occur during fossilization and subsequent thermal alteration determined via a proxy, experimental maturation of a modern analogue fern species, Dennstaedtia cicutaria. Samples of the modern fern were heated in a closed, anoxic system at 250 °C for lengths of time ranging from 2 to 500 hours. Individual cells from these fern specimens were analyzed with a Raman spectrometer using a UV laser source. Results were compared to those obtained from individual cells seen in thin sections of the fossil fern using the same system. Bulk samples of the modern fern altered under the same conditions as well as acid macerated samples of the fossil fern were analyzed using nuclear magnetic resonance spectroscopy and pyrolysis-gas chromatography/mass spectrometry. Results from all of these techniques show that the rate of chemical change was quite rapid at the beginning of the experiment and then slowed with longer periods of heating. The structure changed from mostly polysaccharidic carbon to a mixture of aromatic and aliphatic carbon.

P-129. VENDIAN (EDIACARAN) BIOTA FROM THE LESSER HIMALAYA, INDIA AND SOUTHERN CHINA WITH SPECIAL REFERENCE TO EARLY EVOLUTION OF LIFE ON EARTH

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Himalayan mountain chain was formed as a result of collision of Indian Plate with Asian Plate. The fossil evidences of early evolution of life are well preserved in the Lesser Himalayan Proterozoic sedimentary basins from NW to NE region of India. The newly established Ediacaran Period (650–540 million years) confirmably overlying the Cryogenian Period represents the evolution of the soft bodied animals on earth just after the Neoproterozoic glacial event. The record of Vendian/Ediacaran biota from the Lesser Himalaya (Krol–Buxa belt in India) and Doushantuo and Dengying Formations of China strongly supports that palaeogeographically these sedimentary basins were very close or attached to each other. The Blaini diamictite with pink cap carbonate in the NW Lesser Himalaya and identical diamictites in the NE Arunachal Himalaya and the Sinian diamictites of the Chinese region are correlated with the global Marinoan glaciation. During Terminal Neoproterozoic time (Tewari, 2001, 2002, 2003, 2004). Major palaeobiological and carbon isotopic changes occurred in the Indian Lesser Himalaya and the Yangtze Platform of Southern China leading to rapid evolution and diversification of multicellular life (Tewari, 2003, 2004). Large acanthomorphic acritarchs, calcareous algae, Vendotaenids, sponges (micrometazoans) and Ediacaran soft bodied animals appeared in the Infra Krol-Krol Formation of India and Doushantuo Formation of Southern China. This major event was followed by Cambrian Explosion of life (animals with hard parts and small shelly fossils) found in the Lower Tal Formation of the Lesser Himalaya which corresponds to the phosphatic Meischucunian Zone I of China. The carbon isotope chemostratigraphy of the Krol and Buxa Formations from the Lesser Himalaya and the Doushantuo Formation from the Yangtze Platform indicate very high positive carbon isotope values. This Ediacaran event is also global and has significance in early organic evolution of life on Earth. The Pan African orogeny (Xingkanian orogeny in China) around 500 Ma brought about palaeogeographic changes in this region and the sea regressed from the Himalaya.

P-130. ORIGIN AND EARLY EVOLUTION OF SMALL ANIMAL PHYLA: PRIAPULIDA

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Although priapulid worms form a small phylum in present-day marine environments with only 18 described species (5 families, 7 genera), they were important elements in Cambrian endobenthic communities. These worms are especially well represented in the Early Cambrian Maotianshan Shale of China (ca. 520 Ma) and the Middle Cambrian Burgess Shale of Canada (ca. 505 Ma). Priapulid worms have a very remote origin that can be traced back to, at least, the Precambrian-Cambrian boundary, as evidenced by important trace fossils such as Trichophycus pedum that was probably produced by priapulids. Priapulids were dominant and abundant in early endobenthic communities. At least 6 different body plans are recognized among the priapulid worms present in the Early Cambrian Maotianshan Shale fauna (palaeoscolecidian, selkirkiid, corynetiid, anningiid, tylotitid, and priapuliid; see diagnostic features below). These early Cambrian priapulids show complex morphologies and adaptations (e.g; related to feeding and locomotion).

The morphological features that characterize modern priapulids were present in the Early Cambrian representatives of the group, for example the pentagonal arrangement of pharyngeal teeth and the caudal appendage(s). Resemblances are remarkable between the Early Cambrian and Recent forms, the most spectacular example being the Priapulidae. Close similarities between Recent Priapulidae and their putative ancestors suggest that no major anatomical changes occurred within the priapuliid lineage since the Early Cambrian, thus providing strong evidence for evolutionary stasis over the past 520 Ma. All priapulids of the Maotianshan Shale fauna were predators and burrowers. Other worm groups are represented in this fauna, for example sipunculans and annelids. Annelids are extremely rare though. Priapulids and sipunculans co-occur in the Maotianshan Shale fauna but are unlikely to have been direct competitors (priapulids were predators of smaller invertebrates whereas sipunculans were non-selective deposit feeding). The assumed slow burrowing movement of priapulids added to the competitive pressure exerted by other worms groups as soon as the Middle Cambrian (e.g. co-occurrence of abundant polychaetes in the Middle Cambrian Burgess Shale fauna) may account for the unsuccessful post-Cambrian evolutionary history of Priapulida.

Priapulid disparity: main characteristics

1. Selkirkiid (Paraselkirkia)-Tubiform worms; introvert armed with scalids; trunk specialized (chitinous tube) with tapering shape and fine annulations; pharynx spiculose with subdivisions.
2. Corynetid (Corynetis) – Contracted introvert smooth except the anterior circlet with long spines; annulated trunk spiculose, caudal projection posteriorly; collar developed; spiculosed pharynx very slender.

3. Anningids (Anningvermis)-Contracted introvert smooth with or without anterior circlet of spines; trunk annulated and spiculosed; smooth caudal appendage present; collar short; pharynx very slender, divided into basal section with pentagonal cuspidate teeth and distal, elongate and spiculosed section.
4. Palaeoscolecidans (Maotianshania, Cricocosmia, Palaeoscolex, and Tabelliscolex) – Very elongate worms; introvert poorly developed, armed with rows of scalids anteriorly; no neck; cylindrical trunk well annulated, armed with various cuticular ornaments; paired hooks at posterior end of trunk; collar short; spiculosed pharynx with subdivisions.
5. Tylotitid (Tylotites) – Introvert poorly developed, armed with rows of scalids; no distinct neck; trunk annulated and armed with spines; small caudal projection present; collar short; pharynx divided into a section with pentagonal cuspidate teeth and a spiculosed section.
6. Priapuliids (Xiaoheiqingella, Yunnanpriapulus, and Paratubiluchus) – Swollen introvert armed with 25 longitudinal rows of scalids in its anterior section; neck as a constriction; trunk well annulated, with or without posterior papillae rings; caudal appendage(s) present; collar short; pentagonal pharyngeal teeth armed.

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P-132. LINKING MOLECULAR TAXONOMY WITH ENVIRONMENTAL GEOCHEMSITRY IN ENVIRONMENTS RELEVANT TO ASTROBIOLOGY: THE ANAEROBIC OXIDATION OF METHANE IN COLD SEEPS & DEEPLY BURIED MARINE SEDIMENTS

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The linking of molecular taxonomy (including 16s rRNA) to environmental geochemistry is a powerful way to work out the interactions, metabolic activities, and food webs of microorganisms in their natural setting, whether it is sediment, soil, or a water column. To this end, we developed a method for coupling an extant microorganism's genetic information with geochemical data derived from the direct analysis of its cell. FISH–SIMS combines fluorescent in-situ hybridization (FISH) with secondary ion mass spectrometry (SIMS). FISH is a culture-independent technique used to visually identify naturally occurring microorganisms by staining their ribosomal RNA. Secondary ion mass spectrometry (SIMS) is a method by which geochemical information can be obtained from microsamples. Using FISH-SIMS, a researcher can measure a target cell's isotopic or elemental composition in a mixed environment.

The identification and study of methane-consuming microorganisms is an important step toward understanding the methane cycle and microbial response to methane release. The recent identification of two distinct Archaea capable of anaerobic methane oxidation was in part accomplished using FISH-SIMS. Because natural methane is highly depleted in 13C, FISH-SIMS is particularly powerful at determining if a particular cell, collected from the environment, and consumed methane as a substrate for its cell carbon. This research demonstrated that both the ANME-1 and ANME–2 Archaea from the Eel River Methane Seep are highly depleted in 13C due to growth on methane.

The deep marine biosphere is thought to contain abundant microbial inhabitants, estimated to be a tenth of the Earth's total biomass. Sediments from this environment were recovered during Ocean Drilling Program (ODP) Leg 201, and were analyzed by both molecular biological and organic geochemical techniques. Of particular interest in these sediments were four sulfate/methane transition zones seen at ODP Sites 1227, 1229 and 1230, two of which coincided with strongly elevated cell counts. Archaeal cells in these zones were analyzed for abundance and d13C composition by whole cell analysis (FISH-SIMS) and intact membrane lipids (HPLC-ESI-MSn). Cell counts showed greater archaeal abundance than bacterial, which was reflected by intact membrane lipid abundance. Isotopic compositions by both techniques (often around $-20‰$) suggest that methane is not an important carbon source for these cells. Autotrophic carbon fixation appears to be an unlikely metabolism given the relationship between the isotopic composition of DIC and archaeal biomass. The isotopic evidence suggests that the bulk archaeal community is heterotrophic, possibly mediating the oxidation of methane without consuming it as a carbon source.

The importance of these techniques is that the cells targeted for study can be environmental species that cannot currently be grown in the laboratory. These techniques promises to become critical for working out the interactions, metabolic activities, and food webs of microorganisms in their natural setting, whether it is sediment, soil, or a water column.

P-137. MARTIAN METEOROLOGICAL MEASUREMENTS USING GROUND-BASED TELESCOPES

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The loss of ESA's Beagle 2 lander threw into sharp relief some of the inadequacies of existing Martian meteorological data sets and highlighted the need for continued research in this area. Ground-based observations are particularly useful in this regard, as they allow simultaneous global coverage and use of high-resolution spectroscopy to complement orbital measurements. Aside from the perils of atmospheric turbulence (correctable to some degree using adaptive optics), ground-based infrared observations of planetary atmospheres face another challenge? correcting for the presence of telluric spectral lines. Based on atmospheric simulations using the SMART radiative transfer modelling tool, we will present evidence that the current technique of mitigating the effect of Earth's atmosphere by observing a nearby star of known spectral type (the 'standard star' method) can generate significant errors. Indeed, our simulations of measurements of the Martian 2-micron carbon dioxide band at a resolving power of 1000 produced variation between 'standard reduced' spectra and original modelled spectra of up to 50%. Furthermore, we will outline our proposed computational technique of iterative reduction by progressing modelled parameters towards observed values (which negates the 'standard star' issue), and present results to date.

P-139. SUB-VENT BIOSPHERE: PHOSPHATASE ACTIVITIES IN 308 DEEP-SEA HYDROTHERMAL SYSTEMS AT SUIYO SEAMOUNT, IZU-BONIN ARC, WESTERN PACIFIC OCEAN

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1. Abstract A high-temperature deep-sea hydrothermal system related to dacitic arc-volcanism was drilled using a tethered, submarine rock-drill system as a part of the Archaean Park Project. The benthic multi-coring system (BMS) employed allowed for direct sampling of microorganisms, rocks and fluids beneath hydrothermal vents. The samples examined in this study were from sites APSK 05 and APSK 07 on the Suiyo Seamount of the Izu-Bonin Arc in the Pacific Ocean. Based on the vertical distribution of samples derived from this vigorous sub-vent environment,

a model of deep-sea subterranean chemistry and biology was determined detailing optimal microbial activities. Deep-sea hydrothermal sub-vent core samples of dacitic arc-volcanism obtained at the Suiyo Seamount, Izu-Bonin Arc, Western Pacific ocean were analyzed for acid and alkaline phosphatase enzymatic activities. Useful biomarkers of acid phosphatase (ACP) and alkaline phosphatase (ALP) enzymatic activities were positively correlated against each other and was greatest at the partial middle core sequences; ACP and ALP activities determined were as high as 5.10 nmol/min/g-rock and 6.80 nmol/min/g-rock, respectively. Biochemical indicators of ACP and ALP were consistent with the origin of biogenic amino acids occupied in the sub-vent region and microbial cell number in the fluid. The significant enzymatic activities demonstrated in this study provides crucial evidence that sub-vent regions represent part of the previously unknown extreme-environment biosphere, extending the known subterranean habitable spaces of, for example, extremophilic microbes. This boring trial was first example of discharging high temperature hydrothermal activities at the frontal arc volcanoes. 2. Significance of enzymatic activity as a "Bio-signature" Acid and alkali phosphatases (orthophosphate monoester phosphohydrolases) are considered crucial enzymes in catalytic reactions involving phospho-monoesterases. Many phosphatases have been characterized since the 1960s including the Escherichia coli alkaline phosphatases, which have been widely studied in terms of biosynthesis, structure and catalytic properties. The fact that acid phosphatase (ACP) and alkaline phosphatase (ALP) have been widely found in nature in taxonomic groups ranging from bacteria to mammals, suggests their importance in fundamental biochemical processes. Enzymatic activity is also generally recognized as playing a key role in the degradation and utilization of organic polymers by bacteria, as only compounds with molecular masses lower than 600 Da can pass through cell pores. The cycling of nitrogen compounds is largely influenced by the C/N ratio of organic matter in sediments, and the bacterial carbon conversion efficiency is inversely related to age of the detritus. Temperature has also been identified as a factor that controls enzymatic activity, but with a few notable exceptions. Investigating thermostable enzymes can, in addition to increasing our knowledge and understanding of life in extreme environments, provide the basis for the industrial application of ALPs exhibiting thermostable characteristics. Recently, interest in the limitations of life in high-temperature environments has been growing. Since the discovery of hyperthermophilic microbial activity in hydrothermal fluids recovered from "smoker" vents on the East Pacific Rise, the widely accepted upper temperature limit for life has risen from below 113°C, while many microbiologists seem willing to speculate that the maximum may be closer to 150°C. The recent discovery of a microbe living at 121°C has broken the established temperature limit and extended the zone of microbial habitable temperature. It would be of interest to examine microbial activities within thermal gradient zones of sub-surfaces. Deep-sea hydrothermal systems represent natural laboratories for the study of organic geochemistry regarding vigorous microbial habitats in extreme environments. The historic discovery of the Galapagos deep-sea hydrothermal systems has lead many researchers to consider that deep-sea hydrothermal systems are suitable environments for chemical evolution, with possible implications for the origins of life on the Earth. The extremophilic characteristics of these environments have attracted interest from many scientific perspectives including geology, oceanography, biology, chemistry and physics. In fact, a number of submarine ecological colonies have been identified near black or clear smokers and the sub-seafloor environments. While the existence of a deep bacterial biosphere in oceanic sediments has been reported and is a remarkable discovery, sub-vents, or areas seafloor hydrothermal vents, are only recently being explored through deep-sea floor drilling experiments at submarine hydrothermal vents. Here we present the first determination of enzymatic activities below deep-sea hydrothermal systems through the use of coring investigations. In an effort to construct a consolidated model of the extreme environments in submarine hydrothermal vents and the interactions, we present the first report detailing crucial evidence of a sub-vent biosphere. 3. Geological location of field study The Izu-Bonin Arc lies on the eastern rim of the Philippine Sea plate. This arc is about 1,200 km long, extending from the Izu Peninsula (35 °N, 139 °E) to Minami-Iwojima Island (24 °N, 141 °E). The arc belongs to the circum-Pacific island-arc system and is adjacent to the Northeast Japan Arc to the north and the Mariana Arc to the south. Many volcanic islands and submarine volcanoes run parallel to the Izu-Bonin trench and form the volcanic front of this intra-oceanic island-arc system. The southern Izu-Bonin Arc, which is divided by the Sofugan tectonic line from the northern Izu-Bonin Arc, is thought to have become active at around 42 Ma. The Shichiyo seamount chain forms a volcanic front around which the arc crust is thought to be thinner than that in the northern part. The Suiyo Seamount, one of the volcanoes in the Shichiyo chain, has two major peaks, located on the eastern and western sides of the seamount. The Suiyo Seamount is an active submarine volcano, where vigorous hydrothermal activity has occurred on the caldera floor atop the west peak. Arc volcanoes often have a magma chamber inside the edifice at rather shallow depth, which act as a heat source for fluid circulation. Dacitic rocks of a calc-alkaline rock series and low-potassium andesites have been recovered from this area, and preliminary reports of seafloor hydrothermal alteration at Suiyo have been documented with respect to geochemical and mineralogical characteristics. Numerous short black smokers and clear smokers were observed on the sandy floor. Hydrothermal circulation reaches the region adjacent to the magma source, and volatile constituents are extracted by water-rock interactions.

P-140. ALGAE COLONIZATION AND SUCCESSION IN DESERT SOIL

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Microbiological crusts are attractiong much intrest in view of their possille uses in environmental conservation and ecological restoration of the arid and semiarid regions, where the natural environment is similar to the early earth, so it maybe give some clues for the origin of life on earth. Because aldae play an irreplaceable important role in early formation and strength-maintianing of microbiological crusts, they are paid much more attention than other cryptogams. In this paper, an overview of the current knowledge on the fine structure and development of microbilolgical crust, expressing method of algal biomass, algal influential factors, vertical distribution, succession, eohesion of stabilization soil, cementing mechanism for soil particles and their extracellular polymers is given, with particular emphasis on our researches, and some prospects are put forward as well.

P-141. STUDIES ON THE ADAPTATION MECHANISM OF DESERT ALGAE TO UV-B IRRADIANCE

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Radiation is one of major space factors which affect greatly the living of earth life in space, the evolution of earth life colonizing in extraterritorial environment and the origin of life in early earth. For the studies on the effect of UV radiation on cyanobacterium, we studied the effects of UV-B irradiance on PSII activity of the dominant desert algae isolated from desert algal crust in Shapotou. It was found that PSII activity of Microcoleus vaginatus, Scytonema javanicum, Nostoc sp., Phormidium tenue and Chlorella vulgar was sensitive to UV-B irradiance, it decreased significantly after treated with various UV-B irradiance, and restored partly after placed in dark at lower intensity irradiance. PSII activity of Chlorella vulgar was higher, it decreased rapidly and didn't restore to normal after placed in dark for 24h; PSII activity of Mvaginatus and Ptenue was lower, it was partly inhibited after treated for 4h and partly restore after placed in dark; PSII activity of S. javanicum and Nostoc sp. didn't have a significant change after treated with low intensity UV-Birradiance, but decreased rapidly after treated with higher intensity for 4h, and restored to normal after placed in dark. The results suggested that the fine vertical distribution of desert algae in desert algal crust was attributed to the sensitive and restoring characters of PSII activity. We also found that UV can affect algae's Antioxidant Enzymes Activity, carbohydrate metabolism and signal transduction related to nitric oxide. The next plan is to understand molecular mechanism of the changes related to the effects of UV radiation.

P-142. STUDY ON NOVEL PEPTIDE FORMATION PROCESS IN ORIGIN OF LIFE UNDER MICROWAVE IRRADIATION

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Peptide formation of amino acids in the presence of polyphosphate in aqueous solution was in situ studied with NMR and ESI/MS. We found that magnesium ion has catalytic effects for the condensation of amino acids to peptide with polyphosphates, conversion yield of peptide amounts to 10% even at room temperature (Table 1); both the rate of peptide formation and conversion yield can be further enhanced under microwave irradiation (Kingston and Haswell, 1997). Hydrolysis of polyphosphates in the peptide formation and its regeneration from polymerization of phosphates were studied and it was found that magnesium ion (Dugas, 1996) and microwave irradiation can also make those processes enhanced it was found for the first time that peptide can be formed in aqueous solution with amino acids, orthophosphate and magnesium ion under microwave irradiation. Based on above results, we have found and proved a recycle, which consists of both peptide formation with polyphosphate and regeneration of polyphosphate by polymerization of phosphates in the system containing amino acids, phosphates and magnesium ion under microwave irradiation. Ideally, peptides will be continually formed by only inputting microwave into this system (Figure 1).Thus we propose that the above recycle maybe the most possible process for primitive peptide formation in origin of life; and microwave or electromagnetic may imperceptibly enhance the primitive peptide formation and origin of life.

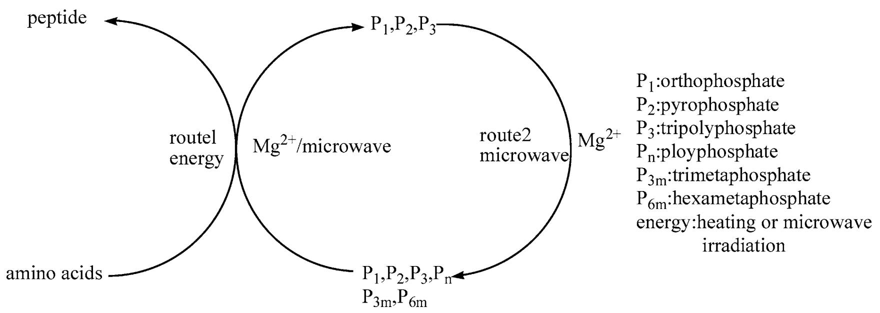

Figure 1.

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P-150. NACL ENHANCED OLIGOMERIZATION OF O-PHOSPHO-L-SERINE

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The presence of NaCl significantly enhances the formation of longer peptides in N,N′-carbonyldiimidazole (CDI) induced oligomerization of O-phospho-L-serine (L-SOP) in homogeneous aqueous solution. The enhancement effect of NaCl on oligomerization of L-SOP was observed in the presence of NaCl from 0.01 M to 4 M. The highest yield of longer oligomers was achieved in the presence of 1 M NaCl, where the longest oligomer detected is 8-mer while 6-mer is the longest peptide formed without the additive.

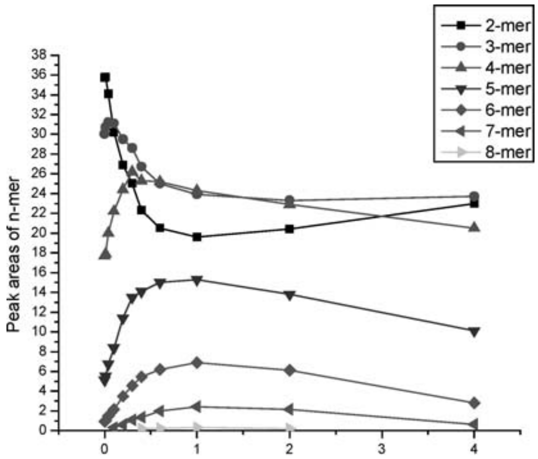

Figure 1. The oligomer formation in CDI-induced polymerization of 50 mM L-SOP (pH 8.0) in presence of different concentration of NaCl.

The presence of NaCl increased the yields of longer peptides and decreased yields of short prptides (Figure 1). The yield of 2-mer and 3-mer were about one-half and four-fifth, respectively, of the amounts without addition of NaCl. The yields of 5-mer and 6-mer were about 3 and 7 times, respectively, of the amounts without NaCl. The percentage yields of 5-mer and longer oligomers to total peak areas of oligomers were increased from 6.76% without NaCl to 26.9% with 1 M NaCl. The percentage yields of 6-mer and longer oligomers to total peak areas of oligomers were increased from 1.06% without NaCl to 10.4% with 1 M NaCl. Na_2SO_4 gave rise to the similar enhancement of longer oligomers of L-SOP to that of NaCl. The highest concentration of Na_2SO_4 screened was 0.25 M because of its low solubility. And the most efficient enhancement was achieved in the presence of 0.25 M Na_2SO_4. The oligomerization of L-SOP was also enhanced in the presence of $MgCl_2$ with an optimal concentration at 0.1 M, with 8-mer as the longest peptides, in agreement to the results by L.E. Orgel, etc. (A. R. Hill & L.E. Orgel, Origins Life Evol. Biosphere 26: 539–545, 1996).

The weak interactions between the Na^+ and negative-charged phosphate group of oligomers of L-SOP are assumed to be responsible for the enhancement of the oligomerization of L-SOP by NaCl. Since RNA also has negative-charged phosphate group, we believe the possible enhancement of the RNA formation such as the oligomerization of ImpA, ImpC, ImpG and ImpU by Na^+.

P-151. NA$^+$ ENHANCED OLIGOMERIZATION OF L-GLUTAMIC ACID

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The presence of Na^+ was found to significantly enhance the formation of longer peptides in N,N′-carbonyldiimidazole induced oligomerization of L-glutamic acid in homogeneous aqueous solution. The polymerization of 50 mM L-glutamic acid without additive yielded 10-mer as the longest peptide. The enhancement of Na^+ on polymerization of L-glutamic acid was detected in the presence of as low as 0.01 M Na^+. The highest yield of longer oligomers was achieved in the presence of 1 M Na^+, where the longest oligomer detected is 15-mer and the yields of 3-mer and 4-mer are about one-quarter and one-half, respectively, of the amounts without addition of Na^+. The percentage yields of 8-mer and longer oligomers to total peak areas of the trimer and longer oligomers without Na^+ was increased from 7.03% to 40.1% with 1 M Na^+. The yields of 10-mer and the longer oligomers are less than 0.2% of the total peak areas of 3-mer and longer oligomers without addition of Na^+. However, in the presence of 1 M Na^+, the corresponding yield is 54 times more than that without addition of Na^+. Increasing the concentration of Na^+ to 2 M, 3 M and 4 M gave rise to slightly inhibited longer oligomer formation compared to that with 1 M Na^+. The similar enhancement of the polymerization of L-aspartic acid by Na^+ and that of L-arginine by both Cl^- and many other common anions were also observed. We did not observe significant effect of ions on the polymerization of glycine and L-alanine.

We have eliminated such factors as the ionic strength, the slightly pH changes as the cause of observed effect. Also the formation of the activated monomers, the elongation of the monomeric amino acids and the corresponding dimers were not affected by the presence of the opposite-charged ions. The weak interactions between the ions and the opposite-charged side-chain groups of the formed peptides were assumed to be responsible for the enhancement.

In view of the inevitable presence of Na^+ and Cl^- in the primitive oceans, the effect observed was interpreted to indicate the much easier longer peptide formation in primitive oceans than previously expected.

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P-152. ALKANES TO DIAMONDS: A SPECULATION ABOUT TITAN

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Titan, the largest of Saturn's moons, is essentially a giant frozen spinning ball of methane, ethane, and other likely carbon sources that have been subjected to hard UV radiation from the Sun the geological compression forces for five billion years. In summary, available carbon plus great pressure plus an eon may produce on Titan a desirable allotrope of carbon – diamond. The possibility exists that such UV radiation has split alkane C-H bonds on Titan with subsequent recombination of resulting hydrongen radicals (i.e. hydrogen atmos) into H2 and recombination of resulting alkane barbon radicals, through progressively larger intermediates, eventurally into extended all-single-bonded carbon lattices, that is, diamonds. The process of diamond formation from alkanes on Titan may be catalyzed by geological compression forces on this geologically actice moon just as diamonds are similarly made on Earth form carbon sources under high compression forces. Thus, there may exist on Titan diamonds floating through liquid methane oceans or buried in solid thane continents. Any H2 molecules that are fomed on Titan form breaking C-H bonds with subsequent recombination of aromic hydrogen would have escaped form Titan due to the low gravity of this moon. On Titan, scarcity of oxygen means carbon would preferentially be channeled into self-reaction pathways, with reduced σ bonds (not oxidized π bonds) predominating, and eventually end up in reaction-impervious diamond.

The Huygens probe that recently landed on a solid thane surface of Titan was ont able to detect diamonds on this moon, if they are present, because the probe lacked proper equipment for this purpose.

However, it may be possible to approach testing this diamonds-from-alkanes idea here on Earth in the following manner: If we take tetramethylmethane, also known as strong radiation with a tunable UV laser at a frequency just right for splitting C-H bonds but not C-C bonds or H-H bonds, and we simultaneously subject the eeop0entane to high pressure, we might be able to generate diamonds from the eeopentane. Becarse neopentane already has a diamond-like nucleate structure, unlike ethane or methane, it should be easier on earth, if at all possible, to make diamonds from neopentane rather than from mentnae or ethane.

Acknowledgements

We with to thank Prof. Claude Wintner for insights derived from his Organic Chemistry Reference lectures web site http://www2.haverford.edu/winterorganiccchem and we with to thank Mr. Anthony Lankford and Dr. Larry Fox for stimulating discussions.

P-154. PLAUSIBLE METABOLIC PATHWAYS AND ENERGY CYCLING ON TITAN

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With the Cassini-Huygens Mission in orbit around Saturn, the large moon Titan, with its reducing atmosphere, rich organic chemistry, and heterogeneous surface, moves into the astrobiological spotlight. Environmental conditions on Titan and Earth were similar in many respects 4 billion years ago, the approximate time when life originated on Earth. Life may have originated on Titan during its warmer early history and then developed adaptation strategies to cope with the increasingly cold conditions. If organisms originated and persisted, metabolic strategies could exist that would provide sufficient energy for life to persist, even today. Metabolic reactions might include the catalytic hydrogenation of photochemically produced

acetylene. The energy yield of this reaction is 107.7 kJ/mol (?G = −107.7 kJ/mol or ?5.7 kcal/mol) under standard conditions, and about 100 kJ/mol under Titan surface conditions. Both acetylene and hydrogen are present in Titan's atmosphere at significant concentrations. Since acetylene is produced high in the stratosphere from solar UV radiation and then mostly condenses and falls to the surface, it provides a potential means of transferring high altitude solar UV energy to surface chemical reactions. Spectroscopic evidence suggests that the product of this reaction, methane, is found to be isotopically lighter than would be expected from theories of Titan's formation, and thus may hint toward microbial fractionation. Or, metabolic reaction may involve the recombination of radicals created in the atmosphere by UV radiation such as CH_2 radical + N_2 radical to CN_2H_2 or 2CH radical + N_2 radical to 2HCN. These reactions produce a high yield of energy and may take place at the surface of Titan. On Earth, the energy-rich reactions involving radicals are very difficult to control and would cause internal damage to any organism. On Titan, however, at surface temperatures of less than 100 K, these reactions may proceed at a reasonable pace, and may constitute a feasible energy-yielding reaction for a metabolic pathway. These radical reactions have the interesting side effect of producing the biologically important compounds cyanamide and hydrocyanic acid, respectively. Metabolic activity may also contribute to the apparent youth, smoothness, and high activity of Titan's surface via biothermal energy. Our calculations indicate that biothermal melting would be a possible explanation for the smooth surfaces observed by the Cassini-Huygens mission. Given the low temperatures, the biological effect on Titan, if it exists, should be larger than on Earth. In conditions where the ability to sustain liquid microenvironments is a key limitation on survival, then adaptive pressures could lead to a larger percentage of the free energy of exothermic metabolic reactions going towards heating the immediate environments of organisms living close to the freezing point. On the other hand, much energy has to be expended to reach the liquid state. If volcanic activity or other energy sources are present and significant, it would increase the chances for life on Titan by elevating temperatures and providing potentially habitable geothermal areas and gases that could be used for metabolism. Any liquid water-ammonia mixture is lighter than the surrounding ice and will float if produced at depth. Given the current sample size of one biosphere upon which astrobiologists must base their theories and speculations, our ideas about life elsewhere must remain fluid and not too heavily based upon the specific metabolisms, strategies and structures of terrestrial organisms. The basic requirements of life, as they are understood today, are all present on Titan, including organic molecules, energy sources and liquid media. If surface or subsurface organisms are able to take advantage of upper atmospheric photochemistry, through the continuous downward transport of high energy compounds such as acetylene, they would have vast energy reserves at their disposal which could be used, in part, to maintain the liquid environments conducive to life.

P-155. POSSIBLE SITES FOR ABIOGENIC AND BIOGENIC ACTIVITY ON TITAN

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Titan, the largest satellite of Saturn has a dense nitrogen atmosphere and a large quantity of liquid water under ice cover and so has a great exobiological significance. The most recent models of the Titan's interior lead to the conclusion that a substantial liquid layer exists today under relatively thin ice cover inside Titan. Such putative ocean likely contain an array of endogenic materials incorporated into the satellite during its formation and released during planetary differentiation, including considerable mineral and organic compounds, which could help support life and/or prebiological processes there. The chemical energy has to be the main driving force for these disequilibrium processes. The putative internal water ocean along with complex atmospheric photochemistry provide some new exobiological niches on this body: (1) an upper layer of the internal water ocean; (2) pores, veins, channels and pockets filled with brines inside of the lowest part of the icy layer; (3) the places of cryogenic volcanism; (4) set of caves in icy layer connecting with cryovolcanic processes; (5) the brine-filled cracks in icy crust caused by tidal forces; (6) liquid water pools on the surface originated from meteoritic strikes; (7) the sites of hydrothermal activity on the bottom of the ocean. We can see all conditions needed for exobiology – liquid water, complex organic chemistry and energy sources for support of biological processes – are on the Saturnian moon. On Earth life exists in all niches where water exists in liquid form for at least a portion of the year. Subglacial life may be widespresd among such planetary bodies as Jovanian and Saturnian satellites and satellites of other giant planets, detected in our Galaxy at last decade. The law temperature hypersaline brines has been proposed as habitat for microbial communities on Mars. The existence of rich atmosphere is the main Titan's difference from Jupiter's moons. This atmosphere could supply a large quantity of different organic compounds to the putative ocean, since there are some possible mechanisms for extensive, intimate interaction of the liquid water ocean with the surface of the icy crust. All these environments will be considered along with properties of many kinds of Earth extremophiles which could survive in different exotic environments. Possible metabolic processes, such as nitrate/nitrite reduction, sulfate reduction and methanogenesis could be suggested for Titan. Excreted products of the primary chemoautotrophic organisms could serve as a source for other types of microorganisms (heterotrophes) as it has been proposed for Europa and Mars. The existing of the water salty ocean inside Titan may be constrained from Cassini flyby data, but detection of the signs of life on surface or in that ocean will demand new, more complicated mission. Future Titan missions will wish to study the sample in-situ. There are several

places for such search: (1) the main attention should be paid to cratered regions which could contain signs of recent water activity after meteoritic strikes; (2) the search for a network of cavities using subsurface sounding radar could give information on place which might be of special interest in a search for life; (3) radar could also identify areas with recent cryovolcanism has occurred and in turn where aueous/organic chemistry may have occurred; (4) the search for thermal anomalies also could give information about active cracks which may have biological signatures.

P-156. METHANOGENS: A MODEL FOR LIFE ON MARS

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The recent discovery of methane in the Martian atmosphere by four independent research teams is arguably one of the most important discoveries in the field of astrobiology. The European Mars Express orbiter along with three ground-based telescopes detected approximately 10 ppb methane. With the half-life of methane in the atmosphere being only 300 years, the methane would have to be "recently" replenished to be detected now. There are two major possibilities as to the origin of this methane, both of which are extremely relevant when it comes to the possibility of extant life on Mars. One possibility is that it is being produced by methanogens, not necessarily methanogens as we know them on Earth, but methanogens nonetheless, by definition (an organism that produces methane [methanogenesis]). The second major possibility is subsurface volcanic/hydrothermal activity. Even though this second possibility does not directly point to life, it points to potentially "warmer" conditions below the surface, conditions where liquid water may exist and consequently conditions where extant life may exist. Another possibility, of course, is that the methane arrived via comet and/or meteorite impacts, a scenario that would account for only a fraction of the observed methane, and would probably have little baring on the possibility of life. Because of the hostile conditions at the surface of Mars, research in my laboratory has focused on the possibility of subsurface Martian life. Life in the subsurface would be non-photosynthetic, most likely chemoautotrophic, and relatively "extremeophilic" with respect to temperature and pressure. Methanogens fit this description and for the past 12 years, we have been studying methanogens as a model for Martian life. In 1998, we demonstrated that methanogens could exist on relatively low concentrations (down to 15 ppm) of molecular hydrogen, their primary energy source. Theoretically, molecular hydrogen is present, but if not, carbon monoxide has been measured in the Martian atmosphere, and some methanogens can use this in place of molecular hydrogen as an energy source. We are currently studying methanogens that have been adapted to metabolize carbon monoxide. In 2004, we presented evidence that certain methanogens could grow on a Mars soil simulant (JSC Mars-1). This has been important in trying to simulate the Martian subsurface. Here we present evidence that certain methanogenic strains can metabolize at pressures approaching those observed at the surface of Mars. Using the Andromeda Environmental Chamber at the Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, we were able to demonstrate significant methane production at both 400 mbar and 50 mbar of pressure. Washed cells were exposed to a hydrogen:carbon dioxide atmosphere under reduced pressure in a Mars soil simulant matrix (JSC Mars-1). Species tested were Methanothermobacter wolfeii, Methanosarcina barkeri, and Methanobacterium formicicum. Growth was determined by in situ gas chromatographic measurement of methane concentration during experiments and by re-growth after experiments. Growth under the conditions tested was primarily limited by rapid loss of water by sublimation. Molecular oxygen concentration was reduced by a palladium catalyst box, and one liter of a sodium sulfite solution (4 mM) added to the soil simulant. In initial experiments, when sufficient water was present, all three species produced methane at 400 mbar. In follow-up experiments, the pressure was lowered to 50 mbar and it was observed that all three species produced methane for at least two weeks. At the end of each experiment, samples were removed from the chamber and tested for viable methanogens. In all cases, viable methanogens were recovered. There are reports of organisms surviving at low pressures, but this is one of the first reports of organisms actively metabolizing at such a low pressure. Experiments taking the pressure even lower (ideally down to 6 mbar which would seem to be the lowest pressure at the Martian surface) are in the planning stages. However, it should be noted that pressure in the subsurface will be greater than that measured at the surface. Thus, demonstrating that an organism can survive/grow at the relatively low pressure of 6 mbar may not be necessary to suggest that it can exist in the Martian subsurface. Results from 12 years of research would seem to indicate that methanogens, as we know them, may indeed be able to survive and possibly thrive in the Martian subsurface. The discovery of methane in the Martian atmosphere indicates that we may be heading in the right direction.

P-161. MICROBIAL ORIGIN OF LIFE ON EUROPA

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Europa is a world where life may have existed or still exists. It becomes an important philosophical and practical concern to prevent contamination of this unknown world with microorganisms of terrestrial origin. However, we also need to explore hypothesis that life that originated on Earth was transferred to other planets, namely Europa. Similar hypothesis is more than century old (Arrhenius, 1908) and mostly concerned transfer of life to the Earth rather then from the Earth. The possibility of similar transfer was considered in detail (Mileikowsky et al., 2000) focusing mainly on Mars-Earth transfer but partially also on Earth-Mars transfer. Life proliferation on Earth is primarily based on water in liquid state. Potential planets containing water in liquid state are Mars (deep within the crystalline rocks) and Europa (under the thick layer of ice). It may be more difficult to detect life on Mars due to deep rocky environment than on Europa, where water is expected under the thick water ice. It can be shown that such dormant life forms can be preserved inside meteorite ejecta traveling from one planet to another. Meteorite mass surrounding the life forms provides an extra protection against lethal ionizing radiation. Both the launch and the landing of ejecta meteorites occur during highly energetical processes. Significant fraction of ejecta avoid heating above 100C and shock as they come from layer close to the surface (spall zone) where the shock pressure is reduced by interference of the pressure waves with the surface (Kletetschka et al., 2004; Melosh, 1984). Typical maximum thickness of the spall zone is less than half of the impactor diameter. The absence of shock in ejecta will not reduce ejecta velocity, as the acceleration is proportional to the gradient of the pressure reaching the maximum at the planetary surface containing the spall zone. The size of the ejecta controls the temperature reached due to friction with the atmosphere. Large initial velocity will cause rapid surface heating and this hot surface layer will be eventually stripped down during the altitude increase. The material stripping will reduce the heat sources by the time the ejecta reach the space the thin surface layer will cause size dependent internal heating due to poor heat conductivity of most of the rock compositions. In general the heat-modified layer (fusion crust) is less than 1 cm (depending on porosity and composition) and will not heat significantly rocks that are more than 10 cm in diameter. The transfer of life between planetary bodies hypothetically occurs mostly during the first 1 Gy of solar system existence due to large frequency of impacts. The thicker atmospheres due to impacts likely allowed safe delivery of the biological material inside ejecta material. After ejecta landing, the contact with liquid water would mobilize the biochemical mechanisms and start proliferation of the primary DNA/RNA from the host rock. The first microorganisms created this way would become a subject of evolutionary pathway dictated by Iovian moon environment. This would include adaptation for absence of light under the ice, high radiation doses from Jupiter (radiation belts), and abundance of water ice interface. Existence of such mechanism of life transfer calls for need of verification and appropriate system development capable of microbial life detection. Recent sampling of terrestrial aquifers (Shields, 2004) uses a DNA extraction method (Grunwald, 2001) that does not require designed to avoid cellular collection. The method takes advantage of existence of free-floating cellular-DNA dissolved in the aquifer water (dDNA) upon release upon cell death.. This is possible due to relatively largelong life-spanhalf-life of free floating dDNA in the aquifer before being leased anddegraded and utilized incorporated into a structureby surrounding microorganisms.

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P-162. TITAN MAY HOLD CLUES TO ORIGIN OF LIFE

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January 14th 2005 was deemed to be an uncommon day, because something which can be called miracle happened. The man-made' spacecraft Huygens probe had landed on a planet called Titan which is 1 221 870 km from earth. The greatness is not only due to in the extraordinary distance that our spacecraft had reached, but the similarity that Titan has compared with earth 4 billion years ago. The similarity is unique in the solar system and can help us with getting further understanding of the origin of life. By the information got from Huygens probe, we gradually know the general situation of Titan. First, Titan has a substantial atmosphere, one even thicker than Earth's. (1500 mbar) And nitrogen, methane, traces amount of ammonia, argon, ethane are the composition of the atmosphere. Nitrogen and methane are the main materials for the organic composition. Then, methane on Titan is just like water on earth forming a gas-liquid circulatory system. All the marks of the process of rainfall, the river corroding and machinery rubbing etc can prove that the forming of physiognomy on Titan has most resemblance with that on earth. And then, the soil on Titan is formed by the deposition of the particles of the hydrocarbon in the atmosphere (instead of clay on earth). Still, there are water ice (instead of silicate rock on earth), the mixture of ice-cubes and ammonia jetted from volcanoes (instead of lava on earth). So we can see many similarities, and still there are some difference in chemical composition, and some terrible physical condition: low temperature, huge air pressure, weak sunshine and 384 hours' day, with all the conditions above Titan can be formed. As the largest satellite of Saturn and the second largest moon in our solar system, Titan has long intrigue scientists.

Its atmosphere and surface composition are thought to resemble those of the early Earth (about 4 billion years ago). Titan's atmosphere is composed of nitrogen, methane and other organic compounds, such mixture under the action of different energy source can give rise to variety of organic compounds which play a key role in the terrestrial prebiotic chemistry. In any case Titan will serve as a plane-scale environment in studies of extraterrestrial organic chemistry and processes related to prebiotic chemistry. Early in 1953 the pioneer work in exobiology was done by Stanley L. Miller. By passing electric current through a chamber containing a combination of methane, ammonia, nitrogen and water, Miller obtained organic compounds including amino acids, the building blocks of life. This suggested that life could have arisen from materials and conditions present in early Earth history. In 1983 life scientist Wenqing Wang and co-worker using CH_4, N_2, PH_3, and H_2O as mixed gas did another electric discharge experiment, the experiment yielded 19 amino acids. PH_3 was introduced in this experiment, because it was detected in Jupiter's atmosphere. Recently laboratory simulations in which gas mixtures with the composition of Titan's atmosphere are irradiated with UV light, electrical discharge, or energetic electrons have produced a solid organic compounds-Titan thiolins. The compounds dissolve to yield amino acids that are the basic building blocks of life. So if Titan does have liquid water, there may be amino acids brewing in Titan's version of ‘ primordial soup’. By coupling the data obtained from laboratory simulation experiments, theoretical modeling and observation, scientists can reach a better understanding of the organic chemistry involved in a planetary or a cometary atmosphere. Titan may shed light on how life began. Maybe because of the differences in physical and chemical conditions, the form of life can be different from earth, bearing low temperature and breathing nitrogen etc. But all of these are just imagination. Now we can only see some simple materials and a series of primary chemical processes. But these how chemical processes lead to the origin of life is still a mystery waiting for us to explore.

P-164. LABORTORY SIMULATION OF PHOTOCHEMISTRY ON TITAN AND COMPARISON WITH AVAILABLE HUYGENS DATA

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Solar UV radiation is the principal energy source driving the chemistry in Titan's atmosphere. We have investigated the photochemical reactions occurring in Titan's atmosphere in a flow reactor using the 185 and 254 nm UV emissions from a low pressure mercury lamp (Clarke, et al., 2000; Tran et al., 2003). The mixtures of the gases (acetylene, ethylene, cyanoacetylene and hydrogen cyanide) were irradiated in the presence of methane and hydrogen. The solid product formed is an analog of Titan's presence of haze. Its complex refractive index was determined and compared with the corresponding refractive index derived from the optical data on Titan's haze derived from Voyager 1 (Tran et al., 2003)

The objectives of the present study are the determination the structures of the volatile reaction products and reaction pathways leading to them. Quantum yields for the loss of reactants and the formation of volatile products were determined form the rates measured by gas chromatographic analysis. Irradiation of mixture of acetylene, ethylene, cyanoacetylene, methane, hydrogen and nitrogen generated over 120 volatile compounds the structures of which were determined by GC/MS. The amounts formed of over 70 of these compounds were determined. The similarities and difference in the products obtained photochemically and by plasma discharges will be discussed along with comparison with the data available from the hyygens probe.

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P-170. SENSITIVITY EFFECTS OF CHEMICAL KINETIC UNCERTAINTIES ON PHOTOCHEMICAL MODELING RESULTS: APPLICATION TO TITAN'S ATMOSPHERE

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Kinetic parameters included in photochemical models of planetary atmospheres carry with them a certain level of imprecision. Photochemical models of the giant planets and their satellites are particularly sensitive to this imprecision as the low-temperature and wavelength-dependent photochemistry of their atmospheric compounds is still poorly constrained by laboratory evidence. This imprecision leads to some uncertainties on the mole fractions of chemical species computed in planetary atmospheres modelling, and is thus supposed to be contributing mostly to the differences between observations and computed predictions.

Our vertical distributions of hydrocarbons and nitrogen compounds present in Titan's atmosphere were obtained using an upgraded 1-D photochemical model, focused on integrating recent laboratory measurements and theoretical breakthroughs in a relevant description of the photochemical scheme. Monte-Carlo calculations are being performed on these nominal abundances in order to estimate the uncertainties on the mole fractions as a function of altitude for each compound and to pinpoint then specifically the photochemical parameters that are responsible for inducing the largest errors.

In this way, it is hoped that key reactions will arise and suggest laboratory experiments or/and theoretical studies from which the more accurate data would reduce the uncertainties of the models. This shows that we need to reform the way we think of photochemical models as a mean to study systematically the many chemical and physical aspects of Titan. It can be done mainly by integrating them among several other complementary approaches, such as experimental measurements, simulation studies and, of course, brand new in-situ observations through the Cassini-Huygens mission.

P-175. ELECTRIC ACTIVITY ON TITAN BEFORE AND AFTER CASSINI-HUYGENS ARRIVAL

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Titan is one of the most interesting planetary bodies in our Solar System due to its nitrogen-methane dense atmosphere, and because organic molecules in gas and condensed states have been detected. Prior to the Cassini-Huygens mission, spacecraft and Earth-based observations led to a significant understanding of the characteristics of Titan. Laboratory simulations and modelling studies have also contributed to enhance our knowledge of the satellite. A great deal of new information has started to be released from the Cassini orbiter surveys and from the Huygens probe monitoring activities performed during its descend through Titan's atmosphere. One of the most interesting questions about the atmosphere of Saturn's biggest satellite is the possibility of electrical activity. Hopefully, a definite positive answer to this interrogation is expected soon because searching for electrical activity on Titan is one of the principal scientific targets of the Cassini-Huygens mission.

The pioneering experimental approach to planetary atmospheric-environment research started with the classical work of Miller's prebiotic terrestrial atmosphere in 1953. For the specific case of Titan there has been a great deal of laboratory simulation experiments where mixtures of methane and nitrogen have been subjected to the action of numerous energy sources with the purpose of learning with deeper detail about the complex organic chemistry that develops in this surprising moon. A summary of the last 25 years of gas-phased experimentation in Titan's atmosphere will be presented with the aim of showing the influence of some experimental parameters on the energy yields of some hydrocarbons and nitriles, the main organic families already detected on Titan. The work will also compare the information obtained by different laboratories that sustain the possible presence of electrical activity on the Saturn's satellite with special emphasis in the work develop in our group using cold plasma discharges.

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P-176. THE ORIGIN OF LIFE IN THE NAHUA CULTURE

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How life began has been the subject of speculation and mythology from the dawn of history. Several concepts have been proposed through ages to explain the beginning of life. Awed by the mystery of the world around him, man has invoked a concept of creation, for example the book of Genesis, adopted interpretation from the Western heritage. Similar descriptions can be found in sacred books of other cultures. In Mesoamerican cultures, the origin of the universe and life was fundamental and common subjects of research that reach its highest philosophical form in the "codices" and prehispanic art. In these documents men expressed their thoughts, concerns, and fears of the world, nature, and life. For these cultures, understanding the cosmological vision and general ideas of the macro and micro cosmos have been one of the primary philosophical issues. In this research we analyze the concept of the origin of life from the Nahua perspective. The Nahua civilization flourished in the central plateau of Mexico, in the Mesoamerican world. In this culture, there were intellectual congregations named tlamatini that means "the one who knows". The tlamatini looked for answers about the concept of life by the observation of the world and expressed them through myths and poems. All the knowledge tlamatini possessed was sustained by empirical observation, for they did not have a direct relationship with groups of sorcery or witchcraft. Also, tlamatini and priests were different, but they were intrinsically linked in the high power spheres. The priests consecrated only to religious rituals and the sacred world. Tlamatini tried to explain how the celestial bodies operated within the world. Especially their influence in the creation of life, for this matter, they registered time estimations that can be found in their poems. These intellectuals had access to a knowledge that was the product of their observations and calculations, having as a starting point the origin and evolution of the world. Their most important concern was to understand the events of life and the relationship with the idea of time. These intellectuals played an essential role in the Nahua society, because they controlled the knowledge of time. The tlamatini created calendars to apply their perception of time into everyday activities such as agriculture. Nevertheless, some of the knowledge of the Nahua-Mexica culture came from a compilation of ideas and thoughts from cultures of prior historical periods. From the Nahua perspective, the origin of life is not one, but several placed in different ages or cycles called "Soles" or "Suns" The first period was called "The First Creation of the Earth" and occurred in ancient times. The Nahuas conceived life as an endless cycle of change in an uprising spiral. Each period or "Sol" ends with a cataclysm, but instead of repeating a fatalistic story identical to the last one, each new cycle created better worlds and species of animals, plants and food. The four forces of nature: water, earth, wind and fire (also seen in the classical ideas of the Western and Asian heritage) existed before the first "Sol" Those are the features that characterize the myth of the suns. With these basic elements the Nahua culture tried to understand the origin of life and their place in the Universe. They built a symbolic construction full with philosophical thoughts that still survives in some parts of our country. Like most ancient cultures, the cosmogonist explanation of the Nahua has a mythical and religious aspect. However, these types of expressions do not disregard the veracity of these interpretations. Through the collective unconscious these myths and leg-ends can survive in spite of the progressive rationalization of our contemporaneous culture.

P-179. EARLY IDEAS SUPPORTING SYMBIOGENESIS AND AGAINST CELL THEORY FROM SPANISH-SPEAKING SCIENTISTS

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The endosymbiotic theory resulted from microscopical observations of granullar bodies within nucleated cells in the late 19th century, and few years later underwent substancial development in the early 20th century in Germany, France, Italy and Russia, and the USA (Sapp, 1990). At the time these efforts somehow did not flourished in Western countries, and had little more support in the former Soviet Union where they were somehow efficently nurtured but remained confined because of political and language barriers (Margulis and McMenamin, 1992). The modern serial endosymbiotic theory was proposed by Lynn Margulis, as an original long-standing experimental argument in the late 1960's, and achieved in a slow-paced full academic recognition and support in the 1970's and in the 1980's (Margulis, 1993). This non-gradualistic evolutionary idea was considered a somewhat marginal approach since the very begining. All researchers involved had in common a more or less articulated experimental-based rejection of the German cell theory as backed up with Pasteur's endorsement. Cell theory supporters proclaimed that life had a cellular nature, and that living beings could only be formed from a cell or from a group of cells. In this context, a number of scientists from central – and peripheral ?scientifically developed countries reacted against the cell theory and proposed novel alternatives. Spanish-speaking scientists were not the exception and a few of the most distinguished persons of the academic millieu in their countries also contributed to this early debate from their own trenches. However, they remained excluded, as were marginal scientists from important metropolis, from the mainstream discussion mainly because of language barriers.

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P-180. MECHANISM OF AMPHIOXUS GASTRULATING CELL MOVEMENTS: FORCES THAT DRIVE THE MOST PRIMITIVE FORM OF CHORDATE GASTRULATION

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The process by which embryos acquire the body plan involves the coordination of cell fate decisions with cell movement during gastrulation. Although morphogenetic processes of gastrulation have been studied extensively in various species, only a few phylogenetic notices have been paid to the gastrulation of cephalochordate amphioxus, the closest living invertebrate relative of the vertebrates. The amphioxus shares a similar basic body plan with vertebrates. During gastrulation, it undergoes a primitive and relatively simple morphogenetic procedure to lay down this body plan. However, cellular mechanisms underlying amphioxus gastrulation movements remain unknown. Cortactin, an actin binding and cortical actin assembly activating factor, is well known to regulate cell migration mediated by FGF signaling in vitro. Here it is shown that during amphioxus gastrulation, the invaginating vegetal cells exhibit a marked increase of cortactin cortical activity. Similar expression pattern was also observed with Arp2/3 complex, a synergic co-operator of cortacin to enhance actin dendric polymerization. *Fgfr* was identified to be restrictly expressed in the invaginating vegetal cells. Distribution of cortactin in the cell cortex of these cells was impaired by treatment of the gastrula with an FGF receptor 1 inhibitor, SU5402. This drug also suppressed lammellipodia formation and cause dramatically change on cell surface morphology and cell motility in amphioxus gastrula. The vegetal mesendoderm cells could not invaginate and gastrulation were greatly retarded. These findings reveal an FGF signaling mechanism whereby the invagination movements during amphioxus gastrulation is mediated by cortactin-regulated actin polymerization.

P-181. SYNCHRONOUS ORIGINATION OF CODON STRAND AND CODED PEPTIDE: AN ORCHESTRATION

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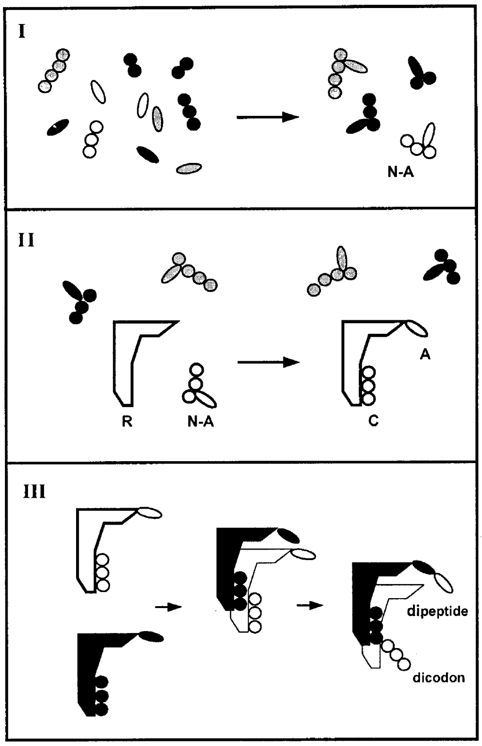
Eigen et al. (1971) first suggested the coevolution of RNA and protein. Zhao et al. (1996) demonstrated such concept with an simulation system mediated by phosphoric amino acid. However, the origin of genetic codon still remains confused. Though various theories have been proposing since the solve of the genetic code, no basic consensus achieved as. yet. However, we found that *contradictory theories*

could become complementary while examining them at successive stages of evolution, namely, stages of steric interaction, frozen information correspondence, and the emergence of colinearity of codon RNA and coded protein. An orchestration of major theories has thus been made.

The simplified diagram is just an approach, providing a platform for various theories to interact complementarily, and most likely resulting in a basic consensus.



Stage I Steric interaction (Woese, 1966) Amino acid (●) have associated with oligonucleotides (●) to form various conjugates (N-A) (Eigen et al,1981;Jukes, 1983;Yarus,1989;Ponnomperuma, 1996; Knight & Landweber,2000). The association of amino acid with the **first dimer** of oligonucleotide is of crucial significance.

Stage II Frozen information correspondence(Crick,1968) tRNA-like molecules have emerged(Eigen,1981),of which a few molecules (R) happened to be able to acylate amino acids and pair with oligonucleotides equivalent to the two components of some conjugates (N-A). They recognized each other, creating C-tRNA-A chimeras. the conjugates dissociated into codon (●●●) and coded amino acid(A)

Stage III Emergence of colinearity of codon strand (ORF) and coded polypeptide (Orgel,1987;Xiao,2002; Joyce,2004) Two tRNA chimeras juxtaposed, and the two amino acids at one end, and two nucleotides at the opposite end polymerized synchronously, resulting in the emergence of dicodon & dipeptides. As the same process went on, the codon strands (ORF) and coded peptides would have also originated synchronously

P-182. STABILITY OF ORGANIC COMPOUNDS IN HIGH-TEMPERATURE AND HIGH-PRESSURE ENVIRONMENTS SIMULATING SUBMARINE HYDROTHERMAL SYSTEMS

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Submarine hydrothermal systems (SHSs) have been regarded as probable sites of the origin of life on the Earth since their discovery in the late 1970s (Yanagawa and Kobayashi, 1992). In prior to generation of life on the Earth, organic compounds could be formed in Earth paleo-atmosphere (Kobayashi et al., 1998) and/or could be delivered by extraterrestrial bodies such as comets (Chyba and Sagan, 19xx).

In these days, deep-sea biological colonies were discovered near SHSs. In addition, presence of novel biosphere in sub-surface of SHSs has been suggested (Takano et al., 2004a). Organic compounds such as proteins are released from *in situ* microorganisms. Nowadays, we can expect both organic compounds of biological origins and those of abiotic origins near SHSs.

These organic compounds released to hot would be thermally transformed. It was claimed that organic compounds, particularly amino acids, are not stable in high temperature environments (Miller and Bada, 1988). We reported that not free amino acids but complex precursors of amino acids could be formed abiotically from either simulated primitive atmospheres or simulated interstellar media (Takano et al., 2004b). Amino acids in proteins are also of combined form. Here we examine the stability of free and combined amino acids and in high-temperature and high-pressure environments simulating SHSs by using a supercritical water flow reactor (SCWFR) (Islam et al., 2003).

Target molecules are as follows: Free amino acids, protein (human serum albumin = HSA), complex amino acid precursors formed from a mixture of carbon monoxide, nitrogen and water by proton irradiation (hereafter referred to as CNW): CNW gave not only amino acids but also carboxylic acids after hydrolysis.

Aqueous solutions of the target molecules were heated in SCWFR at 473–673 K for 1–4 min, and then quenched in ice bath. The pressure was maintained at 25 MPa during the reaction. Amino acids in the resulting products were analyzed with an amino acid analyzer after acid hydrolysis. Molecular weights of the products were estimated by gel filtration chromatography. Carboxylic acids in the resulting products were analyzed by capillary electrophoresis and/or GC/MS after alkali hydrolysis.

Recovery ratio of alanine in HSA and CNW were 30% and 42%, respectively when they were heated at 573 K for 2 min, while that of free alanine was only 0.02%. It was shown that combined amino acids were far more stable than free amino acids in high temperature environments. Moreover, ornthine, β-alanine, β-aminobutyric acid, and β-aminovaleric acid, which are not originally included in proteins, were formed from HSA. HSA was decomposed into shorter fragments during heating, while molecular weight of CNW was little changed.

Carboxylic acids, including mono-, di- and tricarboxylic acids were identified in the hydrolysate both before and after SCWFR-processing. Yield of carboxylic acids was increased after heated. The yield of acetic acid was, for example, doubled when CNW was heated at 573K for 2 min. It is suggested that novel production of carboxylic acid precursors exceeded their decomposition. These results suggest that complex precursors of amino acids and carboxylic acids that were formed prebiotically could survive and evolve in primitive SHSs.

In these days, novel biospheres have been found in subsurface of SHSs through “the Archaean Park Project”. It would be of great interest to find signatures of biological and abiological amino acids in such extreme environments.

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P-183. BIOFILMS ON BIOTIC SURFACES: A LINK IN THE CARBON CYCLE ON EARLY EARTH

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Comparative analyses of more than 200 sequenced microbial genomes indicate that widespread lateral gene transfer has occurred among distantly related microbes over the course of their evolution. Based on these observations, it has been proposed that early cells, having relatively few genes, existed as communities in which cells freely exchanged their genes. Some of these communities would have evolved to efficiently utilize available nutrients and thereby to increase in biomass. Ultimately, significant amounts of carbon would become incorporated into cell biomass. Cell polymers in these primitive assemblages would serve as a readily available source of carbon and energy for other primitive cell communities comprising members that had evolved the ability to degrade these polymers. Presumably, such polymer-decomposing communities played a central role in cycling carbon on the early Earth. In order to degrade insoluble polymers, members of these communities would have evolved enzymes (e.g., hydrolases) that catalyzed the breakdown of biogenic polymers, and the ability to transport these enzymes across their cell envelopes. We suggest that polymer-decomposing cells formed biofilms of growth on the surface of primitive microbial communities, and that the activities of these decomposer biofilm communities played a key role in cycling carbon on early Earth.

Most present-day microbes persist associated with surfaces as structured biofilm assemblages, rather than as free-living planktonic cells. Formation of biofilm communities involves a complex developmental process that results in structures with a characteristic architecture, encased in an extracellular polymeric matrix. Biofilms have achieved a degree of notoriety due to their detrimental effects on human health (e.g., in infections) and in the environment (e.g. within water conduits). However, the impacts of biofilms are not all negative, and recent results indicate a central role for these structured communities in nutrient cycling on Earth today. Their ubiquitous occurrence suggests that biofilm formation may be an ancient behavior that has enabled microbes to persist in their environments. Surprisingly, little is known about present-day polymer-decomposing biofilms that could serve as models for understanding primitive communities involved in carbon cycling on early Earth. As models, we are investigating cellulose-decomposing biofilm communities. Inasmuch as cellulose is presently the most abundantly produced polymer on the planet, we hypothesize that cellulose-decomposing biofilms play a key role in the global carbon cycle. We examined the development of cellulose-decomposing biofilms by three different cellulolytic bacteria, Cellulomonas uda, a facultative aerobe, Clostridium phytofermentans, an obligate anaerobe, and Thermobifida fusca, a filamentous aerobe. In response to different environmental signals, all three species colonized the surface of cellulose, formed structured communities typical of biofilms, and eventually degraded their nutritive surface. These results suggest that biofilm formation is a behavior generally exhibited by bacteria for the efficient degradation of insoluble polymers, and that it may have been a characteristic of ancient communities involved in carbon cycling on early Earth.