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INTERNAL REPORT
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and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

CONFERENCE ON THE STRUCTURE AND MODEL OF THE FIRST CELL

The Alexander Ivanovich Oparin 100th Anniversary Conference

Miramare, Trieste (Italy)
29 August - 2 September, 1994

SUMMARIES

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During the Third Trieste Conference on Chemical Evolution we are honouring the pioneering work of Alexander Oparin, whose 100th Anniversary we celebrate this year. The central theme of the conference is the structure and model of the first cell.

This will be inserted in a programme that will include the early paleontological record, physical, chemical, informational, biological and exobiological aspects of the origin and structure of the first cell.

In this Internal Report we have gathered together some of the summaries of the papers to be read at the Conference, which were available at the time of going to press. The meeting was possible thanks to the generous support of the International Centre for Theoretical Physics, the Commission of the European Communities, the International Centre of Genetic Engineering and Biotechnology, UNESCO, the International Centre for Science and High Technology, and the International Science Foundation.

Cyril Ponnamperuma, Director

Julian Chela-Flores, Local Organizer

10 August 1994

SOME PHYSICAL PROBLEMS IN BIOLOGY:
Aspects of the origin and structure of the first cell

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Abstract. A review is presented within the framework of the theory of evolution, after it has been extrapolated from the population level to the cellular and molecular levels. From Darwin's seminal and persuasive insight - the theory of common descent - we assume, with him, that "probably all the organic beings which have ever lived on this earth have descended from some one primordial form, into which life was first breathed" [1]. We are now aware that this primordial cell may have been a protocyanobacterium, but it has often been called 'a last universal ancestor', a 'breakthrough organism', or a 'progenote', a term introduced by Woese [2] which has gained wide acceptance. Strictly speaking, in the 'intermediate period', ranging from the first living cell to the progenote, life may have evolved in the absence of significant diversity, effectively as a single phylum, incorporating organisms whose genetic systems were already based on DNA. Earlier still, prior to the encapsulation of nucleic acids in microspheres, evolution may already have been at work on RNA molecules (the 'RNA world'). This takes our discussion into the period of chemical evolution, a concept first put forward by Oparin [3], whose principal merit is to have formulated the underlying problem in clear scientific terms. This review does not attempt to be comprehensive. It is mainly devoted to the discussion of certain concepts that may have played a relevant role in the pathway that led to the origin and evolution of the progenote. We do not dwell on the main events of the intermediate period. The topics that we have chosen to include are: the origin of chirality of protein amino acids, the origin of translation, and the origin of the genome. We conclude with some comments on one further aspect of the evolutionary process - the development of biodiversity - by considering the origin of the first eukaryotic cell, an event which, according to the fossil record, may have preceded the evolutionary radiation in the early Cambrian by over a billion years.

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Search for Bioorganic Compounds and Organisms on MARS

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Authors from Russian side will be confirmed at the Conference.

Abstract

From the experiment with accelerator beams, simulating interactions of cosmic rays with atmosphere in primitive planets and satellites, we concluded that the bioorganic compounds like amino acids is easily formed in a simple gas mixture by bombarding charged particles, even if they are not a strongly deduced gas such as CH_4 and HN_3. Organic compounds might be formed in primitive Mars, because a substantial amount of water had existed in Mars 4 billion years ago. On the other hand, we found that cosmic rays is one of the most effective energy source for chemical evolution not only in the heliosphere as well as in interstellar space.

Although neither organic compounds nor organisms were detected in Mars by Viking in 1970's, we can not exclude their existences in Mars. Because, the soil samples, which were collected from the Mars surface, might be irradiated by ultraviolet sunlight and might be strongly oxidizing soils.

We plan to send a new instrument to the places where the traces of water were found or near the poles of Mars. The proposed instrument consists of a quadrupole mass spectrometer to detect chemical compounds and a fluorescent microscope system to detect organisms (cells) and bioorganic compounds in bulk.

We propose to carry out this program as an international cooperative work with scientists and technicians in the world, who are interested or already working in this field.

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Evolution of Enantioselectivity at the Liquid Gas Interface

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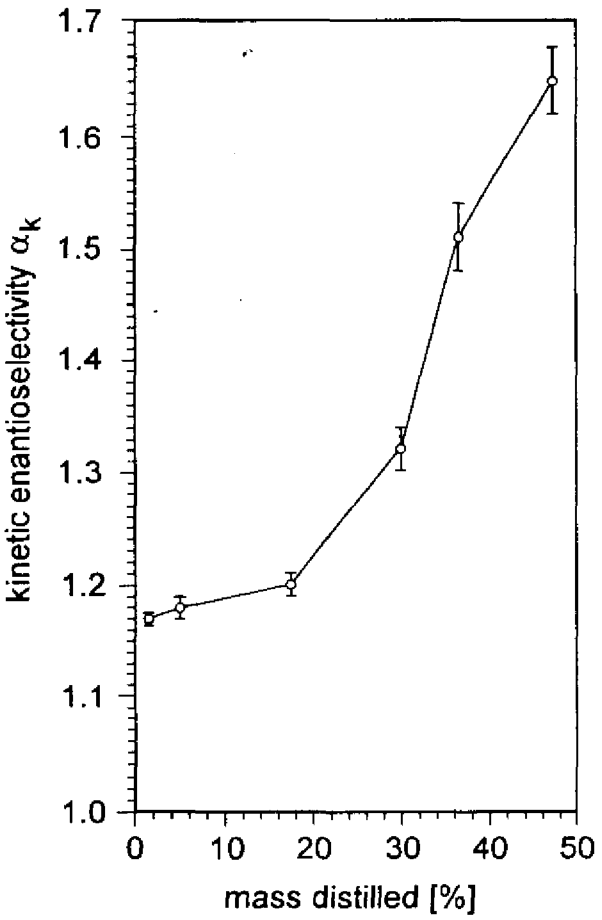
Unexpectedly, scalemic mixtures (> 0% ee) show a significant discrimination during distillation. The most pronounced effects were observed for ***(S>R)***-N-TFA-amino acid esters (valine, leucine, alanine), with differences of up to 20% ee in the fractions, as determined by GC on *L*- and *D*-Chirasil-Val. We define the kinetic enantioselectivity α_k of the phase transition on the basis of the relative rates:

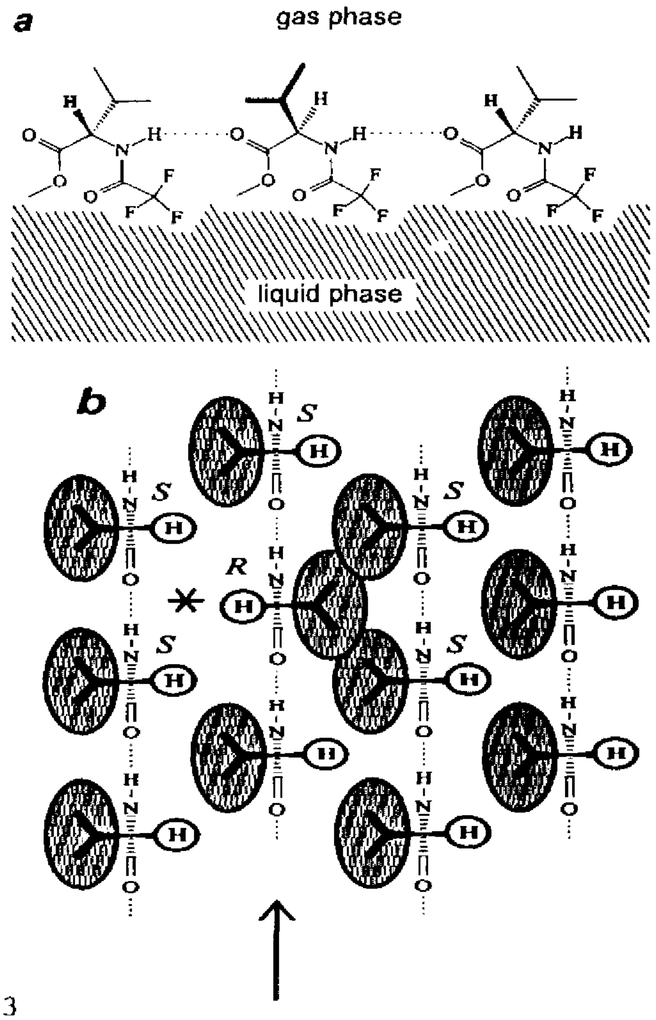
$$\alpha_k = k_R / k_S \qquad \text{where } (k_R = -\Delta[R]/[R]/\Delta t) \geq (k_S = -\Delta[S]/[S]/\Delta t)$$

In contrast, a merely thermodynamic interpretation was ruled out by vapor pressure measurements: The boiling points of *RS*- und *S*-N-TFA-Val-OMe differ by no more than $\Delta T < 0.25$ °C, whereas thermodynamic calculations would demand for $\Delta T > 7.5$ °C. In the course of the distillation, a gradient of ee is built up along the column. The picture of two-dimensional homochiral domains at the liquid gas interface is corroborated by physicochemical studies in the neat liquid, including ^{1}H- and ^{13}C-NMR spectra, surface tensions and excess volumes of mixing of the enantiomers. Like in living systems [1], non-equilibrium effects driven by a flux of energy manifest themselves in transient local ordering of the system.

[1] E. Schrödinger, *What is Life?* (Cambridge Univ. Press, Cambridge, 1944).

from EXPERIMENT **to a MODEL**





HARDWARE AND SOFTWARE IN BIOLOGY: SIMULTANEOUS ORIGIN OF PROTEINS AND NUCLEIC ACIDS VIA HYDROGEN CYANIDE POLYMERS

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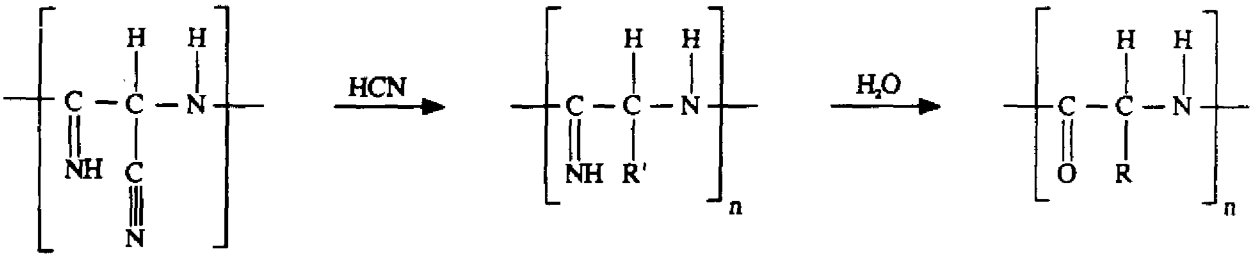
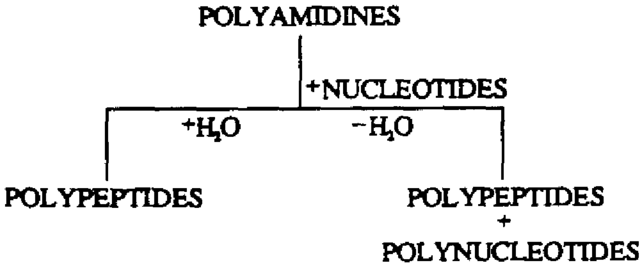
Hydrogen cyanide polymers--heterogeneous solids varying in color from yellow to orange to red to black--could be major components of the dark matter observed on many bodies in the outer solar system, including asteroids, comets, moons, rings and planets. Current studies of these ubiquitous compounds point to the presence of polyaminomalononitrile (I), a polyamidine structure built only from hydrogen cyanide. Cumulative reactions of HCN (or other reactive species) with the activated nitrile groups of I yield other polyamidines (II, with side chains R') which are converted stepwise by water to polypeptides (III, with side chains R):



I II III

Overall, this series of reactions constitutes a route for the direct synthesis of polypeptides from hydrogen cyanide and water without the intervening formation of α-amino acids.

Implications for prebiotic chemistry are profound. Primitive Earth may have been covered by HCN polymers as well as other organic compounds, either through bolide bombardment or by photochemical reactions in a reducing atmosphere. According to this model, membrane material--carboxylic acids, carbohydrates, polypeptides--accumulated in lakes and oceans, while on land polyamidines could have been the original dehydrating agents directing the synthesis of nucleosides and nucleotides from available sugars, phosphates and nitrogen bases. Most significant would have been the parallel synthesis of polypeptides and polynucleotides arising from the dehydrating action of polyamidines on nucleotides:



Metabolic material--hardware--thus arose separately from genetic components--software--as proposed by Freeman Dyson. Subsequent interfacing, perhaps with the help of clays, then produced the first replicating protocells.

On our dynamic planet this polypeptide-polynucleotide symbiosis mediated by polyamidines may have set the pattern for the evolution of protein-nucleic acid systems controlled by enzymes, the mode characteristic of life today.

The Beginings of The First Cell

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Abstract

The early microbe is not emergent (novelty), but a gradual transformation from protocell or protogenome - an active network of oligonucleotides and polypetides, Eigen's hypercycles - for improved selection by confinement. The primal cell could be approached from the prebiotic chemistry or backward as antiquity. The first route was taken by Oparin and Fox. The second by Woese and Eigen through 16S RNA and tRNA respectively. The method of attrition by Margulis to assess the composition of the minimal viable cell from what is known about today's sophisticated cell lacks the rigor of a Dayhoff's matrix or the parsimony method. There were prebiotic amphi philic lipids and sun driven energy conversions. The liposomes easily enveloped or fused with the genomic complex. What was asked of the lipids - ether or ester- was membrane fluidity. The protocell initially a RNA world, highly mutational, led to a variety of cells from thermophilic to cynobacteria contrasted to prsent day restricted cell types due to the cell becoming an attractor in the non-linear dynamic sense. Also, it developed behavior: a sensory perception via ionic channels for information processing of its environs culuminating in our brain which does faster computational prediction.The cell size was sufficiently small to thwart nonlinear dynamic patterns inimical to its cellular function and division of labor. But the cell division was becoming increasingly a Turing process.

In accord with Dobzhansky's early dictum about evolution biolgy, the evolut- ion experiments started by Oparin is becoming a major industry. Oparin's experiments were in gel chemistry. So also was Fox's proteinoid spheres. They believed natural selection took over to bring the first cell. Dyson similarly believed that there were self-replicating enzymes. We know now much about lipids and membranes, nucleic acids and sequences. Evolution experiments with competing macromoecules (Joyce, Shostak) is becoming a standard practice for its biotechnological rewards (S.A. Kaufman). Hypercycles or coevolution is the basic foundation for evolution from macromolecules to ecology. The next step is to encapsulate it. Recent exciting colloborative experiments of Luisi of Zurich and Biebricher of Gottingen to produce replicating protocells using fatty acids and $Q\beta$ replicase would stimulate evolution experiments from the macromolecular basis to the cellular basis.

On the Stability of Proteinoid Microspheres

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Proteinoid Microspheres are stable hollow spheres in the range of 5 fm diameter. Their stability is discussed in terms of macroscopic energies. It is shown that the bulk and surface energy contributions alone cannot lead to stable microspheres. If electrostatic energy, due to transmembrane voltage, is taken into account, stable hollow spheres are proved to exist. For several reasons, however, this should not be regarded as the ultimate explanation of microsphere stability.

ALFONSO L. HERRERA: A MEXICAN PIONEER IN THE STUDY OF CHEMICAL EVOLUTION.

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Over the period of 1905-1942 a series of experiments on the origin of life were performed by Herrera. He devoted forty-three years to the experimental investigation of this problem. He developed a new science call "Plasmogeny" defined as the study of the origin of the protoplasm, the physico-chemical bases of life (Herrera, 1905). Later, about 1935, he started the publications of "Gaceta de Plasmogenia" (in spanish) and "Bulletin du Laboratoire de Plasmogénie": (in french). These bulletins were published until 1942, and many of his experiments were published there.

Herrera was born in 1868 in Mexico City, son of well known naturalist of the same name. He died in his laboratory on September 17 of 1942. Herrera's early experiences were varied. He studied Pharmacy and he graduated in 1889. His interest for biology started in 1885, when he published his first paper related to zoology, later he founded the Mexico City Zoo.

In his research Herrera chose as starting materials ammonium thiocyanate and formaldehyde, also he used polymers from sources other than living organism. Among the products that he reported include vestiges of starch, at least two amino acids, a condensation product of protein character and globules of green, yellow a red pigments (Herrera, 1942). His proposal was based on the ready formation of NH_4SCN in some juvenile volcanic gases (Gautier, 1910). He pointed out many ideas related to the origin of life and the necessity for laboratory experiments. Many of his proposals perhaps are unpromising now, but as Dr S. Fox wrote (Fox, 1965): Herrera deserves credit for historically early experiments in this field.

Herrera, A.L., 1905: Una nueva ciencia: La Plasmogenesis, Bol. de Instrucción Pública , 606-625, México.

Herrera, A.L., 1942: A new theory of the origin and nature of life, Science, **96**, 2479.

Gautier, A.M., 1910: Compt. Rend. **150**, 1564.

Fox, S., 1965: The origin of prebiological systems. Academic Press, New York, p. 357.

SOME ASPECTS ABOUT LABORATORY COMETARY MODELS.

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During the past decades, astronomers have directed their attention toward the study of the solar system bodies, like comets, and they have made many discoveries. These studies have provided profound insights into the formation and earliest story of the solar system.

A complementary role in the study of comets has been played by laboratory research on cometary models. In this paper, we discuss some aspects of laboratory experiments proposed in the literature, specially those associated with the chemical reactions that may occur in the comets. These comments are made the light of chemical composition, energy source, relevant chemical reactions and compounds detected in several laboratory simulations of cometary material.

Biosynthesis of Archaebacterial Membrane Lipids

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Archaebacteria are interesting organisms for the study of origins and early evolution of life. Their biochemistry is different from that of eubacteria, and the comparative studies will give us important clues for the speculations on biochemistry of the primitive cell.

One of the most striking and characteristic differences of archaebacteria from eubacteria and eukaryotes is the chemical structure of membrane lipids. The archaebacterial lipids are either sn-2,3-di-O-phytanyl glycerol (diether) or sn-2,3,2',3'-tetra-O-phytanyl diglycerol (tetraether). The membranes of the halophilic archaebacteria consist of diethers, whereas the membranes of other archaebacteria are comprised of both diethers and tetraethers with varying ratios. The author and his colleagues have focused their attention on the biosynthetic mechanisms of two most remarkable features of the structures of the archaebacterial lipids; (1) the polar head group is attached to the sn-C1 position, that is, the stereochemistry of the glycerol moiety is reversed in the archaebacteial lipids (optically they are dextrorotary), and (2) in the tetraether lipids, two diethers are covalently linked in a tail-to-tail fashion (thus the terminal OH groups of the tetraethers occur in the trans configuration).

The author and his colleagues carried out isotope labeling experiments to clarify the biosynthetic mechanisms of the glycerol moiety of the archaebacterial lipids. The experimental results suggest that (1) in halophilic archaebacteria, a stereochemcical inversion takes place at C-2 of glycerol phosphate before the alkylations, and (2) in acidothermophilic archaebacteria, phosphorylation takes place at C-3 position of a free glycerol molecule.

The author and his colleagues recently found that specific inhibitors for squalen epoxidase inhibit the growth of acidothermophilic archaebacteria. These inhibitors inhibit the biosynthesis of tetraether lipids, and have no effect on the growth of halophilic archaebacteria and biosynthesis of diether lipids. The results suggest that the enzyme responsible for the tail-to-tail condensation of the ether lipids is related to squalene epoxidase, a key enzyme for the biosynthesis of sterols, important components of eukaryote cell membranes.

THE CHIRALITY BREAKING IN THE PHOTOLYSIS OF THE LEUCINE ENANTIOMER AND 5'CMP

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ABSTRACT

In previous studies of weak interactions between amino acids(AA) and nucleotides(NA), a new model was proposed to account for the direct interaction between AA and NA in water solution by presuming that more than one of AA are stacked around NA moving in two-dimension to form a shell through weak interaction mainly hydrophobic interaction. T.U.Selinger et al theoretically predicated the spontaneous formation of complete equilibrium pattern with either 1D or 2D model in the direction of molecular tilt and lead to the chiral symmetry breaking. J.C.Flores suggested the AA phase separation to the postulated P-violating effect and the chiral symmetry breaking in an oriented monolayer of rigid chiral amphiphiles deposited on mica has been reported. Because of the anologous of this separation of chiral phase in two dimension to the sponteneous resolution of enantiomers in three-dimension, and the nucleotide derivatives probably act as three-dimensional chiral substrate, so can cause the difference in photolysis results between D and L-leucine.

It is known that UV irradiation of nucleotide derivatives in O_2 saturated aqueous solution results in the decrease of characteristic adsorption peak near 260 nm mainly through the photohydrate formation, and the quantum yield for hydration of Uracil increases with the molar concentration of water, while for Me_2Uracil the quantum yield depends on the square of the water concentration. The presumed existence of a layer of AA shell around NA will certainly decrease the local concentration of water and "protect" NA from photohydration. So we use photochemistry approach to substantiate our above model.

The results are shown in Fig.1, where the change in relative quantum yield is plotted against the relative concentration of [AA]/[NA]. It is clear from the figure that,the relative quantum yield of cytosine derivatives decreases markedly with the increasing of AA concentration. This is in accordance to the prediction of above model. It is surprising for us to note in the process of photolysis research that even at the level of mononucleotides, D and L leucine behave differently in the interaction with NA. L-leucine seems to adsorp around NA more intensively than D-leucine so the L-leucine is more effective to protect NA from photolysis than D-leucine. The detailed mechanism of the difference between D and L leucine is under the further investigation.

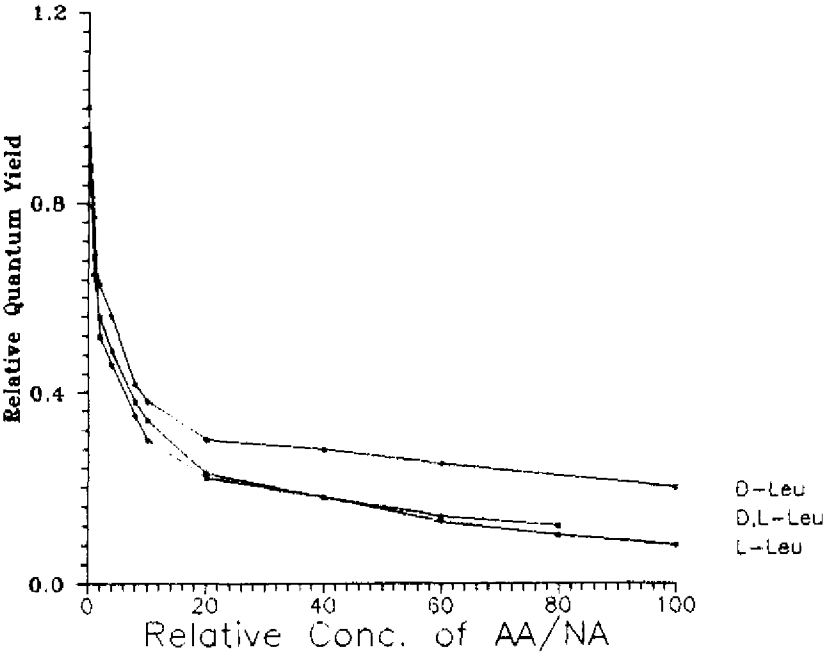

Fig. 1. 254 nm Photolysis of the 5'-CMP and Leu binary system. Relative quantum yield vs. AA/NA

THE OCCURRENCE OF ACRITARCHS IN PROTEROZOIC MICROFLORA OF BRASIL,

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In the region of São Gabriel, State of Goiás, Brasil, it is common to find outcrops of thinly laminated dolomite containing chert nodules and layers, with coloration ranging from gray to black depending on their content of organic matter. Despite the uncertainties regarding the correct stratigraphic position of these outcrops, once São Gabriel microbiota is found in chert situated near the base of Paraopeba Formation (Bambui Group) within the zone of transition with the underlying Paranoa Group (*sensu* Alvarenga and Dardenne), the associate microfossiliferous community is typical of the chert-algal facies of the Middle and Upper Proterozoic (1350-630 M.a.) distributed over all the continents.

The São Gabriel microflora basically consists of allochthonous elements (colonial fragments belonging to the genus Eoentophysalis as well as solitary and colonial planktonic forms).The vestiges of the original microflora, responsible for the cryptalgalaminated *fabric*, refers to preserved organic matter in the form of kerogen and soluble fraction , both syngenetic and derived from the most part of photo-autotrophic benthonic communities.

About 1% of the planktonic microfossils stand out for its morphostructural complexity comparable to species of the genus Kildinella (e.g. *K.hyperboreica* Timofeev, 1966) (Subacius,SMR-,Ciencia e Cultura 37:1945-1956), usually associated with clastics sediments of the Proterozoic. Those sphaeromorphs (≥ 40 μm in diameter) exhibit a robust wall, sometimes ornamented, containing black and compact inclusion inside of membranous structures and morphologic characteristics related with spores and reprodutive cysts of eukaryotic algae (e.g.opercula).

The occurrence of acritarchs in the black chert of São Gabriel is the first formal description of unicellular eukaryotes in the fossiliferous records of the Brazilian Precambrian, and reveals the microfossiliferous potential of the clastics horizons in evolutionary and biostratigraphics studies for helping determine the age of these outcrops.

Physico-Chemical Basis And Mechanisms For Membrane Formation In Pre-Biological Environment

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It is likely that in the pre-biological environment, there has to be mechanisms available to produce membrane bound structures. It is also assumed that there has to be a similarity between the membrane structures around cells in the biological systems at present and the membranes of the pre-biological systems. From surface and colloid science point of view, there are several mechanisms that result in the spontaneous formation of membrane bound structures. These membrane bound vesicles could have served as pre-biological reactors. The reactions occurring within these vesicles or microreactors are determined by the nature of the membranes. This could have contributed to further diversification of types of molecules synthesized by these microreactors. It is evident that the pathway from these membrane bound microreactors to pre-biological cells is not yet delineated.

It has been proposed that collapse of adsorbed films of lipids and polymeric species at the air/water interface, spontaneous formation of vesicles from oppositely charged lipids, the formation of coacervate droplets and spontaneous formation of membranes by monolayer coated aerosol droplets when they impinge on the air-water surface having a lipid monolayer, are all possible mechanisms to produce these membraneous structures. It appears that such vesicles surrounded by a membrane could have produced considerable diversity of chemicals depending upon the local environment such as pH, temperature, salt concentration as well as the nature of various cations (Ca^{++}, Mg^{++}, Fe^{+++}, etc.). The implications of these molecular mechanisms for membrane formation to chemical evolution will be discussed in this presentation.

Repetitive Elements of Protein Sequences: Fossils of Early Evolution

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Conformational energy calculations on protein segments indicate that the overlapping segments of the polypeptide chain are in one of the low energy structure of the respective oligopeptide. The number of these low energy conformations is much smaller than the number of the theoretically possible structures of an oligopeptide. A simple calculation shows that even for a short polypeptide chain of 100 residue, the number of the sequences variationsthat determine conformations in which all the overlapping segments are in low energy conformation is about 40 order of magnitudo smaller than the total number of sequence variations. Therefore protein sequences must evolved from simple sequences conserveing this stability critarion. Poly amino acids and polypeptides with repepitive sequence can be products of gene duplication and represent the most primitive polypeptides in which the overlapping (identical!) segments are in low energy conformations. Many protein do contain repetitive sequence elements. It is very unlikely that a long non-symmetrical heteropolymer could evolve spontaneously into a homopolymer or into a repetitive sequence polymer. It is more likely that the repetitive sequence motifs are remainders of the early stage of evolution.

In this lecture repetitive sequence motifs of proteins and the possible DNA sequences which might code them will be discussed. This analyses can provide insights into the primitive forms of DNA and proteins.

STRUCTURE AND PALAEOBIOLOGY OF THE EARLY CELL : EVIDENCES FROM INDIA

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Early earth's abiotic atmosphere was reducing and dominated by hydrogen since it condensed from a dust cloud about 5 billion years ago. The atmospheric and oceanic conditions for early life on Earth suggest that around 3.8-3 billion years ago oxygenic atmospheric conditions had developed and the earliest unicellular microorganisms (molecular chemical fossils) appeared on Earth which were also responsible for development of **Microbialites (stromatolites)**, the first megascopic evidence of life on Earth. This also supports the evidence for transition from a primitive reduced atmosphere to a highly oxidised one like the modern atmosphere, development of ozone layer and the photosynthesis of Cyanobacteria in the oxic oceans of the world.

Recent biochemical and carbon isotopic evidences from the Indian lithosphere (Archaean-Proterozoic sediments of the Peninsular and Lesser-Himalayan basins) suggest that early Earth's atmosphere-ocean system was buffered by mantle. The structure and palaeobiology of the early cells revealed that uni to multicellularity of cells reflects varying rates of photosynthesis and the mechanism of cell division may be as a result of mitosis or meiosis, recorded in Deoban cells of the Lesser Himalaya, India.

Alexander Ivanovich Oparin in 1924 showed that an input of energy (i.e. lightning, radiation) could bring about the creation of Organic substances in reducing atmosphere such as amino acids (building blocks of proteins), sugars, purine and pyrimidine bases. These organic substances were concentrated in the so called *Primeval Soup* where compounds of high molecular weights were formed (**Macromolecules**) together with proteins, nucleic acids and polysaccharides. It is worth mentioning here that proteins have the capacity to produce enzymes and nucleic acids have the capacity to pass on the information. However, we have yet to explain the triggering of first life whose basic characterstics are metabolism, multiplication and capacity to evolve.

Bacterial communities were widespread on early Earth at least as early as 3465 million years as recorded by Prof. J.W. Schopf from Early Archean Apex Basalt of Western Australia (Schopf, 1993). However, prior to 3.4 Ga the molecular fossils are probably abiotic in origin and do not provide much information on the palaeobiology of the earliest cells.

The most primitive living organisms were *prokaryotes* (without cell nucleus) which lived anaeroibically. Experimentally it has been proved that there can be no "*Spontaneous Generation* in the oxygen rich atmosphere of the present time because organic substances are oxygen depleted and get oxidised immediately in such environment. "*Spontaneous Generation*" is only possible in reducing environments.

These prokaryotes derived their energy by converting glucose to lactic acids, a process which liberates very little energy. It is postulated that to avoid the deadly UV radiations they must have lived at least 10 m deep in the oceans. However, the upper levels of water would have conveniently exposed to UV radiation to facilitate the production of amino acids which served as nutrients for the organisms living in the primeval soup. These organisms were *heterotorphs*.

Almost simultaneously, certain organisms developed the capacity to assimilate carbon dioxide and convert it into carbohydrates in the presence of water where sunlight provided the main source of energy for this conversion. Hence, *chlorophyll* came into existance. These organisms were "autotrophs". The chlorophyll bearing oxygen producing these organisms were *Cyanophytes*, the blue green algae. Now they are proved to be cyonobacteria.

The above phenomenon was followed by the concerntration of atmosphere in oxygen and those animals evolved who were able to respire oxygen and derived their energy from it. At the same time, ozone layer began to form in the upper layers of the atmosphere, which screened the earth from the UV radiation of the Sun. Presently also there are organisms which can either live aerobically or anaerobically depending on the availability of oxygen. The transition from one life to another life is called *Pasteur Effect* which occurs when the oxygen content is only 1% of the present day atmosphere. It is convincingly believed that once this critical level of oxygen was reached, Organisms started respiration so to say the begining of the metazoans started. The evidences of metazoan evolution are now recorded from the Lesser Himalaya of the India.

Just prior to the metazoan fauna, when the oxygen level was from the Pasteur Level the resulting increase in available energy brought about the evolution of *Eukaryotic* cells which are considerably more differentiated than Prokaryotic ones. In addition to the nucleus, they can possess **mitochondria**, **chloroplasts** specially differentiated **flagella** and other organelles. They might have been created by the process of *endobiosis* (Union) of various prokaryotic cells in a proto-eukaryotic host cell. Such cellular structures have been recorded from the *Deoban chert* microbiota of the lesser Himalaya.

THE ORIGINS OF CELLULAR CHIRALITY

In the 1920's speculations were first made by the Russian scientist, A. I. Oparin, that living organisms arose naturally on the primitive earth through a lengthy process of chemical evolution that began in the early atmosphere. Subsequent investigators including Haldane, Urey, Miller, et alia have expanded upon this primordial atmospheric genesis of life.

In this process various sources of energy, including lightning, shock waves produced by thunder, meterorites and comets, and radiation from the young sun provided the energy that transformed simple atmospheric molecules into more energized organic compounds. These compounds then rained out into the more protective marine environment– shallow seas or oceans. There through watery reactions or agglomerations they eventually became the prototypes of proteins, sugars, nucleics and other precursors to the molecules of life. The prerequisite to all of this activity was presumed to be a *strongly reducing atmosphere, one rich in hydrogen and devoid of free oxygen.* Had oxygen been present, the organic molecules would have been destroyed by oxidation (1).

The marine hydrothermal vents, or "black smokers", provide an entirely different environment for the genesis of life. Their discovery is especially interesting because molecular phylogenies based on the analysis of biological molecules have shown that all heat- loving prokaryotes occupy the short, deepest branches of universal evolutionary trees; that is, they are the oldest recognizable organisms. But again, there are objections to this ancestral lineage. High temperatures lead to a rapid and irreversible hydrolysis of unprotected organic compounds and thus to very short lifetimes incapable of known forms of evolution (2).

The above samples of the chemical environments proposed for the origins of life are but a few of the many that are contained in the literature; however, none appear to address the concept of chirality or handedness, let alone offer a rationale for this arcane but transcending feature of life. One of the most striking properties of life is the fact that of the twenty indispensable protein amino acids, all (except glycine) are left-handed, that is, they rotate polarized light counterclockwise. In contrast, biologic sugars are all right-handed. Synthetic amino acids and sugars of nonbiological origin contain equal numbers of handed molecules. One cannot make spiral molecules of DNA out of synthetic, achiral amino acids and sugars (3).

Chirality is not a unique feature of cellular molecules. It is exhibited at the atomic level under the action of the the "weak force" which causes electron orbits to become right- handed helices in the vicinity of the nucleus (4). On the macroscopic level, chirality is a very common human characteristic, and it is also expressed through Coriolis forces that result in the counter-clockwise spiral of hurricanes in the Northern hemisphere.

This treatise will speculate on the origins of cellular chirality in a unique geochemical setting for the precursors of life– the bubble columns in the surface environment of the World's oceans. This model may offer a bridge to the atmospheric and sea floor models mentioned above. This "more protective" environment envisaged by Urey may also provide the sedimented source for our oldest phylogenies in the geothermal "smokers".

A case can be made for the concept that bubbles in the ocean possess many of the properties of "life": (1) they exhibit anabolic negentropy, with total material and energy increases as they expand with the decreasing upward pressures, (2) they exhibit chirality due to Coriolis forces acting on their helical paths to the surface, (3) they "intake" selective hydrophobic materials through the process of adsorption, (4) they synthesize new materials through surface and photic energies, (5) they are "replicated" in multitudinous amounts by the action of wind and wave, (6) they do not replicate by themselves any more than human cells do, but they participate in a macro-replication of new born materials in the much larger entity of seawater, sun, wind, wave, land inorganics--an ergodic ensemble with innumerable generative cycles.

The seabubble is only one in a long series of geophysical events, but perhaps a very important one for what we differentiate as "life". Its birth is preceeded by the capture of a small amount of our atmosphere in the curl of a breaking wave. This atmosphere and the wave are themselves the product of a long series of cosmological events; from the dynamics of sun driven weather, water originating from volcanic outgassing, planetary *accretions, supernovae, galaxie formations, and a myriad of events going back to the Big* Bang.

The breath of captured air is forced downward a few meters into a primordial "soup" of seawater where it gives birth to a multitude of tiny bubbles of gas, surrounded by a liquid environment containing dissolved, colloidal, and particulate solids. This three phase system represents an elemental sample of the varying configurations matter forms in a universe of structure, temperature, and gravitational pressures. The gas comes from our atmosphere, the liquid from the hydrosphere, and the solids from the lithosphere, the three primary partitions of our planet. The tiny bubble is born as a focal point in the expression of cosmic dynamics in a unique Earthly environment.

The bubble begins its journey to the surface and soon expresses its "life force" of negentropy. It grows through surface expansion as the pressure decreases, and it gains surface energies with decreasing entropy in opposition to the general rule of increasing entropy in the universe. It draws this energy from the reordering of the water molecules surrounding the bubbles expanding surface. Instead of death and the dissolution of energy the sea bubble is an open system experiencing anabolic processes and the accumulation of energy and material from its surroundings (5). These increasing energies soon convert the tiny bubble into a forming "vesicle" that accumulates a skin of aquired solids from its materially rich environment. It is now a viable, growing, three phase system of speculated proto-life.

The vesicle's accumulation of matter involves the complex processes of adsorption and the "love/hate" relationship that materials in solution have with water. They are hydrophilic in their love for their supporting surroundings, and yet they must maintain a hydrophobic hate for the medium if they are to maintain their identity and not succumb to the total dissolution powers of the watery medium. The more hydrophobic materials will leave home waters when attracted by the surface powers of the dynamic, passing vesicle. The vesicle "intakes" these materials by adsorption as a beginning step of its metabolic processes. The continual "bioparticulation" of dissolveds and colloids in the few seconds of rise of the vesicle lifetime are orders of magnitude more massive per unit of time than those of photosynthesis, the primary production process of living materials (6).

The vesicle's journey to the surface is not always in a straight line. Many paths can result because of the currents and complexity of the environment. A prominent path is a swirling helix. The helix path is of interest because it has a "handedness" or chirality– in that it must swirl from right to left or left to right. This assymetry may be influenced by the weak force (which is very small) in the processes of phase changes but is much more likely ordered and amplified by Coriolis forces. Assuming this is the case, the vesicle on its upward path is ordering its material, influenced by helical patterns with chirality– expressing some very important features of life.

As the rising vesicle accumulates energy and material in an informed manner it soon learns how to "create" or synthesize new materials. Its energy can break old bonds and form new ones. It can also selectively reject weaker sorbed materials for the stronger in a competitive environment. This productive capability increases as it nears the surface with the addition of the sun's photic energy impacting on its surface. Ensembles of vesicles are now mature cauldrons of metabolic activity, intaking the more hydrophobic materials from their environment and transforming them in an creative and repetitive manner.

Some of the most chemically important reactions are those of dehydration, condensation, and hydrophobic interactions which are vital to the formation of the giant polymers that are essential to life. The vesicle eventually metamorphises into a creative engine of ordered structure, possibly the precursor of life– if one can sharply delineate these intellectual concepts. Finally, it reaches the surface and with a final burst it breaks and coagulates into new particles of material. The chiral symmetry breaker has achieved its mortal end, which is essential to make way for a new generation of producers. Some of the micro-particles are taken aloft as an aerosol and scattered to the far reaches of the World ocean. Other particulates slowly sink back into the sea to nourish other forms of life or sediment out to the ocean floor. Still others re-dissolve and again are picked up by another attracting bubble or vesicle to follow a new creative destiny.

The above scenario should provide a fruitful path into the arena of amino acids, proteins, enzymes, RNA, and phospholipid membranes. Trillions of bubbles per second performing their functions over a few billion years would not only produce proteins, RNA and membranes, but many phylogeny of these and similar compounds. The ones that exist today are probably the evolutionary survivors of the complex material, energy, and information mixture contained in a ergodic ensemble of our geophysical environment. Some investigators appear to associate the origins of life with the origin of individual life. That is, they consider the beginning of life a "birthing" event, a meteor or bolt of lightning that created the living from the dead. On the contrary, it must have taken eons of an evolutionary continuum to evolve the animate from the inanimate.

It should not be too difficult to test the "Coriolis" hypothesis for the origin of cellular chirality. [Experiment: Obtain samples of dissolved organic materials from both hemispheres (preferrably at mid-latitudes and at depth) and statistically check the chirality of the amino acids and sugars. A portion of the material (maybe small) should be synthesized by oceanic bubbling and give a statistical edge to opposite chiralities in the hemispheres. Note: all samples should be prefiltered to remove as much already chirally formed, organic detritus as possible.]

The above sea bubble model does not rule out the basic atmospheric model suggested by Oparin and expanded by Haldane, Urey, Miller, etc. One of the important happenings in the cycle may have been the volatilization of compounds that were carried up into the atmosphere and activated by ultraviolet light or electrical disharges. However, these compounds would have been very crude building blocks incapable of generating replications until they had received the chiral conditioning by the helical patterns of rising bubbles. These compounds along with aerosols would be rained back to the oceans for innumerable repetitive cycles. The inanimate building blocks may have originated in the atmosphere but chirality and the more unique characteristics of life must have originated in the oceans.

Some of the chiral particulates formed upon the demise of the seabubbles must have slowly found their way to the ocean floor through the process of sedimentation, to provide a source of proto-life for those forms found at the geothermal rifts. Or more probably, later thermophilic forms found their way to these locations while the primitive archean forms from the surface died out long ago.

If the above speculations on the origins of cellular chirality are verified by experimentation, they lead to new interpretations of natural phenomenon. They would provide a much stronger bridge between the geochemical and life sciences than that originally envisioned by Oparin. Darwinian concepts would take on a new dimension, and possibly be extrapolated to a wider range of phenomenon than we usually categorize as "life". Does the negentropy power of sea bubbles expressed in the accumulation of matter, energy and information result in evolutionary processes? Are certain molecules synthesized and collected and naturally selected over other less strongly bonded molecules. Or extrapolating further, can the process of : sun caused thermal gradients; resulting weather patterns; high and low atmospheric pressures; storms; winds, waves, gravity formed curling, the pocketed breath of air, etc., resulting in complex organic polymers – can this ensemble be considered an evolutionary process? And finally, can the Coriolis symmetry breaking, resulting in chirality in the three phase system (7) reproduce one of the most unique characteristics of the Universe?

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LOW TEMPERATURE SPECIFIC HEAT ANOMALIES IN D- AND L-VALINE

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ABSTRACT

The origin of chirality is closly related to the evolution of life on the Earth.Until now,no proposed mechanism has been able to explain how the completely asymmetric roles of mirror-image biological molecules could arise.Recently,Salam proposed that due to the attractive character of the parity violating force in electro-weak interactions,a phase transition at low temperature could eventually lead to enantiomeric purity.

Specific heat measurement is one of the powerful method to investigate the mechansim of second order phase transitions.A series of experimental tests has been undertaken and we have studied the differential specific heats of D and L Valine in single crystal state with sample mass being 100mg and 30mg respectively by differential scanning calorimetry in the temperture range 77-320K. Experimental data are presented on the temperature dependence of the specific heat in Figure.The specific heat jump at Tc 272K indicates the symmetry breaking of D-Valine.There is a smooth line of Cp-T(K) with L-Valine sample in the same temperature range.Furthermore,a specific heat peak at 272K has also been found with L-Valine as the reference sample and D-Valine. It seems to undergo a phase transition only in D-Valine .

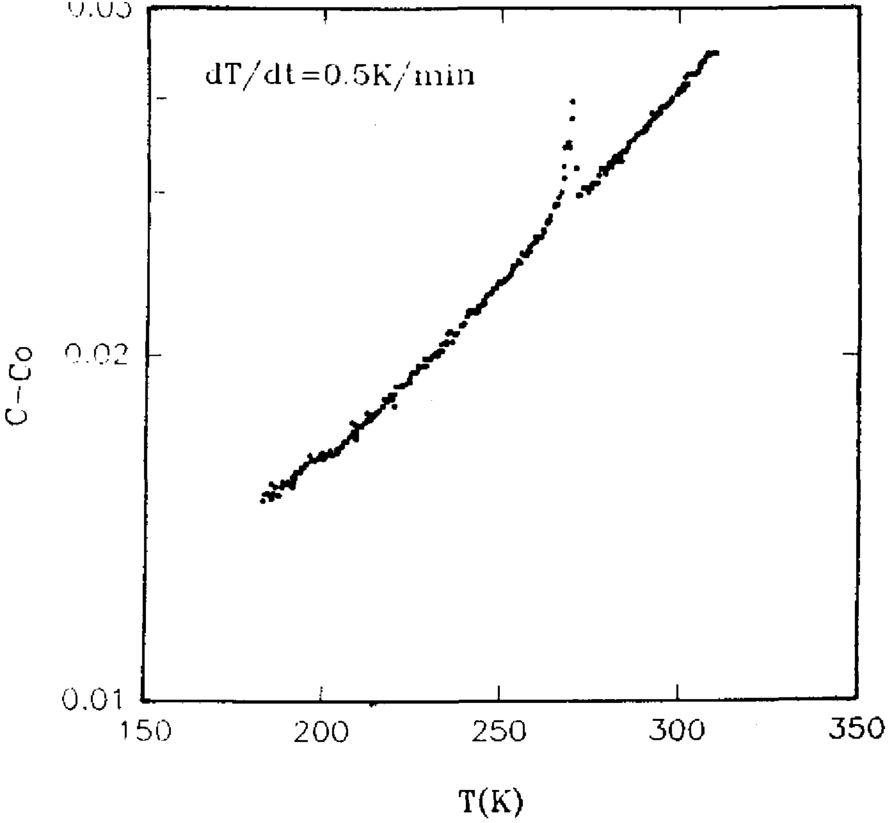

Fig1　Specific heat of D-Valine measured by temperature increasing DSC method (sample:single crystal,100mg)

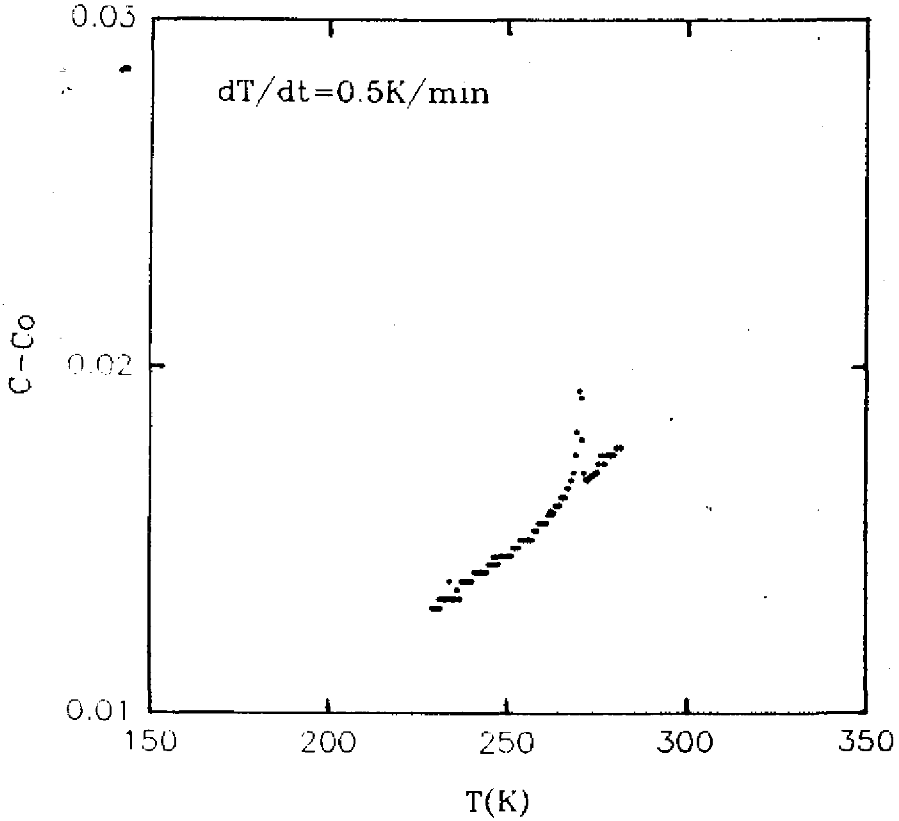

Fig2　Specific heat of D-Valine measured by temperature decreasing DSC method (sample:single crystal,100mg)

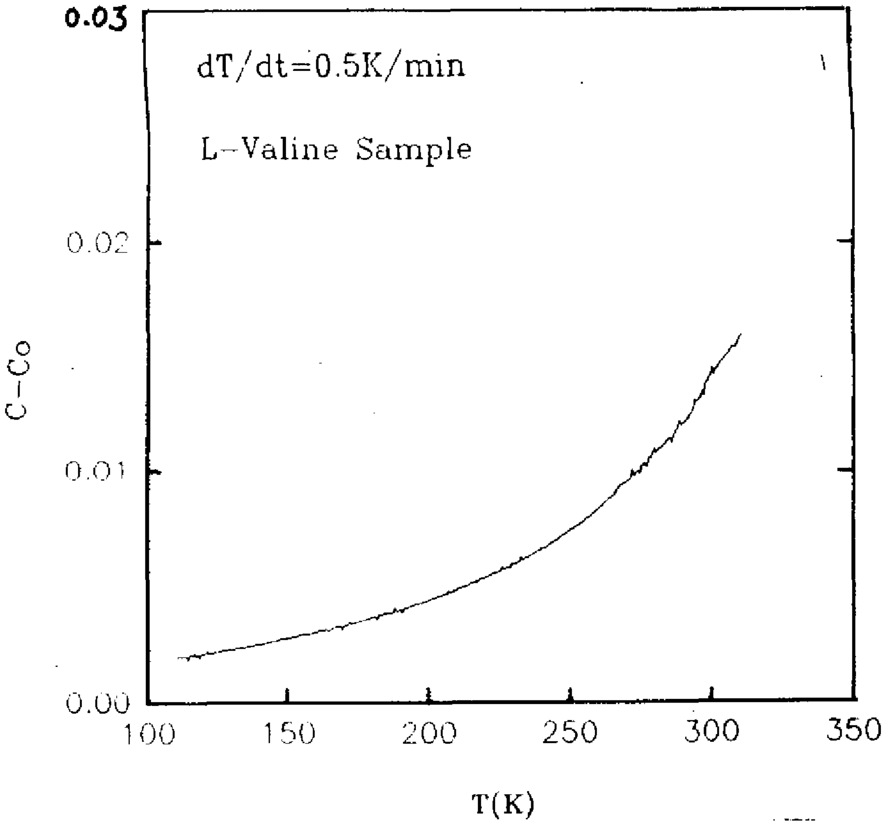

Fig3 Specific heat of L-Valine measured by temperture increasing DSC method (sample:single crystal,30mg)

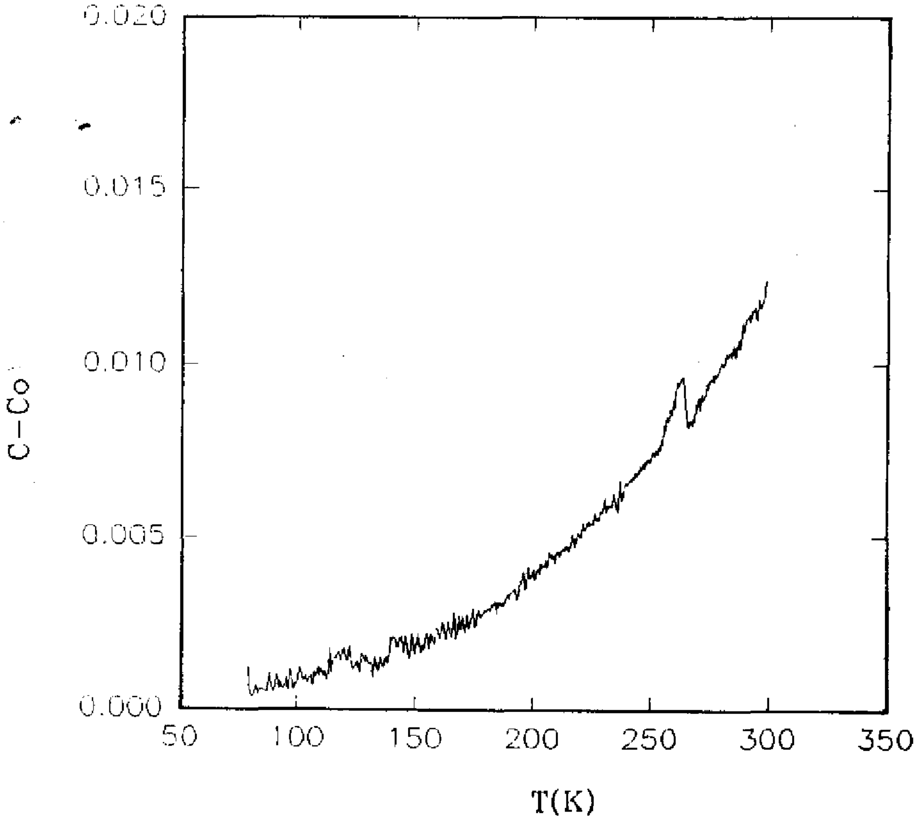

Fig4 Difference of specific heat between D- and L-Valine measured by temperature increasing DSC method (sample:single crystal , D-Val , 30.28mg ; L-Val , 30.25mg)

A Model for the Basic Element of Life Chemistry

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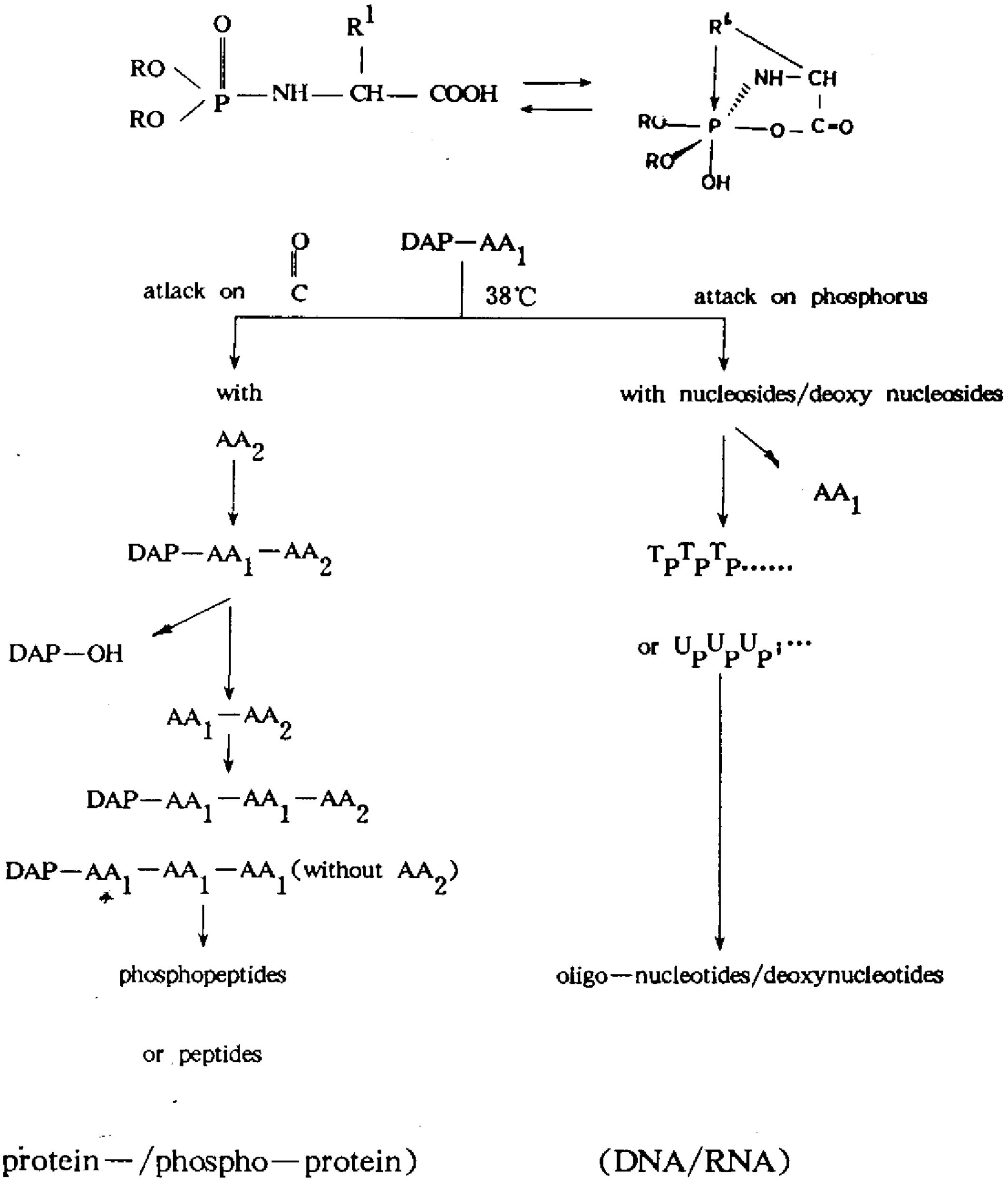
Abstract: A series of model compund (DAP—AA) composed of the amino acid (AA) and dialkyl phosphoryl group (DAP) is set up as the basic element of life chemistry. The self—catalysis of DAP—AA gives the self—assembly oligo—peptides in the direction of N—terminal to C—terminal, even in aqueous medium at 38℃. The oligo—nucleotides could also be assembled from nucleosides through the assistance of DAP—AA. The DAP—AA could be the energy source as well as the phosphoryl donor for the prebiotic synthesis of bilological macromolecules. A general expression for the model is proposed.

Key words: basic element of life chemistry, model expression, phosphoryl amino acids.



A general expression is proposed for this model:

$$F(P)=\sum_{n=i,j,k}^{n} f(P)_i \cdot [f(ch)_j+f(aa)_k]$$

Scheme 1. DAP—AA as the common energy source and phosphoryl donor for the prebiotic synthesis of phospho—protein and nucleic acids.