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By Victor Ostrovskii & Elena Kadyshevich

Karpov Institute of Physical Chemistry, Russia

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Life Origination Hydrate Hypothesis (LOH-Hypothesis): Original Approach to Solution of the Problem

Victor Ostrovskii ^α & Elena Kadyshevich ^σ

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I. INTRODUCTION : PECULIAR FEATURES OF THE LIVING-MATTER ORIGINATION PROBLEM, OF PREVIOUS HYPOTHESES, AND OF OUR APPROACH

The Life Origination Hydrate hypothesis (the LOH-hypothesis) [1–13] is the original one and has no common features with any other hypothesis that considers mysterious and stirring origination of this phenomenon. This hypothesis has been developed by us for about ten years. It was presented at different steps of its development at about 20 International physical, chemical, thermodynamic, biological, geological, and specialized conferences in the form of lectures or oral presentations [14]. This hypothesis considers the mechanism of life origination, and it can be applied to any celestial body, where the appropriate conditions exist.

The problem of the border between the animate and inanimate has been discussed since 1935 when Stanley pioneered isolation and crystallization of the tobacco mosaic virus [15]. Several opinions expressed in this discussion are considered in [4]. Pauling has no reason to consider this question as a scientific one;

indeed, it reduces to the definition of the notion. If a living organism is defined as a material structure capable of self-reproduction, then plant viruses should be reckoned among living organisms. If it is assumed that living organisms must be capable of metabolism, then plant viruses must be regarded as mere molecules having a molecular weight of about 10^6 and a structure allowing them to catalyze, in a certain medium, a chemical reaction leading to the synthesis of molecules identical with them" [16].

We emphasize that Pauling's opinion is not faultless in the light of modern knowledge. It has been many times demonstrated in the past decades (see, e.g., [17]) that not only nucleic acids but even simpler organic substances are capable of self-replicating with consumption of certain chemical elements from the surrounding and excretion of unspent molecular residues. Should we call such a process "metabolism"? The answer can be deduced only from the practice of using the term. Today, viruses and even viroids are regarded as biological substances and are studied by biologists, although a vast field of activity remains open to physicists and chemists. Each of these species contains DNA of a specific composition.

In our opinion, it is therefore justified to regard the appearance of nucleic acids in the course of evolution as the onset of the simplest pre-cellular life. We believe that, once nucleic acids originated and propagated and a medium appropriate for their existence and replication had appeared, the appearance of cellular life was merely a matter of time; if a living system were devoid of nucleic acids, with its protein content preserved, the vital activity would surely cease; if a living system were devoid of its protein, with the nucleic acids preserved, the vital activity of the system supplied with nutrients might normalize with time.

A number of rather different definitions of the phenomenon of life are available. Because the subject of our paper is the process of life origination, we are forced to define the phenomenon that is the subject of our consideration. Meanwhile, we consider the primary life only and, therefore, no one of the widely distributed definitions is entirely appropriate for our consideration. Besides, using one of the available definitions, we took

Author α : Karpov Institute of Physical Chemistry, Moscow, Russia.

E-mail : vostrov@cc.nifhi.ac.ru; ostrovskii.victor@mail.ru

Author σ : Obukhov Institute of Atmospheric Physics RAS, Moscow, Russia. **E-mail** : kadyshevich@mail.ru

chances to meet the objections of authors or users of other definitions. Therefore, we took a decision to formulate the following unpretentious definition for the subject of our consideration. Life is the phenomenon characterized by a combination of the natural chemical processes that lead to the extended self-reproduction of DNA molecules from generation to generation and by translation of all or almost all significant maternal features to the daughter molecules. The rare changes in the chemical composition of the DNAs will be termed intraspecific transformations or microevolution of DNAs.

Each DNA molecule represents both the initiator of life processes and their smallest individualized product that, being introduced into the medium of a definite elemental composition, determines the direction of life processes. Apparently, DNA molecules are capable of conserving their individual features for a long time outside the medium necessary for the life processes and under rather low temperatures, for example, in Antarctic ices, ancient remains, etc.

With the reservation analogous to that which is made as applied to the definition of the term life, we refer to the term "living matter" as follows. Living matter is a mass of the substance of a cell or of a conglomerate of cells, each containing, at least, one DNA molecule and a set of the source substances capable of synthesizing new DNA molecules. In order that the living-matter function of the extended self-reproduction could be realized repeatedly, the cell or the conglomerate of cells must be connected with the environment by mechanisms of inflowing of source substances and out-flowing of side products of the self-reproduction.

In our opinion, living matter resulted from thermodynamically conditioned, natural, and inevitable chemical transformations governed by universal physical and chemical laws and such an approach underlies the LOH-hypothesis (and the Mitosis and Replication Hydrate hypothesis, the MRH-hypothesis [11, 18, 19]); Nature went step by step by its way from minerals to living matter and decreased gradually the Gibbs free energy at each step. Just as a result of the directedness of natural phenomena, researchers are principally capable of mental doubling back the course of Nature and, thus, of revealing the main milestones in Nature's progression. A naturalist must search for a "hook" in the environment in order to catch onto it and, having the thermodynamic laws as a guiding thread, to guess the logics used by Nature in its development.

The similarity of the principal chemical and structural features inherent in DNA molecules of different species is considered by us as an evidence for the similarity of the conditions of origination of different DNAs and for the long-term constancy of the corresponding natural parameters (such as the temperature, pressure, medium composition,

gravitation, and so on) characterizing these conditions. On the other hand, the wide multiplicity of the DNA structural and chemical peculiarities is considered by us as a result of some dissimilarity in the medium parameters occurring in different regions where the primary DNA molecules had originated. Meanwhile, according to our notions, DNA-like molecules with different sequences of nucleotide links and with different nontrivial N-bases could be formed within one localization.

Origination of nucleic acids (DNA and RNA) had preceded cellular life, while origination of nitrogen bases (N-bases that are pyrimidines (cytosine (Cy) $C_4H_5N_3O$, thymine (Th) $C_5H_6N_2O_2$, and uracil (U) $C_4H_4N_2O_2$) and purines (guanine (G) $C_5H_5N_5O$ and adenine (Ad) $C_5H_5N_5$) and also xanthine (X) $C_5H_4N_4O_2$, hypoxanthine (Hx) $C_5H_4N_4O$, and some others), deoxy-D-ribose (DDR) $C_5H_{10}O_4$ and D-ribose (DR) $C_5H_{10}O_5$, and phosphates had preceded nucleic acids.

In our terminology, the formation of the first proto-cells and development of the mechanism of extended self-reproduction of DNA molecules inaugurated the living matter origination, DNA and RNA molecules being the simplest forms (objects) of the pre-cellular living matter rather than the living matter as such and N-bases, riboses, phosphates, nucleosides, and nucleotides being the living matter simplest elements (LMSEs), i.e., the living matter constituents.

The problem of living matter origination can be subdivided into two sub-problems: origination of DNAs and RNAs as the simplest objects of the pre-cellular living matter and origination of the living matter as such, i.e., the formation of cells and development of the mechanism of extended self-reproduction of the DNA molecules.

In the LOH-hypothesis, substantially the same phenomenon of formation–destruction of hydrate structures, but in its different visualizations, is applied for solution of these two sub-problems.

According to the LOH-hypothesis, synthesizing of the LMSEs, assembling them together, and joining in certain sequences went in the same localization. Many of such localizations existed.

Authors of the previous hypotheses finish their considerations, at least as a rule, at the first or second process; we try to reproduce Nature's entire way from simple minerals to living matter.

The living-matter origination problem has the following peculiar features.

1. In the DNA and RNA compositions, the N-bases, riboses, and phosphate groups are located in strictly determined sequences and the N-bases are limited in sizes, in spite of the occurrence in their composition of chemically active groups, which seem to be capable of further chemical transforming. Therefore, such molecules could originate only under very specific conditions. These

- peculiarities of nucleic acids led us to the idea that they originated inside such a mineral honeycomb three-dimensional solid matrixes which selectively absorbed source substances of definite compositions and whose cavities had sizes that limited the chemical accretion of each individual LMSE but did not hamper polycondensation of LMSEs. It should be expected that such matrixes are not constructed from cavities of one size but include the cavities of different geometric forms, because the sizes of N-bases, riboses, and phosphate groups are different.
2. DNA and RNA molecules and living matter as such generally consist of only five chemical elements: H, C, N, O, and P. This fact means that the set of the source substances that produced DNA and RNA molecules within the "parent" matrix had to include a key component capable of selective reacting with the other components of this set and with no other chemical substance that occurred in the environment.
 3. In the DNA compositions and in the RNA compositions, all riboses are similar in their chemical nature and the diversities of N-bases are rather restricted. These features give us grounds to think that the LMSEs originated as a result of the strict directedness (i.e., of the thermodynamic front) of the chemical reactions inside a mineral matrix and that the thermodynamic front was caused by a low temperature level and, as the consequence, by slowness of the reactions that proceeded one by one in the direction of decreasing in the free energy of the system until the structural cavities are completely filled; after the free volume in the cavities of any one size became too small for ubiquitous formation of the same additional atomic group, the final filling of the cavities was regulated in a special manner.
 4. Such a mechanism could be realized only under the condition of the absence of heat flows, electrical discharges, and weather perturbations capable of destroying any order rather than of creating and maintaining it. The best conditions for the thermostat used by Nature for DNA origination could be provided in the Earth's crust under ground or under seabed.
 5. In DNA double helixes, purines are bound with pyrimidines, but purines are never bound with purines and pyrimidines are never bound with pyrimidines; moreover, Cy is never bound with Ad and Th is never bound with G. These features were discovered in the 1950s and are not explained up to now. It is unlikely that this collection of events is explainable by any cause of non-geometric nature, and, apparently, this cause is hidden in a specific matrix character of the media of DNA origination and reproduction.
 6. How can the DNA monochirality be explained; i.e., why did Nature use only desoxy-D-riboses in DNA molecules, and how did it manage to do this? In our opinion, this phenomenon could have only one realistic explanation. Namely, DNA molecules originated within a matrix of a honeycomb structure with such geometry that only D-riboses could join together the N-bases with phosphate groups. The consumption of D-riboses led to a shift of the equilibrium and formation of new D-riboses. Thus, we come again to the concept of a mineral matrix. We apologize to our possible opponents for the rigidity, but we believe that the solution of the problem of monochirality should be simple, because we are in sympathy with Great Newton who wrote in his "Principles" that "Nature is simple and does not luxuriate in excesses". And it is our principal opinion that the cause of this phenomenon is of chemical and geometrical rather than physical nature.
 7. Oparin's opinion [20, 21] on the necessity of external energy for synthesizing biologically active substances from minerals is disproved unambiguously. Oparin believed that the entropy of biological substances is so low that no enthalpy change is capable of making negative the Gibbs free energy for synthesizing biologically active substances from minerals. Speculations concerning a supposedly low value of the entropy of living matter and the necessity of external energy for its origination are also typical for a number of later hypotheses. However, physicist and biologist L. Blumenfeld [22–24] calculated the typical living body entropy on the basis of the generalized approach of statistical physics and came to the unambiguous conclusion that "...according to physical criteria, any biological system is ordered no more than a rock piece of the same weight" ([23], p. 90). Somewhat later, the standard values of the enthalpy of formation ($\Delta_f H^0$) and of the entropy (S^0) were obtained experimentally for different biologically active substances [25–28]. On this basis, we calculated the standard changes in the Gibbs free energy ($\Delta_r G^0$) for a number of reactions leading to formation of N-bases and riboses from minerals [3, 4]. These works had proved unambiguously that no external energy is necessary for synthesizing biologically active substances from definite minerals, because the free-energy changes in such reactions are negative and rather great in magnitude.
- Thus, the external energy is by no means necessary for synthesizing biologically active substances from some sets of minerals. Furthermore, Nature had to provide removal of the energy that evolved as a result of these natural syntheses. However, this problem did not arise

because the syntheses proceeded under low temperatures and went very slowly.

8. Authors of the previous hypotheses, factually, considered origin of life as an occasional phenomenon, because the gross-process of formation of individual components of DNAs and RNAs and their self-assembling is extremely improbable. Meanwhile, it is now evident that living matter occurred repeatedly; for example, according [29], multicellular organisms appeared independently in the Earth history no less than 24 times.
9. Advocates of most previous hypotheses use Miller's experiments [30, 31] up to now as the ground for their assumptions or as the support for their conclusions, although, substantially, the results of Miller and his followers have only remote connection with the problem of living-matter origination. Indeed, under the action of electric discharges, they obtained some amino-acids, cyanic acid, cyanoacetylene, and other N-, O-, and H-containing substances in gas phase as a result of processing N_2/CH_4 , $N_2/CH_4/H_2$, $N_2/CH_4/H_2/CO_2/NH_3$, and other gas mixtures; in recent years, still wider variety of different aliphatic and aromatic substances was produced under the action of electric discharges on gas mixtures that contained water aerosol [32]. However, it is under question that the conditions of their experiments are close to those that caused living-matter origination about 3900 Myr ago when the first living matter originated according to [33, 34]: the atmospheric compositions and pressures are chosen on the basis of uncertain models, which therewith transform with time [35, 36], and the power, cubic density, and temporal frequency of the atmospheric electric discharges are taken voluntary. It was shown (e.g., [37–39]) that the products obtained in electric discharges, being used in rather large amounts and in sufficient concentrations and powers, are capable of giving N-bases in water solutions as a result of multistage syntheses (riboses are not detected in their experiments (e.g., [40])). However, it is hardly surprising that the thermodynamically feasible reactions proceed under some conditions; such facts have no evidential force for the problem of the mechanism of living matter origination until it is proven that the experimental conditions correspond to the Earth's conditions of about 3900 Myr ago. Besides, the opinion of these authors that the collection of the LMSEs and formation of long polymer DNA molecules of specific structures could occur near the atmosphere–ground or atmosphere–water boundary, where the instability of the conditions should prevent the self-assembling processes, provokes strong

objections. It is no less important that the approach of these authors to the problem under consideration gives no answers to the questions of why only five chemical elements and five different N-bases enter the principal composition of the DNA and RNA molecules, why N-bases are limited in their sizes and in the number of the substituting groups, whence riboses and phosphates came, what is the motive behind the arrangement of the N-bases, riboses, and PO_4^{3-} groups in strong sequences and why these sequences are not random but implicate some sense, what is the source of the monochirality, and what is the mechanism of formation of cells.

In our opinion, the hypothesis of living matter origination should hypothetically answer these questions and propose the natural matrix capable of promoting the meeting and chemical interaction of source mineral substances, synthesizing LMSEs and DNA and RNA molecules, and subsequent origination of proto-cells.

According to the LOH-hypothesis, just the gas-hydrate structure was the matrix that provided living matter origination. Therefore, we should give some information on gas hydrates as on a specific class of chemical substances.

II. GEOLOGICAL, BIOLOGICAL, AND CHEMICAL DATA AND EXPERIMENTAL RESULTS THAT INITIATED THE PRINCIPAL LOH-HYPOTHESIS CONCEPT

a) *Natural Incubator*

Gas-hydrate deposits represent natural incubators for living matter origination. Gas-hydrates [41–43] are honeycomb solid mineral substances with cubic (structure I, $a = 1.20$ nm), face-centered cubic (structure II, $a = 1.73$ nm), or hexagonal (structure H, $a = 1.23$ nm and $c = 1.02$ nm) lattices composed of cavities of two different sizes (structures I and II) or three different sizes (structure H), where the waters (hosts) are the vertices of the cavities and other atoms, molecules, or atomic groups (guests) are housed within the cavities. In gas-hydrates, the guest– H_2O interactions are provided by the Van-der-Waals (V-d-W) forces. As guests, particles of one, two, or three different types can be housed within the cavities. Gas-hydrates that contain guest particles of two or three different chemical natures are termed mixed gas-hydrates. The structure type depends on the size of the guest particles or on the sizes of the guest particles if particles of two or three types are housed within the cavities. Gas hydrate matrixes can exist only under the condition that some guest particles are housed within no less than 80% cavities of, at least, any one size; otherwise, the loose structure collapses and transforms to the usual dense ice. For example, in hydrate structure II, the ideal water-

to-guest ratio is equal to 17 and the critical one is equal to 20–21.

The capability for hydrate formation is a fundamental property of water; it can reveal itself in solid and highly-concentrated semi-liquid systems at sufficiently low temperatures and sufficiently high concentrations (or pressures) of particles of such sizes that correspond to the free sizes of the gas-hydrate cavities; the chemical nature of the guest particles is not of principal importance for the question on the possibility of hydrate formation in any substrate–water system.

The equilibrium between a hydrocarbon, water, and a hydrocarbon-hydrate is determined by the temperature and hydrocarbon pressure, and the equilibrium hydrocarbon pressure is constant at a constant temperature. The temperature is determined by the geological conditions of the hydrocarbon-hydrate bedding. Therefore, the feasibility of hydrate formation depends on the depth of bedding and on the density and degree of softness of the overlying Earth's-crust layers. Natural deposits of methane and other hydrocarbons exist frequently in the form of gas-hydrates under the Earth's surface or seabed.

At an appropriate temperature, the potentiality of molecules or atomic groups to form gas-hydrate structures in the presence of water is determined by their sizes rather than by their chemical properties. For the process of hydrate formation from liquid water and guest particles, the additional decrease in the Gibbs free energy as compared to the decrease in the Gibbs free energy characteristic for formation of usual ice I from liquid water is small and, therefore, hydrates melt as a result of rather weak warming-up; therewith, the phase of guest particles and liquid water form.

Hydrate structures have a unique peculiarity. It is caused by the fact that the structuring is caused by

the weak V-d-W forces and, therefore, the molar free energies of the structured and unstructured states are rather close. As a result, variations in the relative concentrations of the components of both the host (water) and guest (substrate) can change the aggregate (structural) state of the systems. For example, when water enters forcibly and slowly into an amorphous dried water–substrate system capable of structuring, a gas-hydrate structure arises and develops with a decrease in the free energy up to hydrate formation over the entire system; however, entering of excessive water leads to the hydrate-structure disruption, which proceeds also with a decrease in the free energy. It was shown in [11] that this peculiarity of the gas-hydrate structures is of principal importance for the living matter origination and development; it is possible that this peculiarity is the cause of a number of derangements in the regular functioning of living cells and multi-cellular aggregates.

Figures 1(2)–1(6) present schemes of the gas-hydrate cavities of hydrate structures I, II, and H. All they are given in scale. Structures I, II, and H contain 5^{12} and $5^{12}6^2$, 5^{12} and 6^4 , and 5^{12} , $4^35^66^3$, and $5^{12}6^8$ cavities, respectively (above each scheme, the lower-case figures mean the numbers of the edges of a facet and the superior figures mean the numbers of the facets that terminate the corresponding cavity). In these schemes, each vertex responds to the O atom of an H_2O molecule and each edge responds to the sum of the O–H valence bond of any H_2O molecule and the $H\cdots O$ hydrogen bond of this H_2O molecule with any adjacent H_2O molecule. Figures 1(2)–1(6) gives also the sizes of particles capable of being housed within cavities of different types. Figure 1(1) gives the scheme of the unit crystal cell of hydrate structure II. Each unit crystal cell of structure II has the size 1.74 nm and consists of 136 waters, which form 16 small and 8 large cavities with the free diameters 0.48 and 0.69 nm, respectively [44].

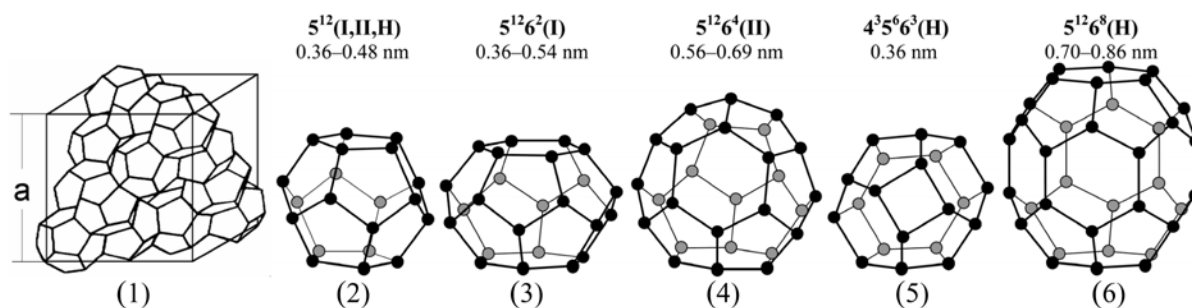


Figure 1 : (1) Unit crystal cell of gas-hydrate structure II (not to scale), $a = 1.73$ nm; (2)–(6) Intra-structural cavities of hydrate structures I, II and H given to scale: the vertexes are the O-atoms of H_2O molecules, and the length of each edge corresponds to the sum of the lengths of the O–H valence bond in any H_2O molecule and $H\cdots O$ hydrogen bond between this and an adjacent H_2O molecule; above each cavity, its free diameter, the number of its facets (the superior figures) restricted with the definite number of the edges (the lower-case figures), and the indexes of the hydrate structures into which this cavity is included are given.

If each large cavity of the structure I or II is filled with guest particles of any chemical nature, the water-to-guest stoichiometry, $n = 7.67$ or 17 , respectively; when all cavities of the structure II are filled with guest particles, $n = 5.67$. Many clathrate compounds of structure II with 17 "host" waters per one "guest" molecule are known, e.g., $C_4H_4O \cdot 17H_2O$ [45], $(CH_2)_4O \cdot 17H_2O$ [46], $CH_3Cl \cdot 17H_2O$ [47], $C_3H_6 \cdot 17H_2O$ [48], and mixed hydrates, such as $C_3H_8 \cdot 2H_2S \cdot 17H_2O$ [49], $(CH_2)_4O \cdot 2H_2S \cdot 17H_2O$ [50], $C_3H_8 \cdot 2CH_4 \cdot 17H_2O$ [51], etc. Note that the term "gas-hydrates" was introduced when it was accepted that such structures can exist in gas-water systems only. However, at present, many liquids are known that are capable of forming gas-hydrate structures. Some of them are written above in this paragraph.

The hydrates of CH_4 , C_2H_6 , and C_2H_4 and of other hydrocarbons are usually crystallized in structures I and II, respectively. Note that the free energy inherent in different hydrate structures with the same guest particles is almost the same, and, therefore, they can metamorphose depending on the external conditions.

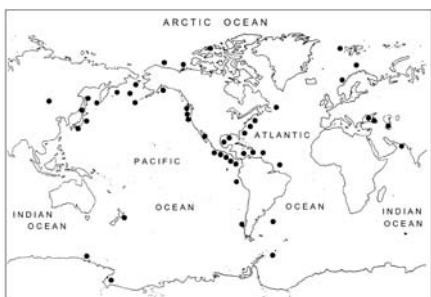


Figure 2: Submarine hydrocarbon-hydrates [52]; circles mark the regions, where submarine hydrocarbon-hydrates or their characteristic features are revealed.

In the Earth's crust, the under-seabed and underground CH_4 -hydrate deposits are widely distributed [53]. Figure 2 gives the map showing the over-world under-seabed methane-hydrate deposits [52]. In 2004, the CH_4 mass in the proven marine CH_4 -hydrate deposits was estimated as $(1-5) \text{ mln. km}^3$ [54], and this estimate grows continuously. Deposits of hydrates of other low-molecular hydrocarbons are also known.

b) Generalizations of Experimental Studies and of Available Information as the stimuli for the LOH-Hypothesis Concept

The LOH-hypothesis was initiated by three principal conclusions resulted from our scientific studies.

(1) In highly concentrated semi-liquid polyacrylamide (PAA)-water and aminoacid-water systems, host-guest structures similar to those in the gas-hydrates form at rather low temperatures and under

undisturbed conditions with no stirring and other disturbances. This conclusion was made as a result of extensive experimental studies of the processes of interaction of vaporous and liquid water with polyacrylamide (PAA), glycine, and alanine by kinetic, calorimetric, sorption, and desorption techniques under atmospheric and vacuum conditions [18, 55–58].

The principal results that led to this conclusion are given below in Figure 3 and in the text.

The PO_4^{3-} , purine, pyrimidine, and DDR (DR) components of the DNA (RNA) molecules are characterized by affinities to water. Therefore, studies of the H_2O -DNA system give no reliable information on the water interaction with N-bases. Meanwhile, the fact is that the DNA molecules in a double helix are joined to each other due to hydrogen interaction between N-bases of the coupled strands; waters with their high dipole moment influence significantly the DNA-DNA interaction and thus the water concentration in the cellular cytoplasm influences significantly the DNA-DNA interaction in double helices and the entire process of DNA replication. Therefore, the H_2O interaction just with N-bases is of particular interest.

In this connection, we used PAA to clarify the physicochemical characteristics and mechanism of water interaction with N-bases, because PAA is a linear polymer like DNA and RNA and because its molecules contain ordered side keto- and amino-groups, which are similar to those included into N-bases. The most principal results of the studies of interactions of PAA and aminoacids with water are summarized in Figures 3 (a-g); the techniques, procedures, and results are detailed in [58] (PAA) and in [18] (aminoacids).

The experiments on H_2O vapor sorption by dried PAA samples from air of about 100% humidity (Figures 3a, 3b) showed that water sorption is very slow and terminates at a water content that corresponds to $(17-18) H_2O \cdot (-C(O)NH_2)$, i.e., $n = (17-18)$.

Figure 3f shows the differential heats of water sorption by PAA (the heats of sorption were measured at $0 < n < 2$ and the heats of desorption were measured at $2 < n < 26$; at $n < 2$ sorption proceeded so slowly that the heat effects cannot be measured). At high water contents in the semi-liquid H_2O -PAA system, H_2O desorption in the deaired system proceeds with the heat of water vaporization; some strengthening of the water-PAA bond is observable at $n \approx 17$, and different special features are observable at $n < 17$ (Figures 3e, 3f). The curve as a whole reflects a nontrivial character of water sorption: indeed, the first H_2O molecule (at $n \leq 1$) is sorbed (Figures 3d, 3f) rather strongly and, at $1 \leq n \leq 17$, complicated changes in the differential heat of H_2O sorption occur, because hydrate destruction in the course of desorption (likely to the process of hydrate

formation) proceeds with a continuous reconstruction of the system and with enthalpy changes at each step of this reconstruction. At $n > 17$, the hydrate structure is destroyed and the system reveals itself as almost ideal

solution; the differential heat of water vaporization is practically equal to the heat of vaporization of pure water.

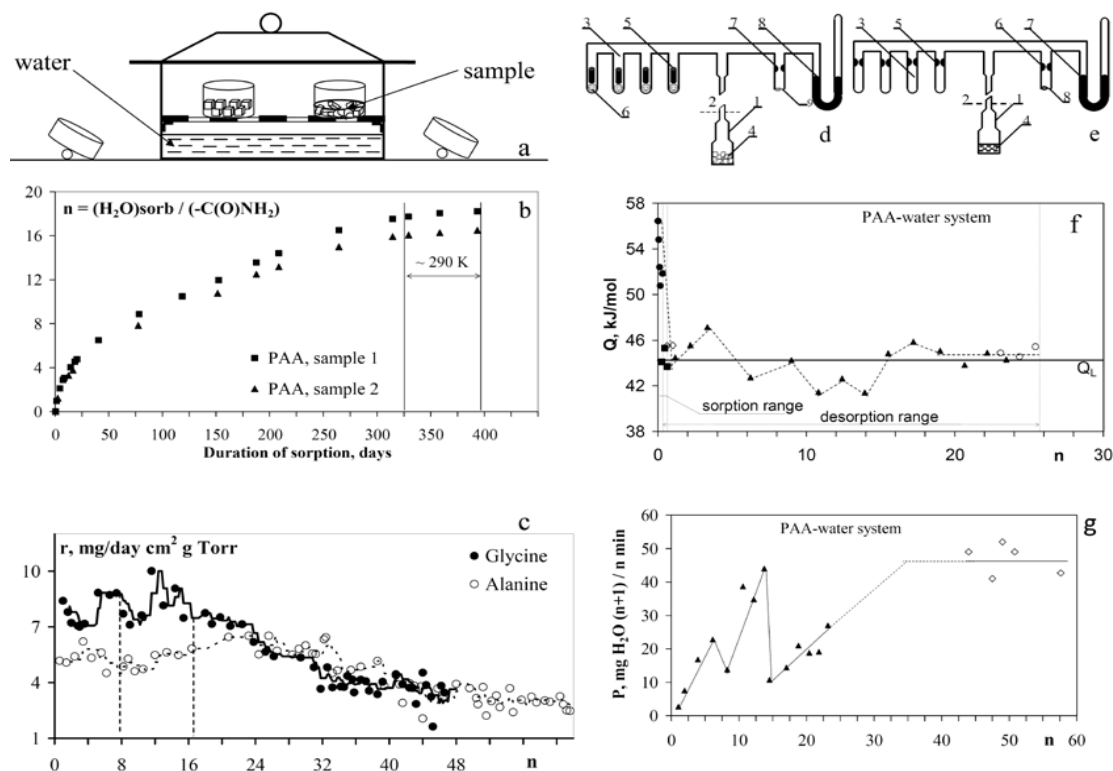


Figure 3 : ([18, 55–58]) (a) Illustration to the procedure of the studies of water-vapor sorption by polyacrylamide (PAA), glycine and alanine from air of 100% humidity at about 290 K; (b) degree of PAA wetting vs. duration of sorption; (c) rate of sorption by glycine and alanine vs. degree of wetting; (d) glass apparatus for sorption experiments in the deaired PAA–water system: (1) calorimetric ampoule, (2) top of the calorimeter, (3) test tube, (4) sample for wetting, (5) “breaker”, (6) sealed water-containing glass sphere, (7) neck, (8) mercury manometer, and (9) tube to vacuum setup; (e) apparatus for desorption experiments: (5) neck (for other notation, see (d)); (f) calorimetric molar heats of H₂O sorption: sorption by sample 8 (●) at 292 K and desorption from samples 7 (■), 9 (▲), 10 (◇), and 11 (○) at 292, 288, 297, and 291 K, respectively (samples 7, 9, 10, and 11 are aged before the experiments for 14, 9, 6, and 16 days, respectively); Q_L is the heat of H₂O vaporization from the pure water surface at 290 K; and (g) probability of desorption of any water molecule into vacuum from the PAA–water system per unit time: samples 9 and 10, 290 K.

Figures 3e, 3g present the desorption apparatus and the data on the n -dependence ($1 < n < 60$) of the P value, respectively. The P value is proportional to the probability of desorption for each sorbed H₂O molecule from the H₂O–PAA system into the deaired volume for 1 min from a unit surface of the system; it characterizes the strength of H₂O binding in the system. The techniques and procedures are detailed in [58]. The P value is constant at high n values and passes through minima at $n \approx 14$ and $n \approx 8$. These minima are associated with some strengthening in the H₂O binding with PAA. It was said above that ideal hydrate structures II and I respond to $n = 17$ and $n = 7.67$, respectively. Thus, the occurrence of these minima is indicative of formation of hydrate structures, in which

the strengths of water binding with PAA are somewhat heightened.

Figure 3c shows that the rates of H₂O sorption from air of 100% humidity by aminoacids decrease at $n \approx 17$ – 20 . This result counts in favor of hydrate-structure formation in these systems, similarly to the PAA–H₂O system. However, in the case of aminoacids, the effect is pronounced not very clearly.

On the basis of these experimental results and a detailed analysis of the available data on the structures of different water–substrate systems, the following conclusions were made [1, 2, 55, 56].

At about 290 K and in the absence of stirring and other disturbances, waters absorbed by PAA and aminoacids at the first stages of wetting of these

substrates form a structure similar to gas-hydrate structure II.

This phenomenon means that the energy of the hydrate structure stabilized by the intracavity guest particles is somewhat lower than the energy of usual liquid water. At the temperatures of the experiments, this energy gain is higher only slightly than the thermal energy of molecular motion. Therefore, hydrate structures can be destroyed by weak (mechanical, thermal, etc.) impacts, including fluctuations. The PAA interaction with water with formation of hydrate structure II can be described by the following scheme.

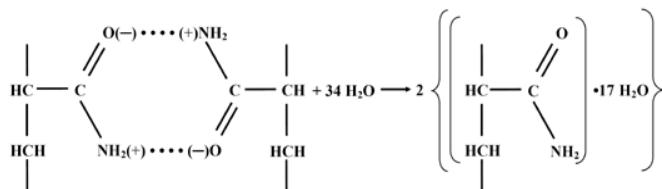


Figure 4 : The scheme of water interaction with a PAA fragment; curly brackets symbolize a large hydrate cavity.

Water-vapor sorption by keto- and amino-groups under conditions of about 100% humidity leads to formation of a semi-liquid clathrate-like hydrate of structure II; after sorption of about 17–18 waters per one $-C(O)NH_2$ group or per one aminoacid molecule, their affinities to water becomes saturated [18, 55–58]. This state of the system is metastable. Upon addition of water into the system, the hydrate structure is steadily destroyed and the system is progressively converted into a homogeneous solution. In all likelihood, similar characteristics of water sorption are typical of other linear polymers with side groups if these groups match cavities in hydrates.

(2) Second principal conclusion is as follows. At the H_2O -DNA double helix quasi-equilibrium *in vivo*, the hydrate structures in the vicinity of each N-basis are being completed, the N-bases become encircled by water envelopes at $n \approx 17$, their pair interactions between the DNA strands become neutralized by the water surroundings, the DNA double helixes become unwound, and the DNA mono-strands float away from each other.

This conclusion is made by analogy with the PAA behavior in the PAA- H_2O medium.

Meanwhile, the term “quasi-equilibrium” requires an additional clarification. The living matter of any scale, including a cell, represents an open system. It is possible to say about immobilization (or sorption) of an equilibrium water amount by DNA molecules outside living matter, having in view the maximal H_2O sorption by them; however, there is no ground to say about an equilibrium water sorption by the cellular DNA, because no equilibrium can be reached in a living cell and the

notions on equilibrium and life are incompatible. We mentioned above about a unique peculiarity of the gas-hydrate structures. In our opinion, it is extremely important in understanding of the common thermodynamic ground of the life as a natural phenomenon. Let a system contain DNA double helixes all just formed and the water amount in the system be deficient for hydrate-structure formation around all N-bases. When waters (and nutrients) diffuse into a semi-liquid system that contains DNA double helixes and too little water for formation of hydrate structure, the process goes to hydrate-structure formation up to $n \approx 17$, because this process is thermodynamically caused. At $n > 17$, the DNAs begin to dissociate and the DNA mono-strands float away from one another because just this process is thermodynamically caused under these conditions. Each DNA mono-strand begins “to accrete” nutrients, and two “daughter” DNA double helixes originate. Now, the system contains again too little water and the process of hydrate structure formation around the newly formed N-bases becomes again thermodynamically caused and the system “imbibes” water again from the outside, etc. In the real systems, the DNA molecules are at any moment in different phases of their interaction with water, however, the physicochemical situation is basically the same. Thus, the process of the alternate formation/destruction of the hydrate structure promotes wonderfully the DNA replication and thus makes life possible.

In [1], it was stated on the basis of a comparative study of the available data on the structures of PAA, N-bases, and their hydrates, that the structural characteristics (the interatomic bonds and valence angles) of the keto- and amino-groups in PAA are almost identical to those in each of N-bases. In addition, as was mentioned above, the PAA molecules are linear like DNA and RNA. Therefore, it should be expected that the water interaction with PAA and with N-bases are similar under comparable conditions.

The composition of the DNA-water system used in [59, 60] to identify the B-form of DNA was far from the quasi-equilibrium [1, 2]. It is commonly supposed that the B-DNA double helix characterizes the DNA state in living matter. However, its structural parameters obtained in different works differ noticeably. For example, values of 10.6 ± 0.1 [61], 10.4 ± 0.1 [62], 10.1 [63], and 9.95 [64] were obtained for the number of the purine and pyrimidine bases corresponding to the full turn of the double helix. Such a scatter in these values is too wide for works on specification of the structural parameters, and the nature of this scatter requires a special discussion.

The multiple experimental and calculated data considered in [1] show that the DNA structure in the natural semi-liquid highly-concentrated aqueous systems depends on the H_2O concentration, that the water content in the crystal DNA samples used for

specification of the DNA structure is much less than the water content in sperm, and that, therefore, the actual DNA structure in vivo differs from the well-known Watson–Crick model.

A new understanding of the H₂O effect in biological processes was proposed on the basis of the assumption on the principal role of water structuring and de-structuring in the vicinity of individual groups of biologically important substances in highly-concentrated semi-liquid H₂O–substrate systems [1, 2]. According to the calculations performed with regard to an analysis of the structural data reported in [59, 60, 65, 66], the quasi-equilibrium degree of wetting (maximal water immobilization) corresponds to the following state of DNA molecules. Under the quasi-equilibrium, each pair of DNA molecules is characterized by hydrate structure II. A full double-helix convolution corresponds to 11.25 intervals along this axis. A double helix convolution is housed in 45 large cavities of structure II. It is known that the helix axis length per pair of N-bases increases with wetting from 0.255 nm in the A-form to 0.34 nm in the B-form [59, 60]. According to [1, 2], this fact means that the degree of twisting of DNA molecules decreases with wetting of the system.

(3) Third principal conclusion is as follows. The components of the DNA (and RNA) molecules are in size conformity with the cavities of the gas-hydrate structure.

Figures 5b and 5d are designed in scale; the diameters of the large and small circles respond to the free volumes of the hydrate structure II large and small cavities, respectively. It is seen that the sizes of N-bases and phosphate-ions correlate well with the sizes of the large and small cavities, respectively. Thus, in this hydrate structure, the large cavities are as if created as the moulds for the N-bases and the small cavities are as if created as the moulds for the phosphate-ions. DR and DDR molecules are somewhat smaller than N-bases and, therefore, each of them also can be housed inside a cavity of the gas-hydrate structure. Note that the sizes of the amino-acid molecules involved into the living bodies allow housing of each such molecule within one gas-hydrate structural cavity.

According to our two-dimensional consideration, structure II is appropriate to house DNA and RNA molecules [3–5, 13].

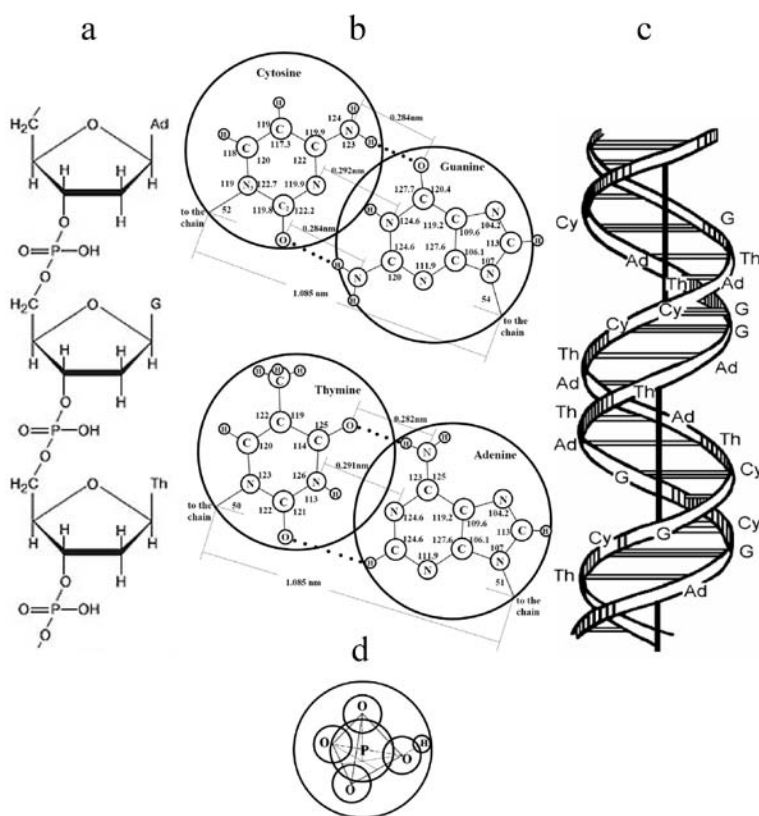


Figure 5: (a) Fragment of a single DNA molecule; (b) scaled schematic representation of pairing between N-bases of two DNA molecules in the double helix structure; the valence angles are given in degrees, circles of diameter 0.69 nm correspond to the free diameter of the large cavity in hydrate structure II; (c) schematic representation of a double-helix fragment formed by two DNA molecules; (d) scaled schematic representation of a phosphate group inside a small cavity of hydrate structure II; a circle of diameter 0.48 nm corresponds to the free diameter of the small cavity

III. LIVING MATTER ORIGINATION: FROM MINERALS TO PROTO-CELLS

a) *General Concept of the LOH-Hypothesis*

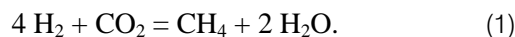
As a result of generalization of the three general conclusions formulated and grounded above, we assumed that the LMSEs and DNA and RNA molecules originated within the gas-hydrate structure of methane or, maybe, of any other aliphatic hydrocarbon and that the phenomenon of formation of the gas-hydrate structures was the key one that provided living matter origination and development.

Once the concept of the necessity of a mineral solid matrix as an "incubator" for simplest living matter origination has been taken, we should choose between three well-known and widely distributed structures: zeolites, phosphates, and hydrocarbon-hydrates. Among them, just the hydrocarbon-hydrates and, very likely, methane-hydrate, which is most abundant of them, is in our opinion most perspective. It almost certainly occurred in the Earth's crust over the rather cold periods of its history, contains two elements (C and H) necessary for the living matter formation and water, can be easily liquefied as a result of diffusion of excessive water or an increasing in the ambient temperature, and has other preferences considered below.

Methane-hydrate was produced in the Earth's crust much earlier than the living matter originated. The hypothesis of the Solar System formation (the PFO-CFO hypothesis) [67–75] describes the mechanism of its production as follows.

After the first steps of nebula compressing and development of the processes of formation of the physically formed objects (PFO), namely, of the cold planets and their satellites, further nebula compression initiated chemical reactions over its warm region. As the nebular-disc compression increased, chemical combination reactions between metal and metalloid atoms accelerated exponentially with time. These reactions stimulated localizations of the substances and reaction heat and initiated compressible vortexes, within which hot cores originated, and triggered the process of formation of the chemically formed objects (CFO). In the vicinities of the giant vortexes, low-pressure and gravitational-attraction zones arose. They stimulated flows of light cold vaporous and gaseous substances and asteroid-like agglomerates from the outer space to the hot cores. The flows precipitated over the hot CFO-core surfaces and cooled them. Progressively, the "sandwiches" resulted from these processes became the young terrestrial planets and their satellites. The space dust and agglomerates were filled with H₂ because it prevailed in the nebula and because it is capable of chemisorbing at different substances. Therefore, H₂ was widely distributed in the Earth's crust. water was mainly captured from the nebula by the Solar

System objects located in the behind-Mars orbits (the cause of this phenomenon is considered in [4]). However, some water amounts were captured by the Earth, apparently, in the form of icy agglomerates (in our days, some celestial objects represent icy bodies). Progressive cooling of the hot Earth's core led to heating of the Earth's crust, melting of the icy agglomerates and forming of oceans and underground water basins, hydrogen desorption from minerals, destruction of crust carbonates of nebular origin and CO₂ liberation, formation of storages of H₂ and CO₂ in the underground cavities and deposits of porous minerals (such as zeolites and sands), and interaction between H₂ and CO₂, according to the reaction



At present, hydrogen exists in the Earth's crust [76, 77] (a number of fields contain natural gas with 10–50% of H₂ [76]) and the raw natural gas contains up to 8% of CO₂ [78].

As a result of the heat losses by the Earth's core and of ice-deposits melting and formation of the oceans, the conditions for methane-hydrate formation arose in the Earth's crust in the vicinities of oceanic beds and underground water basins. These processes led to formation of methane-hydrate deposits and to DNA and RNA origination within their structure.

As was said above, along with methane-hydrate, the honeycomb hydrates of other aliphatic low-molecular hydrocarbons are also available. The changes in the Gibbs free energy under standard conditions for the reactions of CH₄, C₂H₆, and C₃H₈ formation from H₂ and CO₂ are equal to 130.6, –192.1, and –263.6 kJ/mol, respectively [3, 4]. These decreases in the Gibbs free energy are sufficient for these reactions to proceed under the conditions of the Archaean Earth.

Taking that the LMSE origination should start from formation of N-bases and riboses and bearing in our hearts the Newton's aphorism that Nature chooses the simplest ways for its superb performances, we try to find such a mineral that could produce all these substances together as a result of its interaction with CH₄. Such a mineral, if it exists in nature, should contain N- and O-atoms and be the oxidant relative to the C-atoms of hydrocarbons. The cause of the last requirement is that the mean valence number of C-atoms in methane, ethane, propane, ethylene, and propylene (the hypothesis considers all these hydrocarbons as the possible LMSE precursors) is equal to (–4), (–3), (–8/3), (–2), and (–2) respectively; meanwhile, in Th, Cy, G, Ad, U, DR, and DDR, it is equal to (+1.2), (+1.5), (+2.4), (+2.0), (+1.5), 0, and (–0.4), respectively. (The mean valence number of one C-atom is calculated as the opposite-sign value of the ratio of

the algebraic sum of the valences of H-,N-,and O-atoms to the number of C-atoms in the molecule.) In N-bases, the valence number of N-atoms is equal to (-3). Below, we will show that thermodynamics could allow Nature to use niters for formation of N-bases by reactions with hydrocarbons. This means that any nitrogen oxide (NO, NO₂, etc.) could be also used for these reactions, because it is known that transformation of these oxides into niters goes with a decrease in the Gibbs free energy. Meanwhile, by the following causes, we believe that Nature gives preference to niters. First, nitrogen oxides are rather active and it is unlikely that they could exist in the Earth's crust; for example, volcanic gases contain no nitrogen oxides. Second, even if a nitrogen oxide had existed in the Earth's crust, it would be, most likely, in the form of a mixture with other reactive gases and selective formation of N-bases would be questionable. These considerations give us grounds to believe that just reactions of niters with CH₄ (or with another hydrocarbon) had led to formation of N-bases and riboses.

It is well-known that alkanes are capable of reacting with HNO₃ under pressure of alkanes with formation of nitro-alkanes as the primary product (M. Konovalov's reaction, 1888 [79]). One would expect that similar reaction could proceed within the methane-hydrate phase. Under room temperature, Konovalov's reaction proceeds extremely slowly, and its rate can be measured only above 400–500 K depending on the hydrocarbon nature. The rate of the CH₄ nitration is the lowest as compared with that of other hydrocarbons, but Nature has nowhere to hurry. Nitro-methane is capable of subsequent reacting with methane and NO₃⁻-ions giving more complicated molecules. It is a very active chemical substance. It reacts in the form of nitronic acid H₂C=N⁺(OH)(O)⁻ (IUPAK term: azinic acid), which exists at temperatures near 0°C and below [80]. Nitro-methane exists in two forms, according to the following equilibrium (Figure 6).

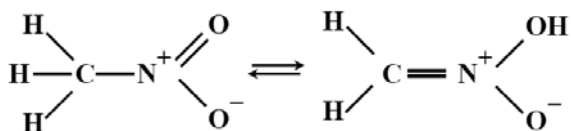


Figure 6 : Nitro-methane – nitronic acid equilibrium.

Nitronic acid anions, H₂C=N(O₂)²⁻, are degraded to ketones and can be alkylated on oxygen and used as a dipole in the so-called 1,3-dipolar cycloadditions (Huisgen's reaction), which leads to formation of pentamers rings and can initiate different other chemical transformations.

Two substances, NO₃⁻ and CH₄, being together inside gas-hydrate matrixes could produce all N-bases and riboses necessary for living matter origination under

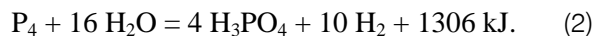
the conditions that thermodynamics allows such interactions and that a cause exists that terminates the subsequent chemical transformations of these DNA (and RNA) components within the hydrate matrix.

The Earth's crust contains not many different substances with nitrogen in an oxidized form; and the most widespread ones are nitrates (niters), such as NaNO₃ and KNO₃. For example, many million tons of NaNO₃ (termed also caliche or saltpeter) was mined in the Atacama Desert in Chile and these deposits are not fully exhausted. Some hold the opinion that niters result from decomposition of the bird metabolism products (BMPs). Meanwhile, it is known that, in the BMPs, the percentage of phosphoric acid (13%) is higher than that of nitrogen (9%). If birds in abundance would had visited this region in former times, this should mean that there had been a sufficient amount of water and that well-soluble niter rather than poorly-soluble phosphate should be predominantly washed out by water from the BMPs; if the birds had been "abstemious" and this region was always desert, the niter should be mixed at present with phosphate. Meanwhile, NaNO₃ occurring in the Atacama Desert contains significant admixtures of soluble iodine and sulfates and does not contain phosphates. Apparently, there are no doubts that this niter is of natural origin and that such a deposit is by no means unique.

One more doubt may arise, whether the regions where the hydrate and niter deposits are at rather small distances occur at the globe. We cannot resolve this doubt entirely for the Earth's crust state that had occurred 4000 Myr ago. However, we can say that, at present, the probability of such a coincidence is rather high and there is no reason to believe that it was lower in the distant past. The map given in Figure 2 shows the locations of the submarine natural hydrocarbon-hydrate deposits (it is necessary to take into account that underground hydrocarbon-hydrate deposits exist also at continents). It is seen, for example, that several gas-hydrate localizations occur along the shelf of the California, Oregon, Peru, etc. Meanwhile, according to [81], several localizations of sodium and potassium niters are known over the coastal continental heights of Chile, Bolivia, California, etc. At present, niter deposits are known in desert regions only. However, their occurrence in present, in spite of high solubility of niters in water, means that, 4000 Myr ago, niter deposits had been much more abundant and frequent.

From the phosphorus-containing minerals distributed widely at present, apatite Ca₅X(PO₄)₃ (X = F, Cl, or OH) could be considered as a possible source material for the natural formation of DNA. It is commonly accepted that apatite is of mineral origin [82] unlike some other fossil phosphates, which are apparently of the animal, in particular phosphorobacterial, origin. It is also not impossible that the young Earth had contained

elementary phosphorous, which had reacted as follows [82] under the action of reduced metals catalyzing the process



Thus, the preliminary analysis of the problem allows the assumption that DNA and RNA origination proceeded inside a matrix, from three natural substances (methane, niter, and phosphate) and so slowly that just the thermodynamic front determined the direction of chemical reactions, i.e., the reactions proceeded at a rather low temperature and their rates were, apparently, limited by diffusion processes inside the solid matrix. Why should this set be composed just of a triad of substances? Because the searching of a pair of different natural molecules that are sufficient for DNA or RNA formation is, apparently, hopeless, and because the repeated meetings of four different molecules all together are unlikely.

This analysis allowed us to solve the problem of searching a triad of appropriate substances capable of forming the DNA, RNA, and aminoacid set whose gathering in some one localization was realistic for the Earth of about 4000 Myr ago and of searching an appropriate matrix and conditions capable of promoting selective absorption of these substances, their chemical interaction, and putting the reaction products out to "free swimming".

We also have set ourselves the problem on a hypothetic forecasting the essence of the replication mechanism as applied to the first DNA-like molecules and to the "ripe" DNA molecules of the following generations on the basis of our notion that the process of replication is determined by chemical and physical laws and results from interaction between DNA and environment. In our opinion, the process of replication of the first DNA-like molecules and the process of replication of the "ripe" DNA molecules must be governed by analogous laws. The principal difference between these processes is that the former uses only simple mineral building materials and synthesizes nucleosides from it, while the latter slivers the organic "food" and uses nucleosides as the building material; therefore, the latter proceeds much faster than the former. When the organic "food" material arose in abundance over the environment, the living articles learned to destroy and use this material. The reactions of destroying and of synthesizing proceed as the consequent ones. The total change in the Gibbs free energy is near zero, because the initial and final states are almost the same.

The LOH-hypothesis considers all above-listed issues and gives answers to many questions connected with formation of the first DNAs and cells and with the mechanism of DNA replication. Of course, these

answers are hypothetical, but we propose a hypothesis and neither a gospel nor a sacred cow. Our answers are mutually noncontradictory and are verifiable.

We understand that any presentation of an idea on the mechanism for any complicated chemical process is a rather thankless pastime, because alternative notions on a complicated chemical process are possible almost always if not always. We propose an experiment for verification of the LOH-hypothesis [3, 4] and think that it must be performed on an international basis. For a start, DNA- and RNA-like substances must be produced from minerals. After that, the problem whether they are self-replicating should be, apparently, solved with no impediments. Our opinion on the mechanism of replication processes is described in [11, 18] as a hypothesis. It is senselessly to discuss in advance, whether the artificial nucleic acids will be self-replicable or not. Nature is more ingenious than any Homo sapiens.

b) From Minerals to DNA- and RNA-Like Molecules

First, N-bases, riboses, and nucleosides formed from CH₄ and nitrate-ions as a result of NO₃⁻ diffusion into the hydrate structure, and then nucleotides and DNA- and RNA-like molecules formed as a result of phosphate-ion diffusion into the structure. N-bases and phosphate groups were localized within the large and small structural cavities, respectively. Riboses can be housed within small or large cavities. (The large cavities of structure H are somewhat "more roomy" than those of structure II, and we cannot exclude that structure H is the matrix for LMSE formation).

The reactions of LMSE formation proceeded in the Earth's crust at significant depths under a CH₄ pressure of several MPa and at 273 ± 20 K, i.e., under the conditions when CH₄-hydrate is stable and the equilibrium in Figure 6 is shifted to formation of chemically active nitronic acid.

In order that the hydrogen bond arise between purine and pyrimidine bases, the distance between them should be strictly fixed. Apparently, just the hydrate structure with its systematically-located large cavities creates the geometric conditions necessary for such binding.

It is important that the CH₄-hydrate structure provides a nonrandom arrangement of atomic groups in the DNA- and RNA-like molecules, and just this specificity of the nucleic acids produced inside the hydrate structure provides their specific characteristics in the further interactions with the environments. The importance of nonrandom arrangement of N-bases was stressed in [83, 84]. We consider two types of the non-randomness. They are caused by peculiarities of the CH₄-hydrate system.

Consider the system peculiarities that cause the non-randomness of the first type. We must take into

account that most of the hydrate deposits do not represent compact homogeneous strata similar to the strata of coal or salt but are associated with underground solidified sandy or frothed rocks. The hydrate crystals transform the sand to a rather dense monolith mass or fill up the porous rock structure. The methane-hydrate crystallites have usually millimeter-range sizes and are integrated with the parent mineral material. Each CH_4 -hydrate crystal can be a source of, apparently, one DNA-like or RNA-like molecule. The chemical processes that proceed within each crystal are slow and thermodynamically controlled. When NO_3^- -ions diffuse into CH_4 -hydrate crystals, uninuclear pyrimidines form step by step in the large cavities of the hydrate structure. After their formation, uninuclear pyrimidines transform to two-nuclear purines in those large cavities where the geometry allows such transformations. Therewith, the requirement that any two atoms not bound chemically to each other should be arranged at a distance no less than the sum of their V-d-W radii should be fulfilled. When the large cavities within any hydrate crystal are already almost filled with purine and pyrimidine nuclei and some their side groups are already formed, a specific situation must arise, at which the appearance of any additional side group (term it "a key side group") in the composition of one of the N-bases determines unambiguously the chemical nature and geometrical positions of the side groups that should terminate full filling the hydrate structure over a significant portion of this crystal or even over its entire volume. The unambiguity of the composition of these terminating side groups follows from the chemical feasibilities (i.e., from the nature of the source chemical substances), geometric features inherent in the system under consideration, and thermodynamic preferences. The point of location of this group and its chemical composition can be considered as the random ones with some qualifications that the cavity must have a free space and that this side group must include no atoms but C, O, N, and H. However, the composition of this key side group and the point of its location provide specific nonrandom positions and chemical compositions for all terminating side groups in the newly originated N-bases and in the hydrogen-bound purine-pyrimidine complexes formed then on the basis of these N-bases. The purine-pyrimidine complexes react with riboses that are produced within the small cavities and diffuse over the hydrate structure and with phosphate-ions that diffuse into the crystal from the outside. Steadily, DNA- and RNA-like molecules form. After that, chemical reactions in any crystal may be continued in the direction of lengthening of the nucleic acid and of its thermodynamic improvement, if these processes are not finished earlier; at that, the nucleuses of the three-nucleus purine-pyrimidine complexes remain immobilized but their side groups may transform in the direction of minimization of the free energy of the system, if additional transformations are necessary.

Consider now the peculiarities that cause the non-randomness of the second type. It is known that, in any double helix, the DNA mono-strands are bound to each other by H-bonds that arise between purines and pyrimidines of different strands but not between their purines or pyrimidines. What is the cause of this phenomenon? The point is that, according to a two-dimensional analysis of the geometry of the system, the hydrogen-bound purine-purine complexes are too prolonged to be housed within two neighboring large cavities of gas-hydrate structure II and the pyrimidine-pyrimidine complexes are too short for two pyrimidines of different strands to be bound to each other by the H-bonds and each of these pyrimidines to be also bound by the covalent bond to the ribose located within a small cavity. In addition, the energy of the system should be minimized, i.e., the dipole moments of the N-bases should be mutually neutralized. Our geometric analysis gives grounds to conclude that the purine-pyrimidine hydrogen-bound pairs originate within hydrate structures as early as in the period of origination of N-bases from simple mineral substances.

Thus, a combination of the matrix effect with the effect of thermodynamic controlling of the chemical reactions in the system under consideration can create conditions for specific and by no means random locations of N-bases in the resulted DNA-like and RNA-like molecules; the processes of nucleic acid formation proceed in different methane-hydrate crystals independently from each other, and, therefore, a variety of nucleic acids characterized by different sequences of N-bases can originate in any one methane-hydrate localization.

Polycondensation of N-bases with riboses and PO_4^{3-} -groups is stimulated by crystallization of the emitted waters with the CH_4 -hydrate formation caused by the excessive CH_4 pressure. From Figure 5d, it is seen that PO_4^{3-} -ions can be housed inside the small cavities. Apparently, just the hydrate structure provides the regularity of location of N-bases, riboses, and PO_4^{3-} -groups in the DNA (and RNA) molecules and just the CH_4 chemical inertness provides the selectivity of CH_4 interaction only with NO_3^- and PO_4^{3-} . Methane-hydrate reveals itself as a selective reactive membrane.

It is important that the thermodynamic equilibrium established in the process of origination of a DNA double-helix between this double-helix and its environment is reproducible after any coercive disjunction of the DNA strands from each other and their housing into the same environment if the ambient conditions are invariable and the medium contains all components necessary for duplication of these strands and no additional components capable of transforming the DNA strands with a greater decrease in the Gibbs free energy than it is in the process of DNA double-helix reproduction. As a result of such a procedure, two daughter DNA double-helices should originate, following the laws of chemical thermodynamics.

In our opinion, just the thermodynamics furnishes the clue to the nature of the so-called “genetic (biological) codes”. The DNAs inherent in different present-day species originated under somewhat discriminate conditions and were perfected with time because the conditions of their reproduction varied in the subsequent generations. The initial perfections occurred after liquation of hydrate structures, and they are described below. DNA double-helices cannot be reproduced after their disjunction and the lines of their generations come to the ends if the chemical composition of the medium or ambient conditions changes sharply.

The LOH-hypothesis allows a plausible explanation of the mysterious phenomenon of monochirality of all known species of living matter. The point is that, the RNA and DNA molecules contain in their composition only D-ribose and desoxy-D-ribose but not L-ribose and desoxy-L-ribose, respectively. Meanwhile, the D- and L-forms of any substance are identical in their chemical compositions, reaction abilities, and sizes and any chemical reaction of their formation produces them in almost equal amounts. Such isomeric molecules have only one distinctive feature; namely, they are the mirror images of each other. Many physicists, biologists, and chemists tried unsuccessfully to guess the riddle about the cause of monochirality of DNAs, RNAs, and aminoacids.

According to our hypothesis, the DNA and RNA monochirality is a natural inevitable consequence of the gas-hydrate matrix geometry: within hydrate structures, only D-ribose, but not L-ribose can “touch” both, an N-base and a phosphate group, by the active groups of their structures. Apparently, only under such conditions, each PO_4^{3-} -group is capable of “touching” two riboses and thus of joining together two nucleotides and of lengthening DNA or RNA chains. At the temperatures around 270 K, when CH_4 -hydrate is stable, CH_4 reacts utterly slowly on the laboratory-experiment time-scale. The subsequent interactions of the intermediate products with NO_3^- -ions and CH_4 and the diffusion processes are also extremely slow. It is possible to expect with a high degree of certainty that increasing of the length of DNA-like (RNA-like) molecules continues on the geological time scale. The longer is the process in any one locality, the lengthier are the nucleic acids. In different localities, the processes that led to DNA and RNA origination could start in different epochs and, although the laws of reacting were universal, the directions of the reactions could be not identical as a result of differences in the ambient conditions. Two last conclusions are rather important, and we attract the attention of researchers to them.

The molecules within the hydrate cavities grew with time as a result of interaction between CH_4 and NO_3^- -ions in the direction of purine, pyrimidine, and

ribose formation up to filling of the cavities and as a result of nucleoside formation and their attaching to the polymer chains through the PO_4^{3-} -bridges. As was said above, seemingly, the purine–pyrimidine pairs also originated within gas-hydrate structures. Chemical ordering of this complex multi-component system went progressively in the direction of the DNA and RNA formation, because just this direction coincided with the progressive decrease in the Gibbs free energy of the system. There was plenty of time for purine, pyrimidine, ribose, and desoxy-ribose molecules to form, for the purine molecules to meet the pyrimidine molecules and to form purine–pyrimidine hydrogen bonds, and for D-ribose and desoxy-D-ribose molecules to find purines or pyrimidines and to join them through the chemical bonds with formation of nucleoside dimers, which may transform then to elements of DNA dimers or RNA fragments. Phosphates diffused into the hydrate structure by the empty small cavities and could react in the direction of DNA or RNA formation. Each act of such a reaction proceeds under the condition that a PO_4^{3-} -ion diffuses into a cavity located between two adjacent cavities filled with two D-ribose or two desoxy-D-ribose. As was said above, we assume that the hydrate-structure geometry allows location only of D-ribose or desoxy-D-ribose between an N-base and a phosphate-group. This does not mean that the groups with L-carbon do not form. They form, but enable formation of aminoacids. Of course, the desoxy-D-ribose and D-ribose positions between N-bases and phosphates were occupied not right away but after a great number of trials and errors.

Thus, according to the LOH-hypothesis, the phenomenon of DNA and RNA monochirality and all other principal features of DNA, RNA, and aminoacids arose at the earliest step of living matter origination and represent consequences of the mechanism of LMSE formation within hydrate matrixes [4]. The ideas that the phenomena of monochirality and codon directedness arose far back in evolution were also posed by the authors of [85] and [86], respectively, on the basis of other starting positions.

The reactions within the gas-hydrate structures proceeded step by step so slowly that their directions were controlled by the thermodynamics, and, within all cavities, they went in the same direction. Formation of the molecular chains of DNA and RNA that were produced in reality corresponded to the minimum in the free energy, and, therefore, the acts of exchange by functional groups led steadily to the achievement of the optimum positions. For so complicated reactions governed by thermodynamics, any search for answers to the questions of detailed mechanisms is pointless. For example, we have no means to ascertain, why any functional group joins to the position to which it joins in reality rather than to another one, to which it, in our

opinion, could join. Analogously, we have no means to explain why nitrogen atoms enter the N-bases but do not enter riboses. Consider one more example of such a kind. A ribofuranose structure has four chiral centers. Each of the N-bases of RNA offers multiple sites for attachment of a substituent, and each ribose offers three hydroxyl groups for phosphate ester formation. In spite of the seeming feasibility of the formation of different products, Nature chooses the connections resulting in the formation of nucleotides and nucleic acids. Very likely, even our issue will never be able to calculate the details of the thermodynamics for such complicated systems. However, we cannot stint Nature of such abilities. In our opinion, all structural details are, in principle, explainable by the chemical affinity and thermodynamics but our chance of achieving this is unattainable in practice. If the interaction of NO_3^- -ions with CH_4 within a gas-hydrate structure were proceeding infinitely long and if the ambient conditions for different localizations were identical, these processes would lead to formation of nucleic acids of one type. However, such processes are not infinitely long, and the ambient conditions are different for different localizations. Therefore, although the directions of the processes are, in general, the same in all localizations, each localization produces at any time a multitude of different DNA and RNA molecules and different localizations produce different sets of DNA and RNA molecules even under the conditions that the processes within them start simultaneously.

The experimental studies performed in the last decade show that the chemical nature of the polymer-forming group in different genomes is variable. Namely, some prokaryotic genomes contain, along with the more abundant PO_4^{3-} group, the AsO_4^{3-} [87] or PO_3S^{3-} [88, 89] groups, which are close to the PO_4^{3-} group in their sizes, chemical activities, and thermodynamic characteristics. In our opinion, this shows that chemical composition of the polymer-forming group is not of crucial importance for living-matter formation; this group is only a "bridge" that joins nucleosides in the DNA and RNA sequences. However, the sizes of this bridge group should not exceed the sizes of the gas-hydrate small cavities. In Figure 5d, it is seen that the gas-hydrate small cavity allows for some increasing in the size of the polymer-forming group. The chemical composition of this group depends on the chemical composition of the environment. For example, it was stated that water of Mono Lake (California), where the bacteria with the As-containing DNA were discovered, contains As in a significant concentration [90]. Apparently, this means that subseabed minerals also contain arsenium.

Let us formulate an intermediate resume at this step of our consideration.

Thus, (1) DNA and RNA molecules originated in the underground and underseabed layers of the

Earth's crust within honeycomb matrixes of the CH_4 -hydrate structures; (2) they were produced from only three widely distributed minerals (methane and NO_3^- and PO_4^{3-} ions); (3) the processes of DNA and RNA origination went under ambient conditions invariable over a long time and at such low temperatures that the direction of the reactions was determined by the thermodynamic front; (4) in any one CH_4 -hydrate localization, a multitude of similar but somewhat different DNA- and RNA-like molecules originated; different sets of DNA- and RNA-like molecules originated repeatedly in different time periods and in different methane-hydrate localizations (it is possible that analogous processes proceed in our days); (5) the CH_4 -hydrate matrixes sorbed only NO_3^- and PO_4^{3-} (rarely, AsO_4^{3-} or PSO_3^{3-}) ions (because, apparently, only these substances were capable of reacting with CH_4 under the ambient conditions), limited the sizes of the particles that could be produced inside the structural cavities, and determined the monochirality of the resulted DNA- and RNA-like molecules; (6) phosphate-ions represent the most abundant connecting links (bridges) between nucleosides; in the prokaryotic DNAs, the chemical composition of these bridges is variable with no principal effect on the nucleic acids as carriers of life; (7) the length and the degree of ordering (i.e., of thermodynamic perfection) of the primary DNA- and RNA-like molecules were determined by the duration of their maturing in the underground incubators, temperature, sizes of the CH_4 -hydrate crystallites, and other factors, and (8) just the thermodynamics furnishes the clue to the nature of the so-called "genetic (biological) codes"; the DNA double-helices inherent in different present-day species originated under somewhat discriminate conditions and were perfected with time because the conditions of their reproduction varied in the subsequent generations with no mysterious code; and, when the medium or conditions changed sharply, DNA double-helices could not be reproduced and the line of its generations came to the end.

A similar mechanism could be realized on other planets where analogous conditions occurred.

c) *From DNA- and RNA-Like Molecules to Proto-Cells and the DNA replication mechanism*

In any CH_4 -hydrate deposit, formation of the LMSEs and of DNA- and RNA-like molecules from CH_4 and NO_3^- and PO_4^{3-} ions led to a consumption of the CH_4 -hydrate deposit mass and to isolation of significant amounts of water. For the time being, water sorbed gaseous CH_4 and additional CH_4 -hydrate formed. However, with time, a semi-liquid component might appear and its portion might steadily increase in comparison with the portion of the solid methane-hydrate. The semi-liquid component represented a highly concentrated prebiotic soup that contained

different organic and organo-phosphate substances, such as DNA- and RNA-like molecules, N-bases, riboses, nucleosides and nucleotides, aminoacids, and other products of methane oxidation by niter. Liquefaction of the system and formation of this soup could be stimulated by ambient factors, such as diffusion of excessive water into the system or a temperature increase associated with global or regional geophysical and geochemical processes, or with faint-young-Sun period termination, etc. This soup could hold the gas-hydrate structure, because structuring is inherent in very concentrated water-organic systems at about 270 K under undisturbed conditions not only under high pressures of guest substances but even at the atmospheric pressure as it was shown above and in [1, 2, 56].

Under appropriate conditions, the concentration of nucleic acids in the soup could increase. When it reached some critical value, proto-cells arose and the subsequent development of the replication processes, including the cell division, became generally similar to the corresponding processes that proceed within the cells of the present-day organisms. A cell could contain one or several DNA-molecules. Among the cells with several DNA-molecules, evolution selected those whose replication phases were in resonance with each other. The processes leading to the DNA and RNA syntheses could continue in this soup under the conditions of a rather low temperature, which is capable of providing hydrate formation, and of the occurrence of CH₄ and nitrate- and phosphate-ions in the newly formed cells. In order that replication could proceed, the water concentration in the cellular cytoplasm should be rather low. As was shown in [1], the water concentration is dependent on the phase of replication process.

Below, we will consider the hypothetical mechanisms of the processes that provide formation and further extended reproduction of the cells and DNA double helices. However, in the beginning, we will consider some principal similarities and differences between the processes that proceed in the solid and in the semi-liquid hydrate matrixes. The point is that, in semi-liquid media, the rates of chemical processes are significantly higher, the ambient temperature is somewhat higher, and the reaction volume is not limited by the crystal sizes, in contrast to solid crystals. If water, niter, and phosphate diffuse to the semi-liquid medium that formed after the liquefaction of the hydrate matrixes filled with the DNA- and RNA-acids and LMSEs or if this semi-liquid substance diffuses out of its original location to an appropriate point, the thermodynamic equilibrium may become “unfrozen”, and the DNA double helices may be subjected to subsequent chemical transformations.

In the preceding section, we described a plausible thermodynamic view on the nature of the process of DNA replication. This concept does not

contradict the opinion [17, 91–94] that nucleic acids are capable of self-replicating. At present, when the methods of syntheses of artificial DNA-like double helices are available, the experimental testing of the assumption on the possibility of the DNA self-replication could be verified by experts in organic chemistry.

The possible mechanisms of the processes that provide the formation of primary cells and DNA replication are considered in [4, 11, 18].

We assume that the mechanism of cell-membrane formation in the organo-phosphate medium, which is termed by us super-cytoplasm by analogy with cell cytoplasm, is as follows. Immediately after replication, the molecules of nucleic acid are hydrated only slightly and actively sorb water from the super-cytoplasm. Let each DNA molecule in the super-cytoplasm be at its individual mitotic stage. It may happen that a few (or many) molecules that have just completed replication and therefore actively sorb water are simultaneously present in immediate proximity to each other. A situation is conceivable in which the water concentration in the super-cytoplasm is low and the water inflow from the outside to this group of molecules is insufficient to serve their water needs. If other DNA molecules in the vicinity of this group also sorb water, some individual molecules may find themselves in an oversaturated space and, therefore, organo-phosphate membranes precipitate not far from them. These are the first cells. Further replication of nucleic acids and the concomitant formation of N-bases, aminoacids, nucleotides, nucleosides, and other organic substances cause the water content in super-cytoplasm to decrease to a certain critical level. This triggers cell formation in the entire volume of the super-cytoplasm. Each newly arising cell receives water and organic substances only by means of their diffusion through the plasma membrane. As a result, intracellular cytoplasm develops in addition to the super-cytoplasm. Thereafter, nucleic acids replicate inside cells and cell division occurs.

We stress once more that aminoacids could originate in the semi-liquid soup arising after melting of the hydrate structure and that the processes of origination of amino-acids require no additional source substances besides those occurring in this soup. Each amino-acid molecule is synthesized within one hydrate cavity. For their syntheses, the L-carbon groups, which cannot be involved in the syntheses of D-ribose, are used according to the “residual principle”.

We have formulated the physicochemical principles of the mechanisms (not chemism) of the DNA replication, binary fission for prokaryotes, and mitosis for eukaryotes in terms of our LOH-hypothesis briefly in [1, 19] and, in more detail, in [4, 11, 18]. Details of these mechanisms are not discussed here. As mentioned above, we believe that the division mechanism for the primary cells in the super-cytoplasm was analogous to

the binary fission mechanism for the present-day prokaryotic cells. Our understanding of this mechanism is expounded below.

Immediately after replication, sister chromosomes float apart towards opposite cell poles under the action of electrostatic repulsion forces; these chromosomes sorb waters from the cytoplasm at a rate higher than the rate of water diffusion into the cell through the plasma membrane and actively form hydrate envelopes around the DNA-DNA hydrogen bonds. These processes result in a diffuse outflow of water from the cell equator towards chromosomes and in the appearance of a region oversaturated with organic substances of a density lower than the water density in the equatorial zone. As a result, a cleavage furrow forms, organo-phosphates precipitate, a membrane appears, and the cell is divided into two separate units.

The above description of the mechanism of cell formation in the super-cytoplasm and of the mechanism of division of prokaryotic cells includes two principal statements: (1) immediately after replication, nucleic acid molecules are hydrated only slightly and therefore actively sorb water; (2) the floating of sister chromosomes apart from each other immediately after replication is a consequence of their electrostatic repulsion. In [11, 18], these statements ensue logically from an application of the LOH-hypothesis key principles to the binary fission of prokaryotes and mitosis of eukaryotes, i.e., to the cell division processes inherent in a majority of unicellular and almost all multicellular organisms whose cells, at certain mitotic stages, contain a nucleus, complex protein “stuffing”, a variety of organelles (including ribosomes), and a few chromosomes.

Apparently, there are reasons to think that the functions of protein synthesis and transmission of inheritable features in the simplest living organisms were rather weak shortly after their emergence from the super-cytoplasm but gradually developed and consolidated in the course of evolution. This inference, which necessarily ensues from our hypothesis, is supported by the following facts. First, the DNAs of prokaryotes and viruses, i.e., of the simplest organisms, unlike the DNA of eukaryotes, contain scarcely any protein; the cytoplasm of prokaryotic cells contains ribosomes generally regarded as “factory shops” for protein production in accordance with a genetic program, but the amounts of protein in them are generally much lower than in eukaryotic cells. Second, prokaryotes and the simplest unicellular eukaryotes are highly variable, are very diverse in terms of species composition, and undergo frequent mutations (it is for this reason that antibiotics against specific bacteria lose clinical efficiency after a span of time: the bacteria mutate retaining their pathogenic potency); viruses and viroids are even more prone to mutations. In other words, the mechanism of inheritance of characters in

lower organisms is poorly developed and their properties are subject to frequent variations, which are in fact the driving force of evolution. The remark opening this paragraph is of primary importance in terms of understanding the direction of the evolution of living matter, because it pertains to a problem at the border between different hypotheses. Today, however, it would be vain to advocate or to reject it because its validity can be verified only in a direct experiment on the synthesis of the animate from the inanimate.

Thus, the principal processes that proceed after DNA and RNA formation within the solid hydrate matrix are as follows: (1) melting of a portion of the hydrate matrix and formation of a structured semi-liquid water-organic-phosphate soup; (2) diffusion of NO_3^- and PO_4^{3-} ions into the soup and formation of super-cytoplasm and of additional LMSEs and aminoacids; (3) self-replication of nucleic acids, concentrating of the soup, and formation of proto-cells; (4) formation of simplest organelles and diffusion of the first cellular organisms out of their “incubator”.

d) *Thermodynamic Front as the Mover of the Living-Matter Origination Process*

According to the LOH hypothesis, transformation of the primary atmosphere of the Earth and the processes conducive to the origin and the development of living matter were closely interrelated over the entire period spanning from the appearance of protoplanets to the emergence of the first colonies of simple organisms and further on up to the modern era. Changes in the primary atmosphere favored the formation of living matter, whose evolution, in turn, influenced the atmosphere until it acquired its present composition.

The main aim of the subsequent thermodynamic calculations is substantiation of the feasibility of formation of DNA-like molecules within hydrocarbon-hydrate phases under natural conditions. These conditions differ from the standard ones. Meanwhile, all calculations are performed for the standard conditions by the following reasons. First, under the standard conditions, the changes in the partial molar Gibbs free energy in the processes of transition of guest particles into hydrate phases and back are small in magnitude as compared to those in the processes under consideration. Second, gas hydrates are the substances of variable composition, their thermodynamic functions can be determined exactly for some ideal compositions only and the partial molar thermodynamic functions (especially, entropy) of the host and guests can vary for different non-stoichiometric compositions. Therefore, the available thermodynamic data give no possibility for exact calculations and it is unlikely that such calculations would be possible in the near future. For almost all reactions considered in this paper, the molar changes in the standard Gibbs free

energies are so great in their magnitudes that, for the purposes of this paper, the standard values given below are quite sufficient.

We analyze the thermodynamic possibility for the Cy, G, Th, Ad, U, and DR syntheses from two mineral substances: one of the simplest fatty hydrocarbons and a niter. In this paper, the reactions of methane, ethane, and propane with potassium niter are considered. The result would be principally the same if we replace potassium niter by another (e.g., sodium) niter.

The standard enthalpy ($\Delta_f H^0$) and entropy (S^0) values for N-bases are taken from [26, 27]. For DR, which belongs to RNA, the complete set of unpublished thermodynamic data for DR was put at our disposal by Boerio-Goates [28] (her enthalpy value does not differ from the values published in [95, 96]). The full list of the standard $\Delta_f H^0$ and S^0 values for all substances involved in our calculations is given in [3, 5]. Below, we present the results of calculations and discuss them.

At first, we consider the thermodynamic problem whether the coupled reactions of (Cy + G + Ad + U + 4DR) formation under standard conditions from KNO_3 and CH_4 , C_2H_6 , or C_3H_8 with liberation of N_2 are feasible. Such a formulation of the problem requires an additional explanation. It is known that the molar ratios Ad/Th and G/Cy in DNA molecules and Ad/U and G/Cy in RNA molecules are equal to unity. Meanwhile, the ratio (Ad + Th)/(G + Cy) varies in living matter from one species to another. For bacteria, this ratio can be more or less than unity; for higher organisms, the range of variations in this ratio is comparatively narrow, e.g., for

most of animals, it is usually between 1.3 and 1.5 (the Ad, G, Th, and Cy contents in the human sperm are 31, 19, 31, and 19%, respectively); and, for higher plants, it is between 1.1 and 1.7 [97]. We consider a hypothetical averaged situation when the molar ratio Ad/G is equal to unity and analyze the problem whether such a situation could be self-realized under the standard conditions in the system that initially contains a saturated fatty hydrocarbon (CH_4 , C_2H_6 , or C_3H_8) and KNO_3 . Suppose that the reactions of KNO_3 with each of the hydrocarbons under consideration stop, for some reason, at a step of N_2 liberation. As the prove of the feasibility for these reactions, we consider the negativity of the changes in the Gibbs free energy for reactions (10)–(12) listed in Table 1.

It is seen that formation of the set of N-bases and DR from niter and each of the considered hydrocarbons with liberation of N_2 is feasible. For Reactions (3)–(5), the greater is the molecular mass of the saturated hydrocarbon, the smaller is the magnitude of the decrease in the Gibbs free energy. These results mean the following. If deposits of a hydrocarbon-hydrate and a niter are bedded rather closely to each other, RNA can originate in the vicinity of 298 K at peripheries of methane-, ethane-, or propane-hydrate deposits with liberation of N_2 and the highest RNA "yield" can be reached with CH_4 -hydrate. The $\Delta_f G^0$ values are negative in sign and very high in magnitude; therefore, there are no doubts that they would be negative in sign if we take wide variations in the relative equilibrium concentrations of Ad and U to G and Cy.

Table 1: Changes in the standard enthalpy $\Delta_f(\Delta_f H_j^0)$, entropy $\Delta_f S_j^0$, and Gibbs free energy $\Delta_f G^0$ for reactions (10)–(12) of Cy, G, Ad, U, and DR formation from hydrocarbons and potassium niter.

Reaction	$\Delta_f(\Delta_f H_j^0)$ kJ/mol	$\Delta_f S_j^0$ J/mol K	$\Delta_f G^0$ kJ/mol
$28.2 KNO_3(cr) + 38 CH_4(g) = C_4H_4N_2O_2(cr) + C_4H_5N_3O(cr) + C_5H_5N_5O(cr) + C_5H_5N_5(cr) + 4 C_5H_{10}O_5(cr) + 28.2 KOH(cr) + 32.4 H_2O(lq) + 6.6 N_2(g)$ (3)	–9410	–3787	–8281
$20.6 KNO_3(cr) + 19 C_2H_6(g) = C_4H_4N_2O_2(cr) + C_4H_5N_3O(cr) + C_5H_5N_5O(cr) + C_5H_5N_5(cr) + 4 C_5H_{10}O_5(cr) + 20.6 KOH(cr) + 17.2 H_2O(lq) + 2.8 N_2$ (4)	–6832	–2442	–6104
$18.0(6) KNO_3(cr) + 12.(6) C_3H_8(g) = C_4H_4N_2O_2(cr) + C_4H_5N_3O(cr) + C_5H_5N_5O(cr) + C_5H_5N_5(cr) + 4 C_5H_{10}O_5(cr) + 18.0(6) KOH(cr) + 12.1(3) H_2O(lq) + 1.5(3) N_2(g)$ (5)	–5840	–1970	–5253

To verify this qualitative conclusion for the reactions considered above, we calculated the standard thermodynamic functions for several variants of reactions of the type of (3)–(5), taking that the sums of the stoichiometric coefficients for Ad, G, U, and Cy remain to be four in all variants but the ratio between the Ad and U stoichiometric coefficients (the same as the ratio between the G and Cy stoichiometric coefficients)

vary from 0.0625 to 16 (i.e., by a factor of 256) in different variants. The results calculated for the reaction between KNO_3 and CH_4 are given in Table 2.

It is seen that the increase in the relative yield of Ad and U by a factor of 256 corresponds to the increase in the $\Delta_f G^0$ magnitude by 109.0 kJ/mol. The same result, 109.0 kJ/mol, is obtained for the reactions of KNO_3 with C_2H_6 and C_3H_8 . These results mean that

thermodynamics allows wide variations in relative yields of N-bases. For the reaction between 28.2 KNO₃ moles and 38 CH₄ moles, significant variations in the equilibrium relation between produced N-bases correspond to Gibbs free energy changes as small as several tens of kilojoules. For this multimolecular reactions, the Gibbs free energy changes of such an

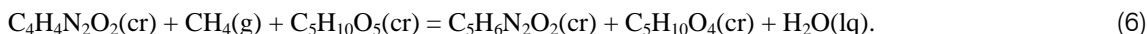
order could result from variations in the reaction conditions and in the nature of reactants (e.g., in the replacement of KNO₃ by NaNO₃). This conclusion is important, because it shows that different sets of N-bases can originate in different historical periods in any one region or in any one historical period in different regions of the globe.

Table 2: Changes in the standard enthalpy $\Delta_f(\Delta_f H_j^0)$, entropy $\Delta_f S_j^0$, and Gibbs free energy $\Delta_f G^0$ for reactions between KNO₃ and CH₄ proceeding with different relative yields of Ad to G ($[U]/[Cy] = [Ad]/[G]$).

no.	[Ad] / [G]	$\Delta_f(\Delta_f H_j^0)$ kJ/mol	$\Delta_f S_j^0$ J/mol K	$\Delta_f G^0$ kJ/mol
1	0.0625	-9385	-3885	-8227
2	0.25	-9393	-3854	-8244
3	1.00	-9410	-3787	-8281
4	4.00	-9428	-3720	-8318
5	16.0	-9436	-3689	-8336

Up to here, the thermodynamic calculations related to the sets of RNA precursors, because the thermodynamic functions for DDR are not available. However, some qualitative estimates for the

thermodynamic feasibility of DDR formation in the chemical system under consideration can be made. Let us consider the reaction of formation of Th and DDR from U and DR.



At first, we estimate the entropy change in this reaction. As the first approximation, we take that the entropy of DDR is equal to the entropy of DR. According to the tabulated data presented in [3, 5], approximately, $\Delta_6 S_j^0 = -84.21$ J/mol K and the contribution of the entropy term to the $\Delta_6 G^0$ value, $T\Delta_6 S_j^0 = -25.11$ kJ/mol. Now, we use the following approach. We suppose that $\Delta_6 G_0 = 0$, calculate the value $\Delta_f H_j^0$ for DDR (C₅H₁₀C₄(cr)), and obtain -781.1 kJ/mol. This result, in combination with the tabulated data [3, 5], means that, for the reaction



$\Delta_7(\Delta_f H_j^0) = -16.09$ kJ/mol. It is known that the reactions of such a type, in which hydrogen reduces organic substances, are characterized by negative enthalpy changes much higher in their magnitudes than the obtained value. This means that the magnitude of $\Delta_f H_j^0$ for DDR is apparently higher than 781.1 kJ/mol. Thus, it is highly probable that the products of oxidation of simple hydrocarbons by niters contain DDR together with Th, Ad, G, Cy, U, and DR. Relative contents of these components depend on the conditions.

Table 3: Changes in the standard enthalpy $\Delta_f(\Delta_f H_j^0)$, entropy $\Delta_f S_j^0$, and Gibbs free energy $\Delta_f G^0$ for reactions (8)–(10)

Reaction	$\Delta_f(\Delta_f H_j^0)$ kJ/mol	$\Delta_f S_j^0$ J/mol K	$\Delta_f G^0$ kJ/mol
4 KNO ₃ (cr) + 5 CH ₄ (g) = C ₅ H ₁₀ O ₅ (cr) + 3 H ₂ O(lq) + 4 KOH(cr) + 2 N ₂ (g) (8)	-1258	-378.7	-1145
3KNO ₃ (cr) + 2.5 C ₂ H ₆ (g) = C ₅ H ₁₀ O ₅ (cr) + H ₂ O(lq) + 3 KOH(cr) + 1.5 N ₂ (g) (9)	-918.4	-201.7	-858.3
2.(6) KNO ₃ (cr) + 1.(6) C ₃ H ₈ (g) = C ₅ H ₁₀ O ₅ (cr) + 0.(3) H ₂ O(lq) + 2.(6) KOH + 1.(3) N ₂ (g) (10)	-787.9	-139.7	-746.2

Table 3 shows that the interaction between hydrocarbons and niters with formation of only DR and nitrogen is also thermodynamically feasible: the changes in the Gibbs free energy for reactions (8)–(10) are negative in sign and rather high in magnitude.

Thus, we see that the coupled reactions of Th, Ad, G, Cy, U, DR, and DDR formation from niter and CH₄, C₂H₆, or C₃H₈ with liberation of N₂ are feasible. The reactions of DR or DDR formation apart from Th, Ad, G, Cy, and U formation are also feasible. Each of the reactions of Th or U formation from niter and each of these hydrocarbons with liberation of N₂ can proceed by itself; however, Ad, Gu, or Cy can not be formed by itself by such a mechanism.

Now, we suppose that the reactions between simple hydrocarbons and niter proceed with O₂ liberation and analyze the thermodynamic feasibility of such reactions. Calculations of the changes in the Gibbs free energy for reactions of such a type led us to the following conclusions. The thermodynamics allows formation of any one of N-bases, but Th and U, and coupled formation of the full set of N-bases under consideration (see Table 4). However, the complete set of N-bases and DR (or DDR) cannot be produced from any hydrocarbon under consideration by the reactions of such a type.

Table 4: Changes in the standard enthalpy $\Delta_i(\Delta_f H_j^0)$, entropy $\Delta_i S_j^0$, and Gibbs free energy $\Delta_i G^0$ for reactions (11)–(13)

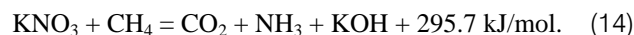
Reaction		$\Delta_i(\Delta_f H_j^0)$ kJ/mol	$\Delta_i S_j^0$ J/mol K	$\Delta_i G^0$ kJ/mol
$15\text{KNO}_3 + 18\text{CH}_4 = \text{C}_4\text{H}_4\text{N}_2\text{O}_2 + \text{C}_4\text{H}_5\text{N}_3\text{O} + \text{C}_5\text{H}_5\text{N}_5\text{O} + \text{C}_5\text{H}_5\text{N}_5 + 15\text{KOH} + 19\text{H}_2\text{O} + 3.5\text{O}_2$	(11)	-3785	-1535	-3327
$15\text{KNO}_3 + 9\text{C}_2\text{H}_6 = \text{C}_4\text{H}_4\text{N}_2\text{O}_2 + \text{C}_4\text{H}_5\text{N}_3\text{O} + \text{C}_5\text{H}_5\text{N}_5\text{O} + \text{C}_5\text{H}_5\text{N}_5 + 15\text{KOH} + 10\text{H}_2\text{O} + 8\text{O}_2$	(12)	-1800	48.84	-1814
$15\text{KNO}_3 + 6\text{C}_3\text{H}_8 = \text{C}_4\text{H}_4\text{N}_2\text{O}_2 + \text{C}_4\text{H}_5\text{N}_3\text{O} + \text{C}_5\text{H}_5\text{N}_5\text{O} + \text{C}_5\text{H}_5\text{N}_5 + 15\text{KOH} + 7\text{H}_2\text{O} + 9.5\text{O}_2$	(13)	-1075	424.2	-1201

From Table 1, it is seen that the stoichiometric ratios KNO₃/hydrocarbon for reactions (3), (4), and (5) are equal to 0.74, 1.08, and 1.43, respectively. If the KNO₃/hydrocarbon ratios are higher, the reactions between KNO₃ and CH₄, C₂H₆, or C₃H₈ could lead to coupled equimolecular formation of Ad, G, Cy, and U with liberation of O₂. Thus, the niter deficiency promotes formation of the full set of substances necessary for DNA (or RNA) formation.

We see that reactions leading to formation of N-bases and riboses from niters and hydrocarbons can produce nitrogen and oxygen in proportions dependent on the conditions.

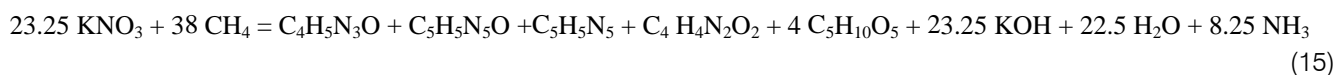
Note some peculiarities of the reactions under consideration. First, the hydrocarbon pressure over hydrates is determined by the temperature independently of the fractional conversion of the hydrocarbon; the super-stoichiometric H₂O converts to liquid phase. Second, the gas pressure over a gas-producing reaction zone located under a rather smooth stratum or under a seafloor is self-regulating because the stratum layer acts as the pressure valve throwing off the pressed gas into the atmosphere or seawater. Third, hydrates are capable of sorbing significant volumes of N₂ obtained as a result of the reactions with niter (the so-called auxiliary gas); this process stabilizes the hydrate structure. The first and second peculiarities are significant for LMSE formation. The point is that the

LMSE are the products of incomplete interaction between hydrocarbon and niter within the hydrocarbon-hydrate phase. Reactions of the type of (3)–(5) represent an initial step of nitrogen reduction. The complete nitrogen reduction could lead to ammonia formation:



Meanwhile, the reactions of the type of (3)–(5) liberate N₂; the gas pressure over the hydrate phase increases up to a limit level, which is determined by the depth of hydrate bedding, temperature of the hydrate phase, and density of the over-hydrate soil layer and seawater column, and then the N₂–CH₄ mixture is thrown off into the atmosphere or seawater. The CH₄ pressure keeps at the initial level due to the first peculiarity formulated above, and the continuous throwing off of the nitrogen that did not achieve the highest degree of reduction inhibits complete oxidation of carbon and thus stimulates stabilization of the produced LMSE.

In a closed system, i.e., under conditions when N₂ is not thrown off from the reaction zone in the course of the reaction between niter and a hydrocarbon, this reaction goes through the state of the system that can be described as the equilibrium between initial substances (niter and hydrocarbon) and such products as N-bases, riboses, and NH₃. For example, when the hydrocarbon is methane, we can write



For this reaction, $\Delta_{15}G^0 = -6146 \text{ kJ/mol}$. We see that the full set of the LMSE can be formed from CH_4 and KNO_3 with liberation of ammonia. For reactions of such a type with C_2H_6 and C_3H_8 , the $\Delta_{15}G^0$ values are also negative, -5198 and -4757 kJ/mol , respectively.

In natural situations, most of the equilibriums considered above can not be reached. The natural reactions of a hydrocarbon with a niter can proceed by a complicated way with liberation of N_2 , O_2 , NH_3 , and CO_2 . The negativity of the changes in the Gibbs free energy shows that the corresponding reactions proceed in the directions determined by the written stoichiometric equations; however, it does not show that they proceed only in the directions determined by only one of these equations.

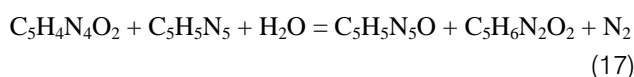
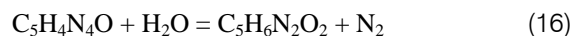
The thermodynamic consideration performed in this section allows the following important conclusions: (i) reactions between niter and CH_4 , C_2H_6 , or C_3H_8 at temperatures in the vicinity of 298 K can lead to formation of all N-bases inherent in DNA and RNA molecules, DR, and DDR; (ii) the relative yields of these substances depend on the conditions and can vary in wide ranges; (iii) formation of N-bases, DR, and DDR from hydrocarbons and niters can be associated with liberation of O_2 , or N_2 , or NH_3 or with simultaneous liberation of O_2 , N_2 , NH_3 , and CO_2 in proportions dependent on the reaction conditions; and (iv) the reactions between niters and hydrocarbons can proceed in different reaction zones over the globe and in different time periods.

The following general conclusions for this section are possible. According to our hypothesis, the fulfillment of the following main conditions is necessary for LMSE origination at any planet. First, the crust of the planet should contain compact deposits of hydrogen or substances capable of decomposing with H_2 liberation, carbon dioxide or carbonates capable of decomposing with CO_2 liberation, niters or other sources of oxidized nitrogen, and phosphates or another source of phosphorous capable of oxidizing to phosphate. Second, the intra-terrestrial conditions, namely, the temperature and mutual arrangement of the above-listed substances, should allow diffusion of these substances within the planet's crust. Third, the temperature within the planet's crust should be appropriate for formation and long-term stability of water, hydrocarbon-hydrates, niters or other substances containing oxidized nitrogen, and phosphates. Fifth, to the above mentioned principal differences between our hypothesis and Oparin's hypothesis on life origination, this section adds the following: according to our hypothesis, ammonia can be formed as a side product of life origination in contrast to Oparin's hypothesis, according to which ammonia represents one of the source substances. To be precise,

we believe that a portion of ammonia liberated in the processes of LMSE origination is thrown off from the reaction zone and a portion of residual ammonia can be used in the subsequent step of formation of amino-acids.

Consider one more question. Why are such N-bases as X and HX not frequent guests in DNA (and RNA) molecules? It appears that, in the nitrogen medium, X and HX can be considered as precursors in the processes of Th, Ad, G, Cy, and U formation.

To confirm this statement, we consider reactions (16) and (17).



The calculations showed that the changes in the standard Gibbs free energy for the reactions of HX interaction with water up to Th and N_2 formation and of X interaction with Ad and water up to G, Th, and N_2 formation are negative and are equal to -106.9 and -115.9 kJ/mol , respectively.

Apparently, just the thermodynamics is instrumental in the selection of N-bases (from those contained in large cavities of the hydrate structure) to be further incorporated in nucleic acids. This opinion is illustrated by the reaction between X and NH_3 yielding G. Equation (15) shows that, under some condition, interaction between methane and niter can lead to NH_3 production. It is not obligatory that reaction (15) goes up to the equilibrium, but it is evident that it is directed to the equilibrium state and it is possible that this equilibrium can be achieved. It is clear that equilibrium in the reaction system suggests equilibrium between all its components, in agreement with the principle of detailed balancing; this allows elucidating whether X ($\text{C}_5\text{H}_4\text{N}_4\text{O}_2$) can exist in a system containing G and NH_3 . For the reaction



The relevant values are $\Delta_{18}(\Delta_f H_j^0) = -43.94 \text{ kJ/mol}$; $\Delta_{18} S_j^0 = -122.9 \text{ J/mol K}$, and $\Delta_{18} G^0 = -7.31 \text{ kJ/mol}$.

In this reaction, the free energy decreases, which means that equilibrium (18) is shifted to the right and X formation is thermodynamically disadvantageous. However, the absolute change of the free energy is small; therefore, nucleic acids may contain X under certain conditions differing from standard ones. Indeed, X is sometimes found in natural nucleic acids.

The majority of the equilibriums considered above are attainable under certain natural conditions and unattainable under others. Also, conditions are conceivable in which a reaction between hydrocarbons and niter develops along a complicated path and is

accompanied by the release of N_2 , O_2 , NH_3 , and CO_2 .

For our purposes, it is inessential whether equilibriums are actually achieved; the possibility of reactions leading to LMSE formation is of much greater importance. The negativity of the standard Gibbs free energy changes proves that the relevant reactions can occur in the Earth's depths at the temperatures that were probably maintained there for a long time.

We demonstrated that the Gibbs free energy changes for the reactions of LMSEs formation from hydrocarbons and niter are not only negative but are rather high in their magnitudes. Of course, the magnitudes of the free-energy decreases in the processes of the LMSEs formation from substances that are simpler than methane and niter (e.g., from the chemical elements) at the boundary between the Earth's surface and atmosphere would be even higher. However, a selective interaction of a large number of single gaseous or dissolved molecules with a growing precursor of any LMSE is much less probable than the interaction between only two phases ($CH_4 + NO_3^-$) and the subsequent interaction with one more phase (PO_4^{3-}) in the interior of the Earth. Besides, the absence of the methane-hydrate matrix would render the DNA and RNA formation process impossible.

e) *Origination of Living Matter and Transformation of Earth's Atmosphere Composition as Interrelated Processes*

Hydrogen was the predominant element of the nebular composition. It is well known that H_2 chemisorbs rather strongly on different metals and metal oxides in a wide temperature range [98–100]. Therefore, the nebular dust and the porous structure of the agglomerated particles that had contributed to the Earth's crust had been covered with chemisorbed hydrogen. As was detailed in Section III.1., just the hydrogen chemisorbed by the nebular agglomerates that formed the Earth's crust triggered the sequence of the processes that had led to the LMSEs formation.

The processes of decomposition of carbonates and formation of hydrates of hydrocarbons in the Earth's crust had led to emissions of CO_2 , CH_4 , and, possibly, other simplest hydrocarbons into the atmosphere by the mechanisms described above. These emissions had caused the greenhouse effect.

The processes of LMSEs origination had proceeded within the Earth's crust and led to gas emission. Apparently, the reactions of formation of substances similar to N-bases, DR, and DDR had proceeded everywhere, where deposits of niter and of hydrates of simplest hydrocarbons had been located in rather close proximity. The natural conditions in some regions had promoted formation of the full sets of the LMSEs and subsequent formation of the DNA- and RNA-like molecules, and the conditions in other regions had promoted formation of only some of the LMSEs.

These processes could proceed with liberation of N_2 ((3)–(5) and (8)–(10)), O_2 (11)–(13), NH_3 ((14) and (15)), and CO_2 (14) or mixtures of these gases. The thermodynamics of several tens of O_2 - and N_2 -liberating reactions of formation of different N-bases and DR from different hydrocarbons and niter are considered in [3]. Some portions of these gases had been thrown off into the atmosphere. Thus, the atmospheric composition had gradually approached to its present percentage. Methane (or other simplest hydrocarbons) that had emitted from the intra-terrestrial reaction zones had partially dissipated in the space, being lighter than O_2 and N_2 , and, in the upper atmospheric layers, had been partially oxidized to CO_2 by O_2 and, possibly, by water vapor under the action of solar radiation.

Thus, transformation of the atmosphere to its present O_2 - N_2 composition had started and had been in progress before the living matter origin, i.e., apparently, 4000-plus Myr ago. The CO_2 and CH_4 of the underground origin and the CO_2 of the atmospheric origin had led to the greenhouse effect, which had prevented the Earth from cooling, had provided the occurrence of water in liquid state on the Earth's surface in the period of the faint Sun, and thus had stimulated the living-matter development. Meanwhile, the faint-young-Sun period had approached to the end and the solar radiation had increased; by this period, the Earth's atmosphere was somewhat enriched with N_2 and O_2 that had resulted from the processes of LMSEs origination.

The available data on the present state of the solar-system planets confirm the likelihood of the Earth's atmosphere metamorphoses proposed by us or, at least, do not contradict them [4]. The atmospheres of the cold giant planets (Jupiter, Saturn, Uranium, and Neptune) are largely composed of H_2 and He like the Sun's photosphere and the primary atmospheres of the terrestrial planets (Pluto is very small and has almost no atmosphere). The atmospheres of the cold giant planets contain no CO_2 , and, most likely, this gas has never been there. The atmospheres of the terrestrial planets contain CO_2 , very small amounts of residual He, and no H_2 . The Mercury's atmosphere is very thin, because the mass of this planet is less than the Earth's mass by a factor of 18 and the gravitational force is small and because the temperature of the Mercury's atmosphere is significantly higher than that of the Earth's atmosphere. Hydrogen of the Venus's primary atmosphere, whose temperature was always much higher than that of the Earth's atmosphere, had apparently dissipated before it could react with CO_2 ; even if CH_4 and H_2O would be produced from H_2 and CO_2 within the interior of the young Venus, these gases would not be able to form methane-hydrate within the Venus's hot crust and, most likely, would diffuse into the atmosphere and dissipate in the space. Thus, the available information on the atmospheric composition inherent in these planets does not contradict our hypothesis.

IV. GENERAL DISCUSSION: THE LOH-HYPOTHESIS AS ACTUALIZATION OF THE PRINCIPLES OF MENTAL RECONSTITUTION OF THE UNIVERSE REMOTE HISTORY AND AS A SOURCE OF A NEW APPROACH TO THE PROBLEM OF THE LIFETIME OF ORGANISMS

The LOH-hypothesis differs principally from all living matter origination hypotheses published earlier. These differences are not only factual but also reflect different world outlooks and philosophies. We consider the life origination process as a sequence of thermodynamically caused regular and inevitable chemical transformations, which are regulated by universal physical and chemical laws. We assume that living matter originated repeatedly in different localizations and that each localization could give rise to a multitude of different living organisms. Different organisms consist of the cells that are similar in their constitution, because they are built by Nature within similar mineral matrixes and on the basis of the same mineral materials and the same physical and chemical laws.

The LOH-hypothesis is the unique hypothesis that fits with the following principles, which are considered by us as the necessary ones when developing hypotheses of gross-scale events that occurred in the Universe in remote ages.

1. The gross-scale processes in nature proceed progressively in the direction of decreasing free energy of the Universe subsystems that can be approximated as the isolated ones.
2. All natural phenomena proceed as a result of regular and inevitable transformations regulated by the universal physical and chemical laws.
3. Newton's principle of simplicity ("...for Nature is pleased with simplicity, and affects not the pomp of superfluous causes").
4. The principle of repetition of supposed events and of the presence of individual features in the reproduced events. (Nature created many similar but somewhat differing events and no unique event without close analogues.)
5. The principle of the unity of the event point. Separation of an event into several sub-events that proceed in different points with subsequent interaction between the sub-events decreases the probability of the resulted event, because it decreases the degree of repetition of the event as a whole.
6. Nature makes no jumps (Nature non facit saltus, in Latin).

The LOH-hypothesis conflicts neither with principal physical and chemical laws nor with

observational and experimental data. In line with the preliminary analysis of the living-matter origination problem that was given in Section I, it is based on the notion that the medium of living matter origination is of matrix nature. According to the hypothesis, this matrix represents the gas-hydrate structure, which is widely distributed over the Earth and, apparently, over other planets and contains methane or another hydrocarbon as the guest substance. Such a medium is unique in nature because it is of water nature and contains two elements (C and H) necessary for living matter origination.

The same physicochemical phenomenon of formation/destruction of the gas-hydrate matrix was applied by us to explanation of living-matter origination and to the pioneering physicochemical explanation of intracellular processes, beginning from formation of a maternal cell to its division and formation of a daughter cell (the MRH-hypothesis). The MRH-hypothesis was progressively developed in [1, 2, 11, 18], and we do not present it in this paper. However, we mention it because the use of the same principles for formulation of physicochemical hypotheses of living matter origination and of living matter replication and development counts in favor of the principles underlying them. These two hypotheses have been developed in parallel for the last twelve years, beginning from [1, 2].

These hypotheses allowed us to explain the double-helix unwinding in the course of mitosis and to understand why, according to [101, 102], the waters located around G desorb faster than the waters located around other N-bases and why, according to [103], the waters located around N-bases desorb faster than the waters located around phosphate groups.

We try to integrate the new concepts of the natural processes responsible for the formation of LMSEs and for the transformation of the Earth's atmosphere and to substantiate their thermodynamic feasibility. The main stages of the LMSEs formation and concomitant atmospheric changes during the Archean period are discussed in [4]. We considered the phenomenon of coupling between the processes that preceded the origin of life and the processes that were involved in atmospheric transformations. On the one hand, hydrogen of the primary atmosphere, together with carbon dioxide that was released within the Earth's crust, provided the formation of underground methane-hydrate deposits, which became starting substances for the formation of living matter elements. On the other hand, the processes of the LMSEs formation contributed, in the course of time, to the appearance of O₂ and N₂ in the atmosphere prior to the emergence of life.

Not proteins nor amino-acids, but DNA and RNA molecules are the first carriers of life. Living matter originated and can originate now everywhere where necessary minerals and necessary ambient conditions

exist and where these conditions are maintained for long periods of time.

Our hypothesis includes an important notion of a “thermodynamic front” whose temporal movement determines the slow (on the human life duration scale) stepwise filling of the gas-hydrate cavities, i.e., formation of purine and pyrimidine nuclei within the large cavities, of riboses within small cavities, and of substituting groups in the purine and pyrimidine nuclei and subsequent formation and lengthening of the DNA- and RNA-like molecules.

The life origination processes cannot be considered, in our opinion, without their time reference and without their discussing in the context of Darwin’s hypothesis of the origin of species.

Let us briefly consider the question on dating the historic period when the first simplest living organisms appeared on Earth. It was recently [104, 105] discussed on the basis of the current knowledge of the Earth Archaean history.

Following the original papers [106, 107], we use two different time scales, the fossil and molecular ones. The former is based on the use of defined time points that are specified from the geological data on the ages of different rocks and of definite geological events; these definite time points are accurately calibrated by the modern radiometric methods. The later is based on the acceptance of consequences from Darwin’s hypothesis, according to which the changes in genomes are accumulated by them with time and the number of the changes is proportional to the time period; thus, it is taken that the positions of points of some genomic transformations on the time scale should allow specification of the positions of other transformations of fossilized genomes on this scale.

According to [106, 107], the early divergence among prokaryotes was 3970 Myr ago (molecular time) or 3800 Myr ago (fossil time) and the origin of eukaryotes was 2730 Myr ago (molecular time) or 2150 Myr ago (fossil time). Note that the dates of divergence among prokaryotes were recently called into question. The point is that this conclusion was made on the basis of indirect data on the isotopic composition of the carbon inclusions within the apatite crystals mined from the Greenland Archaean beds. Meanwhile, according to [108, 109], the apatite crystals and carbon inclusions could be formed much later as a result of metamorphism influenced by the hot fluids. We see that the molecular time and the fossil time differ rather significantly and that the periods of the starts of the Earth prokaryotization and eukaryotization are known rather approximately. These conclusions relate not only to the prokaryotes and eukaryotes ages. Fossil time measurements led to the conclusion that the earliest localities of invertebrate animals lived 600–550 Myr ago and that most of the species of invertebrate animals

occurred in Cambrian period, i.e., their age is less than 510 Myr. However, the measurements of the molecular time give a period of 1500–1200 Myr ago for the development of the first Metazoa colonies and lead to the conclusion that the main branches of the invertebrates developed many hundreds of millions of years before Cambrian [104]. It was mentioned above that multicellular organisms appeared repeatedly in the Earth history [29].

The data of the previous paragraph show, first of all, that the so-called molecular time scale differs greatly from the fossil one; we believe that the molecular scale is based on the questionable principles, and the grounds for such an opinion will be given below. As for the data presented in the fossil scale, they, apparently, give rather clear information on the main temporal milestones in the history of the appearance and development of living organisms and show that the later, along the time scale, a species appeared on Earth, the more complicated is its internal cellular constitution, i.e., the more complicated is its genome [104].

It is an open secret that Darwin’s evolutionary hypothesis on the stick-slip development of living matter from the simplest organisms to highly organized ones limps and the limping does not become less evident with time. The notion of evolutionary accumulation of minor changes in the DNAs of an organism and revolutionary manifestation of summed minor changes in appearance of a new species is scarcely justified.

The experiments with drosophila and other rapidly reproducing species have been performed widely around the world for more than half a century by many tens of researches under different ambient conditions and no less than 10^5 generations were obtained and analyzed, but no new stable species had been observed in spite of the wide variations in experimental conditions. Taking into account that living matter exists on Earth for no more than $(3.5-4.0) \cdot 10^9$ years, it is logical to doubt Darwin’s opinion that Nature created simplest living organisms, that their heritage varied from generation to generation as a result of mutations and natural selection, and that the generations with novel stable characters could originate new superior and more complicated species till the appearance of mammals including *Homo sapiens*. At present, there are strong reasons to assert that no subsequent experiments are capable to refute this conclusion.

According to Darwin, the fossil record should be rife with examples of transitional forms leading from the less to more evolved species. Quite the contrary, “...instead of filling the gaps in the fossil record with so-called missing links, most paleontologists found themselves facing a situation in which there were only gaps in the fossil record, with no evidence of transformational intermediates between documented

fossil species" [110]. The Darwinian hypothetical evolutionary chains have a number of wide gaps, such as between primitive terrestrial mammals and whales or between molluscs and arthropods. However, as was pointed in [111], the punctuationalist hypothesis on the possibility of rapid interspecific evolutionary transformations (macroevolution) resulted from random mutations has neither logical nor geological grounds. It was mentioned above that multicellular organisms appeared independently in the Earth history no less than 24 times [29]. Meanwhile, the today life-origination hypotheses, at least those actively discussed in the scientific literature, are not able to explain the plurality of the life origination phenomenon, because they consider living-matter origination as a random, rare, and single event and, furthermore, most of them proceed from the incorrect principle of the necessity of external energy for synthesis of biologically-active substances from minerals.

Principally new explanation of the variety of living-matter species becomes more necessary over the years. The LOH-hypothesis allows for explaining the living-world variety from naturalistic positions. As was said above, we assume that the DNA and RNA molecules originated from minerals within the natural underground incubators, where they had been forming and upgrading with time and had only a minor contact with the outside. Little by little, they increased in length and their thermodynamic ordering improved. Thus, the longer was the period of DNA and RNA formation within the hydrate matrix and the later the hydrate matrix melted and the DNA and RNA molecules got to ambient water–mineral or soil–atmosphere media, the more complicated organisms developed on the basis of the DNA and RNA molecules matured in their incubators. Apparently, this conclusion explains the statement given above that the more complicated are the internal cellular constitutions of a species, i.e., the more complicated is its genome, the less is the age of this species [104]. According to the LOH-hypothesis, different species of living organisms originated in the period of formation of the DNA and RNA molecules. Perfecting of the primary DNA and RNA molecules in the underground incubators could be interrupted occasionally, and, thus, the complication of the species resulted from further transformations of the nucleic acids was not continuous. Therefore, filling the gaps in the Darwinian series is, seemingly, unpromising. It is quite possible that Darwin's hypothesis is of significance for the survival and adaptation of organisms to the conditions of ambient media, but it scarcely is the leading one for principal transformations of species.

It is known that the simpler are the organisms, the stronger are their variabilities with time. Apparently, the cause of enhanced variability of simple organisms lies in the fact that the DNA molecules that govern their heritage were housed insufficiently long in natural

incubators and, therefore, they were insufficiently ordered in the thermodynamic understanding of this term. Thus, in our opinion, the foundations of the future principal interspecies differences were laid at the steps of origination of the corresponding nucleic acids and proto-cells.

As was mentioned above, the grounds of the LOH-hypothesis were published in 2000 in Russian and its English translation was then published by the MAIK "Nauka/Interperiodica" [1]. After that, the LOH-hypothesis was developed in papers [2–13]. However, apparently, it is still little-known over the world. The following quotation from the book published in 2010 [112] cannot be explained otherwise. Let us quote [112, p. 20]. "The question "How did life begin?" is one of the "biggest unanswered questions" in biology [113]. "More than 30 years of experimentation on the origin of life in the fields of chemical and molecular evolution have led to a better perception of the immensity of the problem of the origin of life on Earth rather than to its solution" [114]. "What creates life out of the animate compounds that make up living things? No one knows. How were the first organisms assembled? Nature hasn't given us the slightest hint. If anything, the mystery has deepened over time" [115]. We agree with the author of [112] when he quotes [113,114]. The question "How did life begin?" is really one of the biggest unanswered questions in biology, and the experiments aimed at verification of Oparin's hypothesis did not lead to solution of the life origination problem. However, the questions formulated in [115] are answered hypothetically by us. According to the LOH-hypothesis, DNA and RNA molecules were produced from such inanimate compounds as CH_4 , NO_3^- , and PO_4^{3-} within solid CH_4 -hydrate matrixes and proto-cells formed in the soups that arose after their melting. Just the occurrence in the Earth's crust of the CH_4 -hydrate matrixes and of only two additional substances (niter and phosphate) allowed the nucleic acids and the first organisms to be assembled. Nature's hints were noted by us, and it is necessary to test experimentally whether we are right or not; no sophisticated reasoning is capable of rejecting our cracking of these mysteries.

The opinion that biological codes of a mysterious origin were inserted into the primary DNAs and have been passed on from generation to generation is widely distributed. Some authors write on unknowable "molecular machines" that allegedly manufactured these codes and dispensed them among DNA molecules. One argumentation of such a kind is as follows [116]. "The genes and proteins of the first cells had to have biological specificity, and specific molecules cannot be formed spontaneously. They can only be manufactured by molecular machines, and their production requires entities like sequences and codes that simply do not exist in spontaneous processes. That is what really divides matter from life. All components of matter arise

by spontaneous processes that do not require sequences and codes, whereas all components of life arise by manufacturing processes that do require these entities. It is sequences and codes that make the difference between life and matter. It is semiosis (symbol translation system) that does not exist in the inanimate world, and that is why biology is not a complex form of chemistry." Meanwhile, each of the statements of this paragraph is controversial, is straightened by nothing, and represents no more than the reflection of the author's world outlook. Therefore, these statements have no advantages over the opposite assertions and the verity can be revealed exclusively by an irreproachable logic or highly reliable experiments. The content of the term "molecular machine" is not specified in [112, 116] and, therefore, is beyond either comprehension or discussion. We assert that the DNAs of the first cells had neither biological specificities nor biological codes and had only chemical specificities and that these chemical specificities, i.e., definite sequences of N-bases in the DNA molecules, arose at the step of the DNA origination as a result of combined action of the effects of gas-hydrate matrix geometry, limitedness of the set of reacting substances, and thermodynamic front. The "congenital" chemical specificities have been passed on from generation to generation under the effect of the same factors; in order that the sequences of N-bases would not be destroyed, the intracellular reactions should proceed under constant and undisturbed conditions and at a rather low temperature when the structural cavities are capable of being occupied as a result of successive thermodynamically controlled chemical reactions. We consider the phenomenon of life as the process of extended reproduction of DNAs and the formation of proteins as no more than a result of side processes. Thus, we consider the phenomenon of life just as the revelation of the universal physical and chemical laws, contrary to the author of [116] who negates such a concept. It is common practice to regard the occurrence and accumulation of proteins as manifestation of the phenomenon of life, but the Sun movement through the firmament was regarded for long as manifestation of the phenomenon of the Sun revolution about the Earth. The author of [116] notes rightly that the DNA molecules are specific and, therefore, they cannot be formed spontaneously. Indeed, none of the hypotheses of living matter origination, but the LOH-hypothesis, takes this feature into account. According to the LOH-hypothesis, just the origination of the primary DNA molecules within gas-hydrate matrixes provides their specificity as was described above. Thus, for origination of specific DNA molecules according to the LOH-hypotheses, no "molecular machine" is required. By the way, we see only the quantitative but not qualitative differences between the specificities in the mineral and biological

worlds; the specificity is characteristic for inanimate world and not just for the biologically active molecules: for example, the designs of malachite crystallized in Somali and Russia are similar and the quartz druses from different countries are almost indistinguishable from each other. Meanwhile, nobody think that these mineral rocks use any mysterious codes, but the natural laws of crystallization.

Let us write something on the problem of the sources of information that is necessary for origination of living matter and on the probability of origination of the complex molecules, such as nucleic acids. The author of [112] writes the following in page 54. "All the known laws, theorems, and principles of information science indicate that codes, complex functional information, and prescriptive algorithmic information cannot arise from physicality....Therefore, based on currently accepted information science, but realizing that science is always subject to change, it seems impossible for life to have arisen purely from physicality.

Those who insist on purely physical causes of life are thus in an untenable position when it comes to known science. Not only can they not prove that it's possible (non-zero probability) for life to come about by the physical interactions of nature, but the information content of life precludes that possibility. "There is no known law of nature, no known process, and no known sequence of events which can cause information to originate by itself in matter" [117]."

We can by no means agree with this multi-author opinion. We wrote above that neither codes nor prescriptive information exist. Any DNA transforms according to nothing more than chemical and physical laws. If the details of these transformations are yet unknown, this means that, up to now, the thought processes have been going in wrong directions. The LOH-hypothesis specifies a new direction for subsequent studies and invites enthusiasts to go in this direction. Of course, every new idea is sure to have its knockers. However, no other realistic approach is available at present. Our approach just is of physical, more precisely of physicochemical, nature. As for the probability of the self-assembling of nucleic acids, the LOH-hypothesis increases it many-fold due to the matrix effect and minimum number of different involved mineral substances. As regarding the information included into living matter reproduction processes, Nature creates ordering, in particular such as crystalline structures and, in our case, methane-hydrate structure; and this ordering can be the source of a secondary information, i.e., ordering is capable of producing information. The principal features of the mechanism of the secondary-information origin from the primary information enclosed into gas-hydrate structures by Nature are described above in Section III.2. It is possible that Nature could find some other ways for the transmission of such

information. The ways of Nature are mysterious, and it is too presumptuous to think that anybody is capable to exhaust mentally all of them.

To support the last statement, we present an indicative example. It is from another field of science which, nevertheless, we know rather well. In 1939, a work on the kinetics of the heterogeneous catalytic synthesis of NH_3 was published [118], where it was written that a kinetic equation which follows from the earlier works [119] and [120] cannot be explaining by nothing but by the heterogeneity of the surface centers of thermally stabilized surfaces relative to their catalytic ability. The community had trusted that conclusion. It distributed over the world; the notion on surface heterogeneity initiated thousands of speculative works, and the corresponding equations and their deductions fell into a number of textbooks. To confirm or reject this concept, measurements of the chemisorption-heat-surface-coverage dependences were necessary; however, as a result of technical difficulties, the results of the measurements were ambiguous. Only 50 years after 1939, it was proved [121–123] that the kinetic equation proposed earlier for the NH_3 synthesis responds also to homogeneous surfaces. As a result, the concept of surface heterogeneity came down [100, 123] and its wreckages covered the results of the works of two generations of the researches who works in the framework of the hypothesis of surface heterogeneity. Such a situation could be impossible if the statement of the author of [118] would be timely ignored. Indeed, the ways of Nature are mysterious. Of course, this is not the unique example of such a type.

As was noted above, we consider the problem of how the Earth's living matter had originated rather than the problem of where it had originated. Nevertheless, we think that it would be improper to ignore the point of view that living matter origination process had started beyond the Earth, especially because all Earth's processes, being considered from the formation of all chemical elements and simplest substances, had started, of course, beyond the Earth.

We criticize neither Oparin's hypothesis nor any other similar hypothesis with the exception of one question, namely, the relation to the thermodynamics, because this question is of principal importance and because we were the first to reveal the absence of any energy-requirement for production of biologically active substances from minerals.

However, it goes without saying that we would develop no new hypothesis if we would be satisfied with any other one. Nevertheless, we do not think that our aim consists in a criticism of any available hypothesis. We prefer argumentation and defend of our own ideas and chose criticism only in rare instances. Let all flowers bloom, let all hypotheses compete with each other, and let the experts who are specialized in criticism rather

than in creation of hypotheses decide which of them has the best prospect.

A number of different approaches to the problem of living matter origination are available in addition to those mentioned above, for example, in [124, 125]; a special issue of the open access journal "Life", 2(1), 2012 is dedicated to this problem. We do not comment on these works and believe that the readers are capable of forming their own attitude toward the degree of likelihood of different hypotheses, basing on their own preferences and, may be, taking into account our opinion formulated in the beginning of this section relative to the principles necessary for formulation of the hypotheses aimed at clarification of the mechanisms of ancient events.

In Section I, we defined the term life as the phenomenon characterized by a combination of the natural chemical processes that lead to the extended self-reproduction of DNA molecules from generation to generation and by translation of all or almost all significant maternal features to the daughter. This definition contains no mention on the protein production. We believe that just the transformations of DNAs should be considered as the proper life and the protein production is no more then the result of side processes that accompanied them. Moreover, we believe that just the accumulation of protein within cells and on DNAs leads to deceleration in the cellular replication and to the cellular senesce. For example, "both in vivo and in vitro in human as well as in rodent cell populations, the rates of cellular replication are significantly decreased with cellular aging" [126].

An opinion exists that this effect is associated with the unrepaired DNA damage accumulation. [127]. However, if it is even so, this is only an associative connection but not the natural-science explanation. In our opinion, such an explanation can not be considered as the constructive one because it gives rise to new questions, for example: what is the nature of this connection? The references to enzymes that allegedly supply the duplication process and cannot continue the duplication process all the way to the ends of chromosomes give also nothing for understanding of this important phenomenon and are scarcely capable of influencing the lifetime.

We assume that the nature of the phenomenon of the DNA tiredness and cellular senescence and dying is, substantially, of the following nature. If nothing hampered the DNA replication process, the DNAs would increased in the number by the law

$$N_1 = 2^n, \quad (19)$$

Where N_1 is the number of the DNA mono-strands produced from any one DNA mono-strand as a result of n replication events. We believe that two most harmful phenomena decrease the rate of DNA replication under favorable ambient conditions with no

agitation: the fatal mutations (N_2), including the mistakes in the replication process, and the DNA covering with protein (N_3). It is quite possible that just the last phenomenon has a determining harmful effect on the replication process intensity and on the life duration; apparently, the DNA strands are overgrowing continuously with protein and thus become centers of protein condensation and log out life development. It is possible to consider the problem of degradation of the rate of DNA replication by the algebraic methods. It is sufficient to specify the realistic laws of N_2 and N_3 increase with the number of the DNA replications and to calculate the n value at which

$$N_1 - N_2 - N_3 = 0. \quad (20)$$

Just this n value responds to the state of death. Apparently, there is one more important cause that influences (*ceteris paribus*) the rate of DNA replication: this is the fullness of cells by excessive proteins that retard the diffusion processes and thus are capable of influencing the intracellular exchange processes. The intra-cellular content of proteins can increase from one generation to another. In our opinion, these two protein effects can be summarized by one term in (20) to a first approximation. The realistic number of the effective DNA replications from the birth of a lot of organisms to their death is available; it is equal to about 50 (e.g., [124]). The data on the frequency of fatal mutations are also available. We think that the analysis of a solution of such a problem would be of interest. It is possible, that either the N_2 or N_3 term could be regulated; apparently, regulation of the N_3 term is most prospective. This idea is our gift for a curious young researcher who will read this rather long paper up to this page.

Basing on the LOH-hypothesis, we see the possibilities to come down to brass tacks on the way to adequate understandings of different subjects. The idea described in the previous paragraph is not the unique one of such a kind. The LOH-hypothesis allows new approaches to the problem of food and energy necessary for living organisms. This follows from fixation of new relations between the living matter, as a multitude of DNAs, and protein, as the side product of the DNAs extended reproduction, and between the living matter and food, as the source of such a reproduction.

Apparently, such substances as C^{-4} , NO_3^{-} , and PO_4^{3-} are sufficient (in the presence of hydrate matrix) for life maintenance and protein production. After our thermodynamic calculations, there is no doubt that these processes require no energy and, furthermore, they evolve much energy. The processes of the primary living matter formation had no difficulties in dissipation of this energy because of their slowness. However, as biota accumulated in the environments, some living organisms began to "feed on" other organisms that were dissipated in the super-cytoplasm soup. The

"organisms-killers" destroyed the bodies of the "organisms-victims" up to N-bases, PO_4^{3-} - and NO_3^{-} -ions, and riboses and used this material for their own extended reproduction. They were the first animals. Other organisms, i.e., plants, continued to use the mineral food. Possibly, origination of the animals and plants was dependent on the DNA concentration in the hydrate matrixes before their liquation and in the semi-liquid super-cytoplasm soup. This "food revolution" increased the rate of the extended reproduction of the "animals", because the necessity of the LMSEs syntheses disappeared and the heat evolution decreased as a consequence of the necessity of the endothermic food destruction. After the "heat revolution", the process of the DNA replication became almost autothermal because the chemical states of the food and of the newly formed organisms were closely related in their chemical composition and structure. To perform an external work, an additional energy became necessary. This led to the consumption of additional amounts of food and to exothermal synthesis of additional protein. This protein was unnecessary for the process of life development and, moreover, it retarded the process of life development; however, it was a necessary source for performance of an outer work by the living organisms.

Thus, we propose a completely new view on the relation between the food, energy, and outer work for animal organisms.

According to our concept that is supported by the thermodynamic calculations, just the DNAs and RNAs or, more precisely, the N-bases and PO_4^{3-} - and NO_3^{-} -ions which are included into the food substances, rather than the proteins, fats, and carbohydrates as such satisfy the biological requirements of the animal organisms in the energy necessary for the functioning of the organisms and for the production of an outer work by them. Moreover, the necessary energy is produced as a result of formation of proteins and other organic products but not as a result of their oxidation in the bodies of living organisms. As a matter of fact, the N-bases and PO_4^{3-} - and NO_3^{-} -ions can be introduced into the animal organisms in the form of these simple substances or in the form of DNAs and RNAs and the necessary amounts of this "food" can be estimated from the real rates of DNA replication. Of course, each present-day animal organism may include not only nucleic acids but also proteins, lipids, monosaccharides, polysaccharides, and different other organic substances, tissues, and fluids and each of the organisms is in need of some food for reproduction or extended reproduction of these components and for the inter-organism circulations and production of an outer work. However, the amount of energy that is necessary for these processes and for the production of any outer work can also be estimated. According to the conclusion from the LOH-hypothesis, the calorie content

in the food does not determine the quality of the food.

Thus, apparently, new notions should be used as the basis for calculations of the nutrition. In our opinion, the way to a prolongation of the life of animals lies through regulation of the composition and quantity of the food in the context of the principles given above, rather than through the search of a gene of the long life. In our opinion, the amounts of the excessive food should be minimized and the necessity of using the C^{4-} and PO_4^{3-} and NO_3^- -ions in definite proportions should be taken into account. The simpler is the food in its chemical composition and the closer is it in its chemical composition (with definite limitations) to minerals C^{4-} , PO_4^{3-} , and NO_3^- and to their proportion in nucleic acids, the longer is the life.

These conclusions on the life duration and food are not far from some empirical recommendations, such as the cereal diet or Bragg's feed system [128]. However, we should caution the riders from premature applications of our conclusions. They are entitled to a careful and many-sided examination. Meanwhile, apparently, their grounds are sufficiently solid. The fact of the matter is that they even do not depend on the content of the LOH-hypothesis as such; they result from our thermodynamic calculations that show unambiguously that biologically active substances can be produced from minerals with no additional energy.

We are sorry to let out a squeak in the harmonious chorus of highly experienced maestri and understand our risks; however, we should express our opinion that each step of the multi-step self-reproduction of a cell is controlled by a physicochemical mechanism rather than by an article termed ferment, which is a unit of a flotilla of four thousands of different amphibian units locked or flung open, each of which appears seasonably at the correct point, acts accurately its function, regardless of the laws of physics, chemistry, and diffusion, and disappears completely to nowhere like a phantom. This our opinion relates equally to the first replication of the newly originated DNAs and to the present-day DNAs and cells; a similar idea was developed in [4, 11]. We try to reveal the physicochemical grounds for the processes of origination of the LMSEs and first DNAs and cells and for the processes of replication of the present-day DNAs. This review is dedicated to the problem of living matter origination. However, in our opinion, these two

problems should be connected by a common physicochemical phenomenon. Therefore, we considered useful to throw some bridges between these two phenomena in this paper. Of course, we do not hope to guess all riddles of the physicochemistry of the origination and development of living matter but we would be lucky to go several steps ahead and to pass on the baton to the following generations of the researches.

Meanwhile, the LOH-hypothesis, apparently, proved its right to life for its twelve-year history by the fact that it was multiply published at different steps of its development in a number of physical, chemical, biological, and specialized peer-reviewed international and Russian journals and was presented and discussed at about twenty international scientific conferences. Let us present one of the opinions given in the preface of the "DNA Replication – Current Advances" open-access book by Prof. H. Seligman, its Editor [11, p. XII]. "But perhaps the most astonishing and challenging novelty in this book is the approach of DNA structure and chemical dynamics by focusing on its interactions with its natural solvent, the water molecules, and the changes in water concentrations through the cell's life cycle (chapter by Ostrovskii and Kadyshevich). This Most interesting hypothesis develops a concept that escapes conceptions established through the force of habit, which frequently result in dominant, yet unproven intuitive truths. This hypothesis will doubtlessly produce new deep insights into every level of DNA associated processes, and probably also general cell physiology, if given the deserved consideration and further developed. Physical properties at a lower scale of natural phenomena, namely the multimolecular dynamical structure of water .

This paper integrates and significantly develops our notions on the living matter origination published for the 12-year period.

V. CONCLUSION: THE FAVORABLE EVENTS AND RESULTS AND THE POSSIBILITIES OF VERIFIABILITY AND FALSIFIABILITY FOR THE LOH-HYPOTHESIS

According to the LOH-hypothesis, living matter originated as a result of the following evolution sequence (Figure 7).

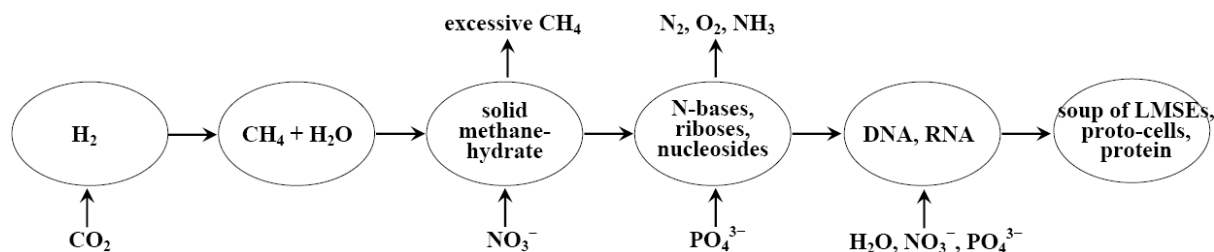


Figure 7: The living-matter origination evolution sequence according to the LOH-hypothesis.

The LOH-hypothesis indicates that DNA- and RNA-like molecules most probably formed in nature (and, maybe, continue to form at present) from only three mineral substances widespread in the Earth's crust: methane hydrate (or other simple hydrocarbons), niter (sodium or potassium nitrates), and phosphate. Nucleic acids formed in the interior of the Earth's crust within the CH₄-hydrate phase or, maybe, within the phases of hydrates of other methane hydrocarbons. N-bases and riboses can be synthesized from only two minerals, methane and niter, that are not only widespread in nature but are also deposited frequently in close proximity to each other in the Earth's crust.

It would seem that the possibility of living-matter formation within the zeolite structures should also be considered. However, had such clumsy molecules as nucleic acids actually formed within zeolites, they would have found it very difficult to make their way out. A similar remark relates also to the phosphate matrixes. Besides, the sizes of the cavities of the zeolite and phosphate matrixes do not correspond to the sizes of the LMSEs. As for the methane-hydrate matrix, things are made still easier for nature by the fact that it contains initially two sorts of atoms (carbon and hydrogen) of the five ones necessary for DNA and RNA synthesis and that it is easily soluble in excessive water or at enhanced temperatures and, thus, favors the formation of the semi-liquid super-cytoplasm soup.

An important feature of the proposed hypothesis is the possibility of its experimental verification. It is sufficient to have an abiotic autoclave, which is temperature-controlled and contains niter, water, phosphate, and pressed methane; then, the researchers should arm themselves with patience. Such an autoclave must have a pressure-relief valve and equipment that provides repeated chemical analyses of the gaseous and solid products with no effect on the reaction condition. Certainly, a number of technical problems must be solved before the experiment is undertaken, but the game is worth the candle. In our opinion, this important, rather expensive, and not simple experiment should be performed on the international basis.

Such an experiment is in principle different from the well-known experiments that were described by Miller and Urey and based on the assumption that living matter appeared on the Earth's surface as a result of one or several stochastic events initiated by electric discharges in the atmosphere. Similar experiments have been performed in many laboratories. However, the idea underlying Oparin's hypothesis was proven to be thermodynamically inconsistent. For the last 60 years, this hypothesis has failed to bring substantial progress in detailing how life originated. In contrast to this approach, we believe that living matter arose in the Earth's crust as a result of gradual and inevitable

chemical reactions between concrete simple mineral substances and that these reactions are governed by thermodynamic laws.

The above-proposed experiment aimed at the DNA formation could prove that living matter is a natural phenomenon that is obligatory inherent in atomistic world during a definite period of its development when water, methane, niter, and phosphate localizations are located not far from each other and that living matter could arise multiply.

Another problem that could be subject to the experimental testing is the possibility of the self-replication of double DNA-like molecules within the highly concentrated semi-liquid organo-phosphate aqueous systems in which DNA-like molecules could be used as the organo-phosphate substances. Apparently, this problem could be solved by the methods of organic chemistry.

The LOH-hypothesis contains a number of hypothetical issues, which could become the subjects of computer studies. A group of tasks can be put for computer simulation of rearrangement of different LMSEs and DNA- and RNA-like molecules within the hydrate structures II and H. One of the tasks that, apparently, could be accomplished on the basis of computer simulation is the clarification of the nature of the monochirality of nucleic acids. We work in this direction. The corresponding computer programs are developed by A. Dzyabchenko and preliminary encouraging results are already obtained.

Several observational and experimental data count in favor of the LOH-hypothesis. Some interesting observations are described in [129–132] and generalized in [5].

Huge colonies of prokaryotes were discovered at water depths from 427 to 5,086 m under the seabed over the entire rock layer down to 400 m (deeper drilling was not performed) in open areas of the Pacific Ocean and along the coastline of Central America; the temperature measured at the maximum depth of drilling was 299 K. The concentration of living organisms in these colonies is higher than 10⁵–10⁶ per cubic centimeter of underseabed rock and does not decrease with drilling depth. The layers that harbor bacteria contain methane-hydrate. In particular, the bacteria are found near the American continent with its large niter deposits. The authors of [131] believe that the living and dead bacteria release methane and, thus, serve as a source of methane-hydrate deposits. However, an alternative and no less plausible explanation of this discovery is also possible. We believe that the bacteria colonies formed as a result of methane-hydrate and niter interaction with formation of N-bases and D-ribose, interaction of these substances with phosphates (widespread in the underseabed layers), and subsequent origination of the cellular living matter.

Thus, in our opinion, the bacteria colonies confirm our hypothesis. A temperature of 299 K measured by the authors of [129] at the maximum depth of drilling requires a special consideration. Normally, the seabed temperature at a depth of more than 400 m is about 274 K independently of water-layer thickness; at vertical underseabed drilling, the temperature increases by 3 K per each 100 m. Therefore, the expected underseabed temperature at a depth of 400 m is 286 K. It is unlikely that the metabolism of prokaryotes would result in a substantial increase in ambient temperature. Apparently, the most probable explanation of the unusually high temperature in the zone of prokaryote activity is the heat production during the formation of DNA from mineral substrates. It is worthwhile to mention that, long before publication of [129], we predicted [133] the possibility of the living-matter origination in the regions of the Earth's ocean and mainland, where water and simplest organic and inorganic substances necessary for synthesizing cellular substances are present and where the temperature and pressure conditions are suited to hydrate formation. A similar conclusion was made in our paper [3]. Conditions in which the prokaryotes discovered in [129] exist are reminiscent of the conditions for the appearance of living matter described in our earlier publications.

Large bacterial colonies were found also under the Earth's surface at depths down to 6820 m [130]. Living matter was associated with a methane medium. Thus, living matter apparently originates and reproduces on the basis of methane-hydrate.

According to several publications (e.g., [131, 132]), the gas sampled from gas-hydrate deposits contained significant amounts of N₂ and very small amounts of O₂: 4% of N₂ and 0.005% of O₂ in [131] and 11.4% of N₂ and 0.2% of O₂ in [132]. It is seen that the ratios between the N₂ and O₂ concentrations were much higher than the corresponding ratios inherent in the atmosphere; it is obvious that N₂ could not be acquired by the samples from the atmosphere during sampling. The possible sources of N₂ formation within the Earth's crust are not numerous, and it is quite possible that N₂ was reduced from niter by hydrocarbons according to reactions similar to (3)–(5) and (8)–(10). These observations count in favor of our concept.

Note also the experimental work [134], where it was stated that the synthesis of pyrimidines from methane and urea does not go in liquid water, but goes in the water ice phase, although, it would seem that cooling should decrease the rates of chemical reactions. It is quite possible that the observed reactions were stimulated by the formation of gas-hydrate structure within the icy reaction medium.

So, presentation of the LOH-hypothesis and its validating draw to a close. The LOH-hypothesis in its present-day state consists of two sub-hypotheses of

origination of DNAs and RNAs and of origination and self-reproduction of living matter as such, both proceeding in the H₂O/CH₄/NO₃⁻/PO₄³⁻ systems and both being governed by the same natural phenomena of chemical interaction inside the gas-hydrate structure and of formation or destruction of such a structure under the effect of the water-content deficiency or excess in it, respectively. It is the only living matter origination hypothesis that is capable of being smoothly transformed into a unique physicochemical hypothesis of DNA reproduction in living cells of the present-day prokaryotes and eukaryotes. Thus, the same natural phenomenon of formation/destruction of gas-hydrate structures under the influence of variations in the concentrations of waters and guest particles in the environment can be used for explaining the both phenomena, origination of living matter and its subsequent extended reproduction. Such universality of these notions indirectly counts in favor of this hypothesis.

According to the LOH-hypothesis, the processes that led to living matter origination were associated with O₂ and N₂ evolution and, thus, influenced the composition of the Earth's atmosphere and approached it progressively to the present-day state. The main destination of the hypothesis is to try to elucidate the enigmatic mechanisms of life origination and living matter functioning. This review is focused on the first of these puzzles posed by nature.

The LOH hypothesis was initiated by experimental results that revealed the possibility of formation of water-substrate structures at about 290 K in highly concentrated semi-liquid aqueous systems that contain polymers and monomers with functional groups similar to those of biologically-active substances, including DNA and RNA molecules, and a similarity between these structures and the solid gas-hydrate structures and by the discovery of a correspondence between the sizes of N-bases and other DNA components on the one hand and the sizes of the cavities in the gas-hydrate structures on the other hand. Just the analysis of these two nontrivial discoveries led us step by step to the formulation of the LOH-hypothesis and, then, of the MRH-hypothesis. To make sure that methane-hydrate, niters, and phosphates occurred in the Earth's crust in the period of about 4000 Myr ago, when the first living organisms appeared on Earth, we developed the hypothesis of Solar System formation, PFO-CFO hypothesis [67–75], because no one of the available hypotheses satisfied us.

The LOH-hypothesis is original in terms of the physical essence, because it suggests that living matter originated in a certain geometric matrix, and in terms of the concrete content, because it considers the ability of water to form structured gas-hydrates as a condition

necessary for the emergence of the simplest living matter. It is also important that the LOH-hypothesis provides a new approach to the solution to the problem of monochirality of nucleic acids.

The LOH-hypothesis comprises the following set of key features that distinguishes it from the other hypotheses of living matter origination:

1. The process of origination of DNA and RNA molecules is interpreted as the formation of a multitude of essentially similar but slightly different polymer molecules that arose from the interaction between one solid phase and ions of one type and the subsequent interaction between the products of this interaction and ions of another type rather than as the formation of individual polymer molecules that arose from the multiple collisions between a great number of source gas or dissolved molecules of many different types and different intermediates;
2. It is suggested that living matter originated on Earth repeatedly and at different points of the planet (it is not improbable that living matter continues to originate at present) and that, in each case, the complete series of chemical interactions, from the source mineral substances to origination of a set of different cells, proceeded at the same point;
3. The composition of the source mineral substances that produced the simplest elements of living matter, nucleic acids, and divisible cells and also the ambient conditions, under which the relevant processes proceeded, are specified;
4. The possibility of the experimental and computer verification of the hypothesis is one of its important features.

The LOH-hypothesis allows an entirely new explanation for the chiral purity of DNA, RNA, and their derivatives: the chiral purity of nucleic acids is a consequence of the effect of the geometry of the matrix in which they were first molded in nature and have continued to reproduce themselves in each newly formed cell of living matter.

The LOH-hypothesis is capable of explaining the occurrence of numerous prokaryotic and eukaryotic species without resort to Darwin's hypothesis on interspecific variations and natural selection as the leading causes of the species diversity of the prokaryotic and eukaryotic living matter. This is an important feature of our hypothesis. The fact is that Darwin's evolution hypothesis is confirmed neither by the experiments with rapidly reproducing species nor by geologic studies; the lack of successes of the evolution hypothesis is used by creationists in their criticism of the materialistic ideology.

Let us note one possibility that might seem for somebody as an idle fancy. The point is that, apparently, a combination of CH₄, niter, phosphate, and water

represents the simplest set of nutrients to maintain life for some organisms at definite low temperatures. By varying the temperature and nutrient composition, the rates of the metabolic processes can be decreased manifold and regulated; therewith, the waste can be minimized. It cannot be excluded that the cellular life could be prolonged due to deceleration of cellular division and that, after a time, the usual rate of the cellular metabolism can be restored by returning to the usual nutrient and conditions. In our opinion, this is an interesting theme for studies, which could be used for verification of our hypothesis.

At the end of the paper, we note that laconism is one of the important features of the LOH-hypothesis. Only two substances enter the widely-distributed matrix and all reactions that are necessary for formation of a plenty of different DNAs and RNAs originate in one localization. Somewhat later, a multitude of cells that are different in the N-base sequences but similar in the elemental composition and structure originate in the same localization. The repetition of thus processes is provided by the abundances of the methane-hydrate matrixes and niter localizations and almost ubiquitous occurrence of phosphates on the Earth. The monochirality is provided by the occurrence of the matrix. It is unlikely that another so laconic hypothesis for so complicated phenomenon could be formulated. Meanwhile, a lot of authoritative philosophers wrote in different epochs that laconism is very desirable in William Occam wrote: "It is vain to do with more what can be done with less". Later, Isaac Newton wrote that "Nature is simple and does not luxuriate in excesses". We are with them. It is generally recognized that this thought expressed in different forms is useful in theology, religion, and science.

The laconism of the LOH-hypothesis and the possibility of applications of the same physicochemical phenomenon of the hydrate structure formation/destruction for explanations of the living matter origination and of the DNA replication, give us grounds for optimism.

VI. ACKNOWLEDGMENT

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