

# Generalized hypothesis of the origin of the living-matter simplest elements, transformation of the Archean atmosphere, and the formation of methane – hydrate deposits

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**Abstract.** The original hydrate hypothesis of the origin of living-matter simplest elements (LMSEs), i.e., the ‘Life Origination Hydrate hypothesis,’ abbreviated as the LOH hypothesis, is discussed. It includes notions of the interdependence and interconditionality of processes leading to the life origin, to the transformation of the primary atmosphere, and to the underground methane–hydrate formation. Saturation of the young earth's crust with nebular hydrogen is taken into consideration for the first time. The origin of LMSEs is regarded as a result of regular and thermodynamically caused inevitable chemical transformations and of the universal physical and chemical laws. According to the LOH hypothesis, LMSEs originated repeatedly and, maybe, are now originating from methane (or other simple hydrocarbons), niter, and phosphate within boundary layers of the solid phases of the hydrates of the simplest hydrocarbons. It is assumed that the phenomenon of monochirality of nucleic acids is caused by geometric features of the structure matrix.

## 1. Introduction

The processes that gave rise to life could not obey biological laws because they proceeded in the absence of biota. Hence, the origin of life is first and foremost a problem of physics and

many related scientific disciplines concerned with mechanisms underlying the development of the atomistic world.

Vitaly Ginzburg, who was awarded the 2003 Nobel Prize, described the problem of the “reduction of the animate to the inanimate” in his Nobel lecture [1] as one of the three great physical problems facing the 21st century. In a recent futurological article [2], he formulated this thought in the following words: “At present, we believe that we know what all alive consists of, meaning electrons, atoms, and molecules. We are aware of the structure of atoms and molecules and of the laws governing atoms, molecules, and radiation. Therefore, the hypothesis of reduction, i.e. the possibility of explaining the life on the basis of physics, the already known physics, is natural. The main problems are those of the origin of life and the appearance of consciousness (mentality). The problem is not solved, and I am inclined to think that it will be unreservedly solved only after ‘life in a test-tube’ is created.”

We propose an original solution to the problem of the origin of living-matter simplest elements (LMSEs), i.e., N-bases and riboses, and of nucleic acids that ensure the protein synthesis and transmission of major traits of living organisms from one generation to another. Our Life Origination Hydrate hypothesis (LOH hypothesis) is based on the assumption that living matter resulted from thermodynamically conditioned, natural, and inevitable chemical transformations governed by universal physical and chemical laws. Immanuel Kant contended that “To get knowledge from nature, the Mind should address to it, on the one hand, with his own principles, which are necessary for concordant phenomena to carry the force of law, and, on the other hand, with experiments intended in conformity with these principles.” [3, pp. 85, 86]. With this in mind, we describe an experiment that can be used to verify our hypothesis if it is reproduced by several laboratories in a coordinated manner with the experimental conditions varied within a certain range. If the hypothesis proves

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valid, this experiment may yield precursors of nucleic acids and possibly DNA-like molecules. It can be expected that the LOH hypothesis will contribute to the realization of the cautious prediction by Ginzburg [2], who noted that he ‘would not be surprised if ‘life in a test tube’ would be created in the 21st century.’”

We first clarify our understanding of the borderline between the animate and inanimate. There is no consensus with regard to this issue. For example, Oparin believed that life development started with the appearance of nucleotide sequences (nucleic acids) when the process of chemical evolution as the struggle among protobionts was coming to an end and competition in the growth rate turned into the struggle for existence [4]. Spirin maintains that “the origin of life in its present cellular form is reduced to the development of a mechanism of heritable protein synthesis” [5], but leaves the problem of acellular life beyond this definition. Galimov calls adenosine triphosphate “molecule No. 1 on a path leading to the origin and evolution of life” [6, p. 215]. In the late 19th century, Friedrich Engels defined life as “the form of existence of protein bodies.” Nucleic acids were unknown at that time, however, and Shnol’ regards this definition as outdated [7].

The problem of the border between the animate and inanimate is far from vain even if its discussion may seem to make no concrete sense. Drawing the line between the animate and inanimate determines the interpretation of viruses (DNA molecules containing genetic information and enclosed in a protein membrane), viroids, and prions (membraneless DNA molecules) as subjects of biological (including biophysical) or organic and physico-chemical studies. This problem has been discussed since 1935 when Stanley pioneered isolation and crystallization of the tobacco mosaic virus. Pauling summarized the situation as follows: “in fact, there is 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” [8].

We emphasize that Pauling’s opinion is not faultless in the light of modern knowledge. It has been many times demonstrated in the past 10 to 15 years (see, e.g., [9]) 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 nonutilized molecular residues. Should we call such a process ‘metabolism’? No reasoning can answer this question, similarly to the question of where the snake’s tail begins; the answer can be deduced only from the practice of using the term. Today, viruses and even viroids and prions 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 precellular life. Such a demarcation between the animate and inanimate is especially logical because, as noted by Kauffman [10], complex organic systems such as DNA and RNA inevitably become self-replicative and their self-replication proceeds

through an autocatalytic mechanism. 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.

Apparently, once nucleic acids had 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. It follows from the foregoing that in our terminology, DNA and RNA are the simplest forms of precellular living matter, while N-bases and riboses are its simplest elements or constituents. We consider it appropriate to expound and substantiate our understanding of the border between the animate and inanimate, bearing in mind the definition of physics by Kant as the theory field that should perceive natural objects by mind and that should determine them *a priori* and “purely, at least partially, and then should do it also on the basis of knowledge sources other than the mind” [3, p. 84].

## 2. Background

The processes that gave rise to LMSEs, the earth’s atmosphere, and deposits of methane hydrate and other hydrocarbons are three fundamental puzzles of nature that many researchers have tried to solve from different standpoints. We put forward the LOH hypothesis that suggests a common mechanism and common chemism of these three seemingly dissimilar processes. This hypothesis was prompted by experimental studies [11, 12] and analysis of the literature on DNA–water systems [13], the early history of the earth, and the origin of living matter; it was further developed in Refs [13–16]. The proposed mechanisms of gas hydrate formation in the interior of the earth and the transformation of the primary hydrogen–helium atmosphere into the oxygen–nitrogen one is not the sole option. We do not exclude the possibility of the contribution of other mechanisms to the development of the above processes.

An attempt to solve the three puzzles simultaneously in the scope of one review may look overambitious, but on the other hand, the attempts to artificially create living matter from an inanimate substance may have failed just because the origin of life has thus far been considered without regard for other global processes. In connection with this, it is worth recalling what Joyce stated over 15 years ago: “The question of life’s origin is one of the oldest and most difficult in biology. The answer, if it is ever known will not be a single statement of fact but rather an extended chronology, beginning with the formation of the earth and ending with the appearance of cellular organisms” [17].

Today, opinions differ as regards the origin of the simplest elements of living matter, N-bases and riboses, and their subsequent transformations that resulted in the formation of nucleic acids. The absence of consensus hampers the development of a common understanding of the conversion of inanimate matter to animate matter.

Oparin [4] suggested one of the earliest scientific hypotheses to explain the origin of living matter. According to him, nature first created protein and thereafter ‘taught’ it to replicate; the processes that contributed to the formation of living matter consumed mineral substances from the interface between condensed phases and the earth’s gaseous atmosphere. Oparin described the development of the first

unicellular organisms as a sequence of the following evolutionary events:

the simplest organic substances in the atmosphere and in the ocean → protein precursors in the ocean → proteins in the ocean → organized hydrophilic protein bodies (coacervates) containing polynucleotides and polypeptides and enclosed in an aqueous membrane → living matter capable of metabolism → unicellular organisms in the ocean and their exodus from the sea to become land creatures. (1)

Later investigations showed that the long-term action of electric discharges on the  $\text{H}_2\text{O}-\text{CH}_4-\text{NH}_3-\text{H}_2$ -atmosphere may give rise to various amino acids (these studies were initiated by Miller and Urey [18, 19]); certain amino acids and N-bases were synthesized in aqueous solutions of  $\text{NH}_3$  and HCN (see, e.g., [20, 21]). But the strength of electric discharges per unit volume in these experiments was very large compared to that supposedly realized in the Archean atmosphere of the earth. Moreover, the composition of that atmosphere may have been quite different from the experimental one used by Urey and Miller; the same is true of the composition of Archean seas simulated by liquid media in experiments by Oro, Kamat [20, 21], and other researchers. At present, scientists agree only that the gaseous component of the gas–dust nebular cloud was largely composed of hydrogen and helium and that primitive living matter appeared on the earth some 3.8–4 billion years ago. At the same time, the majority of researchers do not reject the possibility that the interface between the earth's surface and atmosphere of the Archean may have been the medium for the synthesis of various compounds containing N, C, P, O, and H atoms.

Discussion in the literature also concerns other sources of organic substances on the young earth's surface, such as chemical reactions initiated by subterranean perturbations, collisions of the earth with various celestial objects (comets, meteorites, etc.), solar UV radiation or chemical reactions in hydrothermal media. The results of many discussions are summarized in Refs [22–25]. According to Galimov [6, p. 100], the key molecules utilized for the formation of living matter were adenosine triphosphate (ATP), synthesized in nature under the effect of solar radiation from adenine, ribose, and phosphates. Galimov suggests the following chemical mechanism for ATP formation. Each adenine molecule resulted from condensation of five molecules of cyanic acid that had in turn been synthesized under the effect of radiation in the aqueous medium containing compounds with C, H, and N atoms. Each ribose molecule was produced as a result of condensation of five formaldehyde molecules that had been synthesized under quite different geochemical conditions than cyanic acid: specifically, in the reduced atmosphere of gases containing C, H, and O. Cyanic acid and formaldehyde did not contact each other (their contact would lead to the formation of cyanohydrin) until the condensation processes were completed and adenine in the atmosphere and ribose in the aqueous medium formed. Thereafter, ribose combined with phosphate and the resulting ribosophosphate reacted with water-soluble adenine, yielding ATP.

In the early 1960s, a meteorite found near Orguel was reported to contain traces of organic matter [26, 27]. Further studies of this meteorite gave rise to the so-called panspermic hypothesis maintaining that living matter on our planet has an extraterrestrial origin. Investigations carried out in the

framework of this hypothesis are summarized in Refs [28–30], whose authors advocate the concept of panspermia.

An original idea was suggested by Gold [31]. This author argues that life originated deep (many kilometers) in the earth rather than on its surface, and the primary living matter did not experience the effects of solar radiation or other factors operative in the overlying strata. According to Gold, subterranean life was supported by energy sources in the form of fluids arising from deeper layers of the earth's crust. This idea was confirmed by investigations [32, 33] that demonstrated the presence of underground deposits that could not form in the absence of bacterial activity. But the authors failed to identify living matter, and it was accepted that these deposits are actually remnants of living organisms that had lived on land or at the sea bottom in by-gone times and were later buried in the bowels of the earth by some geological cataclysms.

It was shown in the 1980s that RNA displays catalytic activity in biological systems [34, 35]. These works laid ground for the hypothesis of the primary role of RNA in the development of living matter (so-called RNA World) [35] that incorporated DNA of unknown origin at a certain stage of evolution and has never let it go since then, using it as a transmitter of genetic information. In a few years, the model of autocatalytic replication of RNA was formulated [36]. The RNA World concept was also developed in Refs [17, 37–39]. Orgel with collaborators [9, 40] and other authors (e.g., [41]) showed that enzymes are not indispensable for replication of various organic molecules. Results of the verification of the RNA World hypothesis gave Orgel reason to propose the existence in the past of a biological world without DNA, in which RNA molecules functioned as both genetic material and enzyme-like catalysts [42].

This concept is supported by Spirin with the reservation that the literature offers no hypothesis ideally describing physico-chemical processes that have led to the development of the currently accepted mechanism of protein biosynthesis in the RNA World. Based on his own experience with RNA studies and that of other authors regarding the RNA World as the forerunner of present-day life, Spirin suggested a new variant of this hypothesis focused on its two key postulates. First, abiogenically synthesized oligoribonucleotides actively recombined via a spontaneous nonenzymatic trans-esterification mechanism [43] giving rise to long chains of various RNA. Second, the development of the mechanism of enzymatic (polymerase-dependent) replication of genetic material (RNA and DNA) was preceded by the formation of the primary apparatus for protein biosynthesis based on a few specialized RNA species. It is supposed that “this primary apparatus included catalytic proriobosomal RNA possessed of peptidyl transferase activity; a set of pro-tRNAs specifically binding amino acids or short peptides; another proriobosomal RNA simultaneously interacting with catalytic proriobosomal RNA, pro-mRNA, and pro-tRNA” [5]. However, Spirin notes that the RNA World hypothesis will be difficult to validate so as to overcome the main difficulty, plausibly describing the transition from RNA replication to protein synthesis.

As we have noted, Spirin believes that the inanimate-to-animate transformation became possible after the formation of an inheritable protein synthesis mechanism governed by nucleic acids by means of programming the composition and specificity of the produced proteins and by ensuring reproduction of this program in consecutive generations.

It seems that self-replication is not a unique property of DNA and RNA. According to Kauffman, self-replicability is an inherent property of systems that reach a certain critical level of complexity and is governed by an autocatalytic mechanism [10]. This inference implies that the ability to replicate is not the main characteristic that distinguishes nucleic acids from many other polymers.

There are a few long-known enigmatic aspects of living nature that might very likely give clues to the mystery of the origin of life if they did not elude clarification. These are the optical activity of bioorganic substances discovered by Pasteur [44], the dextral coil of almost all mollusk shells (mentioned by Jules Verne in 20,000 *Leagues Under the Sea*), and the existence of highly developed organisms under an almost 11 km-thick water layer (some 40 years ago, aquanauts D Walsh and J Piccard found fish, shrimp, and mollusks in the near-bottom layer of the Mariana Trench [45]; these organisms must have an internal pressure in excess of 1,000 atm).

Many authors considering the problems of the origin and evolution of living matter have used physical and mathematical methods. Their works have given a number of important and interesting results; some of them are cited below.

Investigations into the origin of the optical activity of biological objects showed that none of the DNA, RNA or enzyme structures has a mirror symmetry (neither a symmetry plane nor a symmetry center, like the human hand). All these structures are monochiral (i.e., composed of molecules of a single mirror antipode); specifically, DNA and RNA consist only of right-hand nucleotides (all their riboses have the D-configuration) and enzymes only of left-hand amino acids (all of them have the L-configuration). Authors of dozens of studies have tried to understand how bioorganic compounds acquired monochirality in the course of evolution in order to use this knowledge as Ariadne's thread (the metaphor is borrowed from [46]) to bring to light the prebiotic stage of molecular evolution. Interesting reviews of these studies can be found in [46–48].

Avetisov and Gol'danskii [46] categorize all scientifically grounded approaches proposed for the explanation of monochirality of biological substances into two groups. One includes studies postulating the primary origin of achiral LMSEs that, for an unspecified cause and by an unknown mechanism, gave rise to monochiral LMSEs in the course of evolution; later, monochiral LMSEs became prevalent 'in all spheres.' The other group comprises studies arguing that the LMSE symmetry was broken at the prebiological, i.e., chemical, stage of evolution, while monochirality first appeared at the stage of polymer synthesis, in other words, in the prebiological epoch.

This striking property of living matter has been attributed to a variety of causes, including the fundamental asymmetry of the universe and weak interactions responsible for beta-decay of atoms [49], augmentation of minor differences between reactive activities of various mirror isomers by large-scale chemical systems [50] (see [51] for this idea), and kinetic properties of autocatalytic processes governing evolution [52]. Frank [53] suggested the possibility of the simultaneous birth of two branches of antipodal chirally pure life and the subsequent death of one of them. Avetisov and Gol'danskii [46] considered this idea and arrived at the conclusion that the existence of an asymmetric biota as a result of the 'struggle for survival' between the two branches of antipodal life should be considered natural rather than paradoxical.

Ten years ago, Avetisov and Gol'danskii concluded their paper [46] with an observation that "this issue needs to be addressed in future studies." Since then, Ariadne's thread has remained unwound. The common opinion may be summarized as follows. First, monochirality could hardly develop from the fight between alternative tendencies because it seems improbable that a single tendency could prevail in all spheres, from prokaryotes to mammals and from underground and underwater to terrestrial forms, many of which only weakly interact with one another. Second, the relation between some of the above models and the living matter as a terrestrial phenomenon is too complicated to be correct. We believe that a certain simple and rigorous (most probably, geometric matrix) mechanism of selection must have existed at the very beginning. The LOH hypothesis suggests such a mechanism, although we refrain from drawing a definitive conclusion until relevant experiments are carried out. Even if our concrete suggestion proves wrong, template matching appears to have been the most likely instrument used by nature to select identical enantiomers.

Some authors postulate a relationship between processes occurring in biological phenomena and the variation of weak electromagnetic fields in the circumsolar space [54]. Publications reviewed in monograph [55] offer interesting considerations with regard to the evolution of enzymes, other subcellular organelles, and cell-to-cell interactions, including those in the nervous system.

Lindenmayer [56] was a pioneer of the application of the fractal method [57] for the description of intracellular processes. The main theorems of fractal geometry were proved almost 100 years ago. This mathematical method is employed in biology to describe transformations of structural entities formed by specific spatial patterns [58].

An important result having major implications for the discussion of the origin of life was obtained by Blumenfel'd [59, 60] based on a simple generalized physical approach. Blumenfel'd writes: "Almost any book on theoretical biology and physics mentions surprising regularity of biological structures at all levels from macromolecules to man. Reasoning on antientropic trends in the animate world and antientropic nature of biological evolution has become a common place not only among biologists but also among philosophers and physicists. In physics, there is only one quantity, entropy, characterizing the degree of order." Blumenfel'd quantitatively assessed changes in entropy associated with the appearance of biological organization unambiguously demonstrated that all speculation about antientropic tendencies in biological evolution stem from misunderstanding and that "in compliance with physical criteria, any biological system is no more ordered than a piece of bedrock of the same weight."

An impression of the marked regularity of biological structures results from the fact that information contained in living nature makes 'sense'; in other words, these structures have the so-called 'meaningful order' [61]. For example, a DNA dimer of a given composition placed in a certain medium under certain conditions is capable of replication giving rise to an identical dimer. Blumenfel'd tried to formulate a hypothetical scenario of the formation of a meaningfully ordered DNA-like construction at the early stages of prebiological evolution based on the purely physical methodology of Kestler. In book [62] finished shortly before his death, Blumenfel'd arrived at the conclusion that this is impossible to do in the framework of the known physical laws

and principles. He prefaced the relevant chapter with the following epigraph, citing the words of Timofeev-Resovsky: "This thing (life) was invented and started by the Lord, but then He busied Himself with other doings and let the rest take its own course." The chapter ends in the following observation: "Animate machines, like inanimate ones, must be designed and constructed in accordance with an existing plan" [62]. We dare to supplement Blumenfel'd's inferences with a remark that inanimate nature also gives numerous examples of surprising 'order' (suffice it to recall amethyst crystals in hollow boulders, garnet druses, huge regularly shaped stone structures in the Negev Desert, etc.) and 'sense' (e.g., a crystal facet imparts its structure to a film of another substance deposited on it). Thus, neither 'order' nor 'sense' is a unique property of living matter.

It is beyond the scope of this review to comprehensively expound current views of the mechanisms, chemical nature, and physical principles of the origin of living matter; indeed, it would be impossible to combine such a goal with the substantiation of a new hypothesis in a single paper. But we hope that the variety of hypotheses discussed in preceding paragraphs illustrates by itself the absence of consensus. We are also aware that the publication of any new hypothesis in such a situation fans the flames, but it is the flame that must eventually give birth to the Phoenix. Let our hypothesis be a fan: we shall be content if it speeds up the solution of the great puzzles of nature. Contrary to the opinion expressed in [62], we believe that nature 'acted by guess-work' rather than implemented someone's 'plan,' but the mode of its actions was predetermined by a starting point and universal physico-chemical laws. We are sure that the composition of that clay from which everything is molded will be determined and the very first stages of life reconstructed.

Unfortunately, only the hypothesis by Oparin of all those proposed thus far lends itself to experimental verification in terrestrial conditions. During the last 50 years, its different variants have been tested in numerous studies in which organic substances were obtained containing atoms of carbon, nitrogen, oxygen, and hydrogen. But no appreciable progress has been made in the understanding of the mechanism and the chemical nature of events that led to the synthesis of nucleic acids capable of replication and producing living cells. Processes underlying the formation of N-bases and riboses, constituents of DNA and RNA, remain as enigmatic as ever; it remains absolutely unclear how molecules of four different N-bases happened to be in one place at the same time, or why they came to interact and give rise to orderly linear polymeric chains composed of regularly arranged monomers with uniformly located side branches 'attached' to these chains in a different sequence.

The general structure of our hypothesis of the origin of LMSEs and their subsequent transformation towards multicellular living entities contains three heuristic elements. One is the postulate that nature must have a certain three-dimensional matrix as its intrinsic property with cavities of different sizes corresponding to the size of functional groups in DNA and RNA molecules; the matrix is able to simultaneously form many such molecules. This matrix must have been repeatedly replicated in nature; it was strictly determined and at the same time slightly variable depending on the surrounding conditions. The second element of the hypothesis is the assumption that matrix cells initially contained certain atoms that in the course of time turned into constituent components of newly formed polymeric mole-

cules. In other words, it is assumed that a certain half-product existed at the very beginning (we have specified this product and suggested a hypothesis of its formation). This problem is akin to those problems that physicists address in terms of fractal geometry, and nature has solved it. The third element consists of the monochirality intrinsic in living nature being dictated by the geometry of the matrix on which nucleic acids are formed.

The main principles of the LOH hypothesis are expounded in Refs [13–16, 63]. The chemical processes that constitute its basis occur rather deep in the earth's crust. Following Gold [31], we consider the problem of LMSE origin in the geological context. But the physical and chemical substance of our hypothesis differs from Gold's reasoning. Specifically, we think that the motive power of the processes responsible for the appearance of LMSEs was a change in the Gibbs free energy resulting from these processes rather than the thermal energy of fluids ascending from deeper crust layers. Also, we assume that LMSEs formed inside a crystal matrix and specify the initial substances from which LMSEs might originate, as well as conditions under which the relevant processes were likely to proceed.

The present review summarizes and further develops our views on the mechanism and chemical nature of LMSE formation and possible modes of their conversion to nucleic acids and eventually to living matter capable of metabolism. In the context of these views, we consider the putative processes of the formation of hydrated hydrocarbons in the interior of the earth and the processes that contributed to the transformation of the hydrogen–helium atmosphere into the nitrogen–oxygen atmosphere at the prebiotic stage of the earth's existence. We were the first to notice that the young earth had been 'soaked' with nebular hydrogen, presumably adsorbed on nebular dust particles and conglomerates of which the earth was being formed, and described the possible role of hydrogen in the development of living matter. It may be assumed that incalculable amounts of hydrogen are still accumulated in the bowels of the earth and continue to strongly influence geophysical and geochemical events on our planet. The LOH hypothesis expounded below is confirmed by literature data and original thermodynamic calculations.

The LOH hypothesis, the subject matter of this review, encompasses other problems, which necessitates their consideration in connection with the substantiation and discussion of the proposed mechanism of the origin of living matter. We emphasize that the LOH hypothesis offers a definitive answer to the question of 'primacy' of DNA or RNA; we believe that DNA and RNA came into being simultaneously within the same places and that such places have been numerous during the earth's history. According to our hypothesis, living matter appeared in the following sequence of events:

deposition of solid precursors of N-bases and riboses in the earth's crust → precursors of DNA and RNA molecules (N-bases, riboses, and phosphates) → precellular nonreplicative DNA, RNA, and amino acids in the earth's crust → living matter capable of replication in the crust → unicellular organisms and their transport to the oceans and the earth's surface. (2)

Our hypothesis postulates that DNA and RNA were the first to appear, followed by proteins [not in the reverse order,

see (1)]; DNA and RNA synthesis was preceded by the formation of N-bases and riboses; LMSEs and nucleic acids were formed in the earth's crust in the solid phase; and each synthetic event gave rise to many DNA and RNA species of different composition but similar structure dictated by the structure matrix. Nature proceeded from simple to complicated and did not squander its resources on trifles when realizing its 'cherished dream' of creating life; that is, it rejected molecules that the sun or Zeus offered one after another. We think that the proposed sequence (2) of formation of life's precursors is universal; this means that if carbon-based living matter ever existed on other planets besides the earth, it was produced via the same sequence of processes. One of the distinctive features of our hypothesis is the possibility of experimental verification of its principal conclusions with regard to the mechanism of formation of the simplest elements of living matter and its close relation to the mechanism of the formation of the earth's atmosphere.

The following basic premises are laid in the foundation of our hypothesis:

(1) Living matter presently existing on the earth originated on our planet rather than elsewhere in the universe. It developed from the simplest inorganic and organic mineral substances as a result of inevitable thermodynamically predetermined chemical processes and general physico-chemical laws, as opposed to random events and essentially nonequilibrium processes, such as electric discharges and the like. We do not reject the possible important role of mutations, but believe that living nature repeatedly came into being and may be originating at present at those sites of our planet where the necessary starting mineral substances and favorable conditions for their transformation are available.

(2) According to the current cosmogonic hypotheses, Earth's primary atmosphere was largely composed of hydrogen and helium similar to the known 'atmosphere' (photosphere) of the sun.

(3) Metamorphoses in nature occur in the simplest mode. Isaac Newton wrote that "Nature does nothing in vain, and more is in vain, when less will serve; for Nature is pleased with simplicity, and affects not the pomp of superfluous causes" [64].

We are of the opinion that the most concise formulation of a hypothesis gives it the best chance to be correct, even though we realize that some readers may think otherwise. For example, Galimov argues that "despite the remarkable inventiveness of nature in creating intricate biological mechanisms, their analysis indicates that almost each given result could be achieved by a simpler means" [6, p. 218]. Nevertheless, most physicists believe that a laconic hypothesis is the best one, as the majority of chess-players think that the simpler a move, the more beautiful it is.

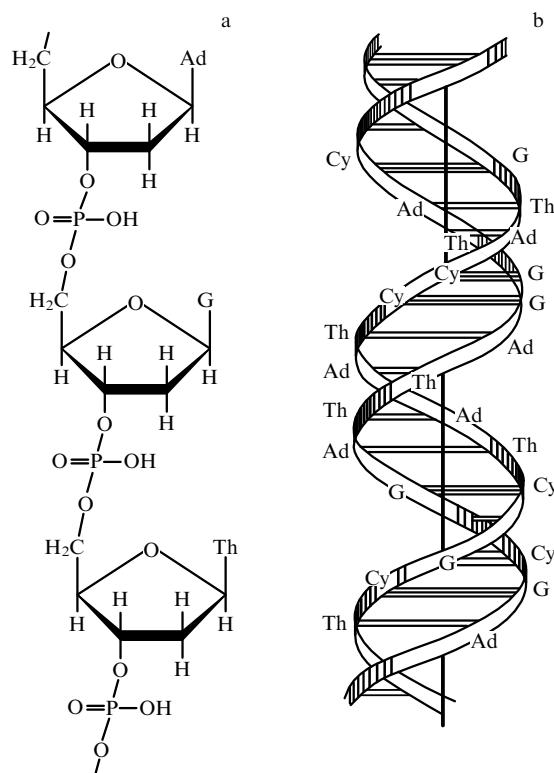
### 3. Hydrate hypothesis of the origin of the simplest elements of living matter

#### 3.1 Preliminary remarks

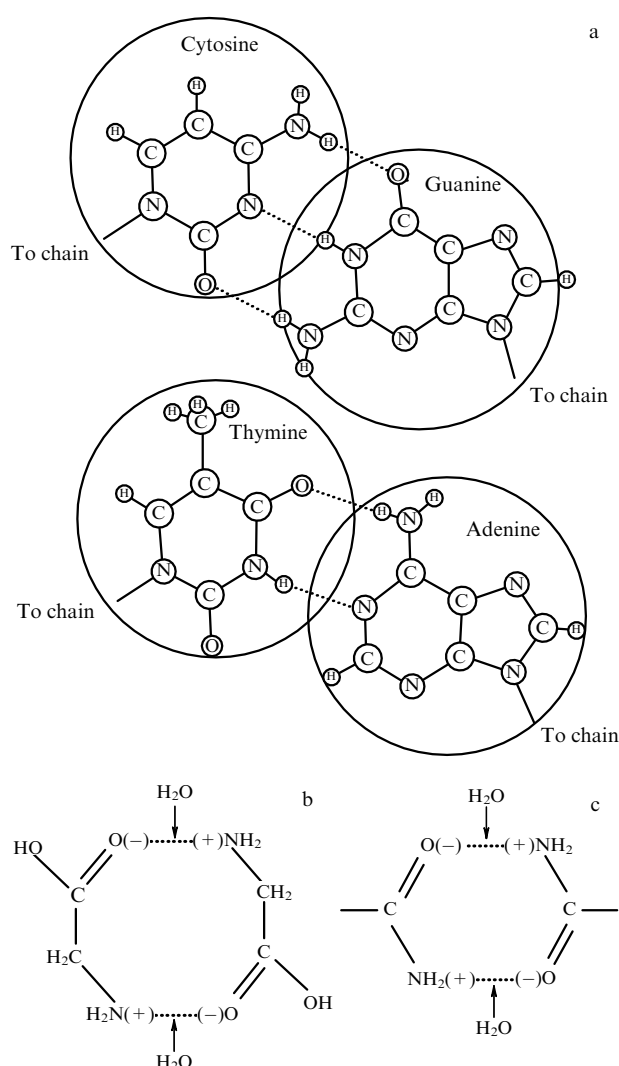
DNA molecules responsible for the reproduction of the diversity of the plant and animal kingdoms, i.e., inheritance of traits, are very similar in terms of chemical composition and structure. Only a few details are different in individual species, but it is these minor differences that determine whether molecules of DNA give birth to a bacterium or a human, a palm or an octopus. We consider the overall

similarity of the main chemical and structural features of DNA supporting the development of the existing plant and animal species (and viruses) as evidence that 'prototypes' of different DNA molecules formed under similar conditions. In other words, natural parameters (temperature, pressure, composition of the medium, gravity, etc.) characterizing these conditions remained constant over a rather long time. On the other hand, a great variety of structural peculiarities and chemical compositions of DNA molecules that are readily apparent despite their general similarity may be attributed to the fact that these parameters could be somewhat different in individual regions where the primary molecules of DNA were synthesized. Moreover, these parameters could not remain unaltered infinitely long in the gas phase or at the interface between phases under the effect of weather and radiation-related factors, or dynamic and other processes. Therefore, we conclude that primary molecules of DNA most likely formed inside a condensed phase, either liquid or solid.

Figures 1 [65] and 2 demonstrate the structure and basic chemical composition of DNA molecules. Each of them is a linear polymer of identical links called nucleotides and composed of the five lightest metalloid elements: H, C, N, O, and P; all atoms except H are tightly bound to one another and do not dissociate in aqueous media. Figure 1a presents a three-nucleotide fragment of DNA. Each nucleotide contains one phosphate group, one ribose, and one N-base. Each DNA molecule basically consists of four N-bases: adenine (Ad), guanine (G), cytosine (Cy), and thymine (Th) (the fragment in Fig. 1a contains Ad, G, and Th). N-bases are planar. DNA strands usually pair with each other, i.e., form double helices. One such helix is schematically shown in Fig. 1b; it can be seen that paired strands are bound by nonvalent (the so-called hydrogen) bonds between their



**Figure 1.** Fragment of a single molecule (a) and schematic of a double helix formed by two DNA molecules (b).



**Figure 2.** Scaled schematic representation of pairing between N-bases of two DNA molecules in the double helix structure (a); scaleless schemes of pairing between glycine (b) and polyacrylamide (acrylamide) (c).

N-bases. The diagram in Fig. 2a shows to scale the chemical composition and structure of N-bases along with hydrogen bonds between them (dotted lines) in double helices (the meaning of the circles is explained below).

We believe that such polymer molecules with periodically located substitutes could form only inside the earth's condensed phase, with its most stable conditions compared with the atmosphere, or at the interface between the condensed phase and the atmosphere. Moreover, their formation was possible only during direct contact between a minimal number of initial geological phases (rather than individual molecules) of different chemical composition and when reciprocal diffusion of the reacting phases was slow enough to allow the establishment of thermodynamic equilibrium at each step of attachment of the next link. The attachment of a new atomic group would not have been so clearly selective if excessive reactant of a different chemical nature had been present in the immediate proximity to the growing polymer chains. Evidently, the mobility of DNA (and RNA) molecules that 'arose' (and may still be 'arising') from simple mineral substances had to decrease as the molecules grew in size. Moreover, their regular growth would have been difficult to maintain if they had moved in

space because each molecule would have 'entangled' itself (the functional groups of N-bases being bipolar and tending to bind to one another in a disorderly manner). Finally, a single molecule like a nucleic acid miraculously formed at the interface between phases or even in a diluted aqueous solution would for the same reason have immediately rolled itself up into a ball, which would hamper further dimerization and replication. All this suggests the advantage of paired molecule formation.

Therefore, it is assumed in the LOH hypothesis that DNA molecules first formed in the condensed phase from only two starting substances and the resulting 'half-products' remained in place to interact with a third substance that diffused into their phase; this process proceeded parallel to polymerization. We think that DNA (and RNA) of all modern species, as well as the amino acids needed for the formation of primary living matter, arise largely from three types of initial mineral substances (usually containing minor admixtures in their natural deposits). To further simplify the work of nature, we assume that all these processes occur in a common solid natural matrix where nothing interferes with pairing between DNA molecules. 'Eureka!' exclaims the reader, 'Natural ceolytes!' He is wrong, however. Had such clumsy molecules as nucleic acids actually formed inside ceolytes, they would have found it very difficult to make their way out. Things are made still easier for nature by the fact that the matrix in which DNA and RNA molecules are supposed to have formed initially contained two sorts of atoms (carbon and hydrogen) of the five necessary for DNA and RNA synthesis. Finally, the LOH hypothesis allows an unexpectedly simple and experimentally verifiable assumption about the nature of the monochirality of DNA and RNA molecules.

Life as we know it, both vegetable and animal, cannot exist without water. There is no case of mitosis, either natural or artificial (experimental), in a waterless medium. The majority of living organisms are composed of more than one-half water (for example, the human body consists of 65–70% water, while the content in jellyfish amounts to 95%). It is therefore natural to suppose that primary elements of living matter originated in water or in a very moist medium.

To understand how inorganic and the simplest organic substances of inanimate nature of the Archean might have given rise to complex organic molecules (life's primary elements) in the aqueous medium, it is necessary to know properties of the water–mineral matter system. Specifically, it must show a property facilitating the needed arrangement of atoms and atomic groups among water molecules, maintenance of this arrangement in time, and interatomic interactions leading to the formation of multiatomic particles of strictly defined composition, structure, and size.

The sole property meeting these requirements seems to be the ability of water ('host') molecules numbering 20, 24 or 28 to form regular dimensional structures of quasi-spherical cavities when the liquid contains 'guest' atoms, molecules or atomic groups having the size of these cavities. The resulting compounds are called gas hydrates because they were first discovered as products of water interaction with some inert gases. It is noteworthy that only the size of 'guest' particles is important for the formation of gas hydrates, whereas their chemical nature is inessential. Gas hydrates were first obtained and comprehensively studied as solids, although it is quite possible that structures corresponding to gas hydrates may also be present in unperturbed fluid systems at low temperatures, at least in the short-range order form.

Mentioning gas hydrates brings to mind one more important property of DNA structure that we first noticed in [13]. The diameter of the disks shown in Fig. 2a is 0.69 nm. It can be seen that N-bases building up the DNA molecule are rather densely packed inside a disk of this diameter [uracyl (U) present in RNA molecules, instead of thymine in DNA molecules, obeys the same rule]. In other words, there is a certain ‘mould’ in which N-base molecules are ‘shaped’ from a variety of sequences of H, C, N, and O atoms before they are fastened to the growing molecule of DNA or RNA.

In the LOH hypothesis, the role of such moulds is played by large cavities of crystal structure II of gas hydrates, which is widespread in nature (see, e.g., [66–69]). The disks in Fig. 2a correspond to the sizes of large cavities formed by water molecules in the gas hydrate structure (the so-called structure II). The size of large cavities in structure II exactly corresponds to the size of N-bases Cy, G, Th, and Ad (the same applies to U).

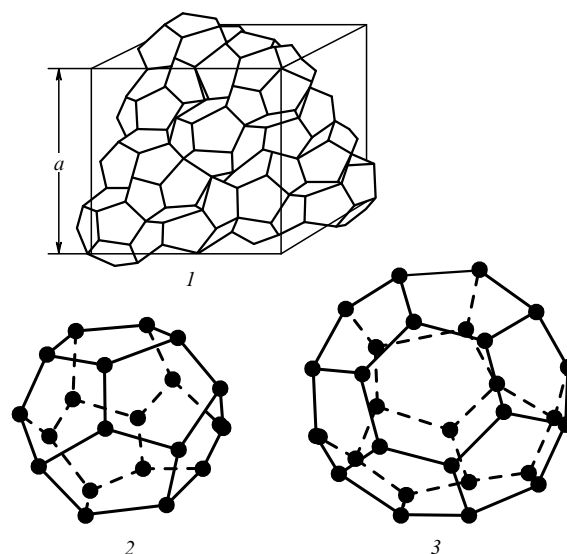
The size of phosphate (three-dimensional) groups corresponds [13–15] to the size of small cavities of hydrate structure II. Figure 3 shows to scale the structure of one such group enclosed in a disk whose diameter corresponds to the size of small cavities of hydrate structure II (0.48 nm).

Moulds for D-ribose, as for N-bases, are large cavities of hydrate structures. Ribose is slightly bigger than a phosphate group but much smaller than an N-base. There is little doubt that ribose may be enclosed in large cavities of hydrate structure II. For this reason, this situation is not illustrated here by a separate figure.

Certain data about gas hydrates necessary to continue the discussion are borrowed from Refs [66–69] and presented below. Figure 4 shows the crystal lattice of hydrate structure II (1) and the general view of small (2) and large (3) cavities of this structure (besides structure II, there is a structure I, which is beyond the scope of this review).

The nodes of the cavities give home to immobilized water (host) molecules. Both large and small cavities may contain either identical or different atoms and their groups (guests). A guest is linked to the host by nonvalent Van der Waals bonds. As mentioned above, the critical factor is the size of the guest rather than its chemical nature.

When a hydrate forms from ordinary ice I and the guest phase, the gain in enthalpy is usually small or absent, while the gain in the Gibbs free energy is largely due to an increase

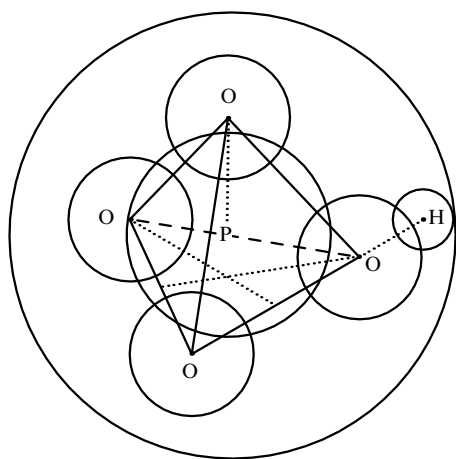


**Figure 4.** Crystal lattice of gas hydrate structure II: 1 — elementary crystal cell formed by 136 water molecules making 16 small and 8 large cavities,  $a = 1.74$  nm; 2 — small cavity: pentadodecahedron,  $d = 0.48$  nm; 3 — large cavity: hexadecahedron,  $d = 0.69$  nm.

in entropy compared with the total entropy of the initial phases. Due to the gain in the free energy during formation of hydrates, they may exist in the solid phase at much higher temperatures than ice I. It seems that the short-range order corresponding to the structure of gas hydrates may also exist in the liquid phase such as unperturbed concentrated solutions at temperatures slightly above 273 K. Gas hydrates are widespread in the earth's crust. Specifically, it has been shown that a small part of methane and some other simplest fatty hydrocarbons are present in the crust in the form of hydrates (see, e.g., [67]).

At the beginning of Section 2, we mentioned that the LOH hypothesis was prompted by the results of original comparative studies on the interaction of water vapor with polyacrylamide (PAA) [70, 71], acrylamide (AA) [11, 12], and amino acids (AAS) (glycine and alanine) [72]. Earlier investigations [73, 74] showed and confirmed that water sorbed by monomers and polymers binds to substrate functional groups; first, monohydrates are formed, followed by dihydrates, etc., if there is enough time for equilibrium to set in. These studies were carried out using sorption–desorption, calorimetric, and kinetic methods. Water was sorbed and desorbed in small portions, its content in the initial specimens and at each stage of the sorption process was known exactly, and the establishment of equilibrium in the water–substrate system prior to and after the experiments was thoroughly controlled whenever it was appropriate. The methods used provided information about interactions between substrates and water at different stages of the hydration of amidogroups.

Polyacrylamide is a poorly soluble linear nonbranched polymer containing amidogroups  $-C(O)NH_2$ , each bound to every other atom of the carbon chain. Removal of water from an aqueous polyacrylamide solution causes its molecules to pair via hydrogen bonds very similar to those between purines and pyrimidines in DNA–DNA helices. For this reason, PAA is the best model material for studies designed to elucidate the mechanism of insertion of water molecules into double helices of DNA and the resulting break of hydrogen



**Figure 3.** Scaled schematic representation of a phosphate group inside a small cavity of hydrate structure II.



bonds between purines and pyrimidines that stabilize the double helix. The binding energy in a DNA–DNA system largely depends on the  $=O \cdots NH_2-$  bonds due to the maximum dipole moments of these atoms. In a PAA–PAA system, the binding energy is determined by the  $=O \cdots NH_2-$  bonds alone. The similarity of bonds in DNA–DNA and PAA–PAA systems is readily apparent from the comparison of Figs 2a and 2c. The interaction between water and purine–pyrimidine complexes cannot be studied directly in double DNA–DNA helices because phosphate groups and ribose also interact with water, and it is impossible to distinguish these interactions from those between water and other functional groups of DNA. An AA–water system in which AA contains the same functional groups as PAA was investigated in order to clarify changes introduced by a hydrocarbon chain in the interaction between water and hydrogen-bonded amidogroups. Interactions of water with amino acid functional groups were studied in glycine–water or alanine–water systems. It was found that dehydration of AAS gave rise to hydrogen bonds between two amino acids (Fig. 2b) similar to AA–AA bonds (Fig. 2c). Bonds between amino acids were similar to the  $=O \cdots NH_2-$  bonds formed in the systems under consideration. Differences between these bonds in dimers of all compounds included in the study were largely determined by their geometric features. It is shown in [13] that these features may be responsible for a substantial difference in the binding energy.

We arrived at the following conclusions concerning the behavior of the systems studied in [11, 12] at 288–298 K. Interaction of water with dehydrated PAA, AA, and AAS leads to gradual neutralization of PAA–PAA, AA–AA, and AAS–AAS bonds and their substitution by PAA–water, AA–water, and AAS–water bonds. In other words, PAA, AA, and AAS exist at equilibrium as dimers or in the form of aqueous solutions of monomers depending on the water content in a given system. At 100% humidity, water is sorbed by all the above systems, but this process is very slow (certain experiments lasted uninterrupted over one year). The binding energy of substrate–water complexes is slightly higher or lower than the binding energy of interacting substrate molecules, depending on the degree of dehydration. Differences between the heat of water vapor binding by a water–substrate system and the heat of water–vapor condensation at the liquid water surface for systems containing more water than dihydrates do not exceed  $3 \text{ kJ mol}^{-1}$ . Sorption of water vapor occurs regardless of the extent of dehydration due to peculiar characteristics of entropy of substrate–water systems. In the water–substrate systems with no agitation, the characteristics changed when the water content varied in the range 17–22 water molecules per amidogroup. The changes are especially pronounced in PAA–water systems. In this system at about 290 K, we observed a long-term delay of water-vapor sorption from air saturated with water vapor, an increase in the differential heat of water desorption, and a decrease in the rate of water-vapor desorption into a vacuum. These data suggest an especially strong binding of water by the polymer at the given degree of system dehydration [11, 12].

Analysis of these observations shows that dehydration results in the appearance of cavities around amidogroups of PAA formed by water molecules similar to the cavities in structure II of gas hydrates; in other words, the arrangement of water molecules near amidogroups submits to short-range

ordering. Further dehydration of the system leads to a water continuum in which the structurization of water in the vicinity of amidogroups becomes thermodynamically disadvantageous and unfeasible at a given temperature. Decreased dehydration is accompanied by dimerization of PAA molecules with the formation of hydrogen bonds between amidogroups. We suggested that similar phenomena can occur in the DNA–water system [13, 14].

Data presented in this section were used to formulate the LOH hypothesis and to describe the postulated physico-chemical mechanism of the processes underlying DNA replication and cell division [72].

### 3.2 Formulation of the LOH hypothesis

The LOH hypothesis asserts that the simplest elements of living matter, N-bases and D-ribose, were synthesized by nature from methane (possibly also from other simple fatty hydrocarbons) and niter within the structure of the simplest hydrocarbon hydrates in those parts of the earth's crust where hydrate and niter deposits occurred close to each other. Apparently, filling the hydrate structure with such compounds corresponded to the free energy minimum in a hydrocarbon hydrate–nitrate system in the presence of excessive hydrates. When purine (G, Ad) and pyrimidine (Cy, Th, U) bases happened to form in the neighboring large cavities of a hydrate structure, they were linked by hydrogen bonds. This created prerequisites for further synthesis of nucleic acid dimers, bypassing the stage of monomer synthesis. N-bases chemically interacted with ribose molecules, giving rise to nucleosides. Due to the internal self-organization of the new substance governed by the arising system of hydrogen bonds, a certain phase located in the boundary zone of the hydrate structure formed and could exist rather long in this form. Therefore, purine molecules had enough time to encounter pyrimidines and 'join hands' to form purine–pyrimidine pairs stabilized by hydrogen bonds. Simultaneously, riboses could find 'their own' purines and pyrimidines and be attached to them 'forever' by chemical bonds; the resulting nucleoside dimers became elements of future nucleic acid dimers. If phosphoric acid or its salt diffused into this phase, they traveled over small cavities of the hydrate structure and organized nucleosides into chains of nucleic acid dimers of different length and sequence of N-bases. Simultaneously, monomer molecules formed. Some nucleosides could not find a partner and remained 'frozen' in the oligomeric or monomeric state. When the temperature increased as a result of various geophysical and geochemical processes, after the period of faint young sun was over or when excessive water or phosphoric acid solution diffused into the system, the hydrate lattice melted and a 'soup' was created. The chemical composition of this soup was such that it allowed the synthesis of amino acids and other basic components found in cells of the present-day living matter (at least in prokaryotic cells).

DNA molecules in double helices are known to be bound by hydrogen bonds between purines of one strand and pyrimidines of the other (not by purine–purine or pyrimidine–pyrimidine bonds). It may be thought that the situation realized in present-day living matter is determined by the hydrate structure and took shape at the stage of LMSE formation. This inference is illustrated by Fig. 2a. Had a purine base molecule arisen in each of the two neighboring large cavities of the hydrate structure, the distances between the groups of different polarity in individual molecules would

have been smaller than equilibrium distances, and the polar groups would have inevitably ‘turned away’ from each other. If another large cavity adjacent to one containing such a purine base had been occupied by a pyrimidine molecule, the purine and the pyrimidine would have been linked by hydrogen bonds because the latter base has a certain degree of freedom inside the cavity, enabling it to take an equilibrium position with respect to the former. Had two pyrimidine bases been formed in the neighboring cavities, it would have meant that they spread loosely and nature would not have failed to pack them by attaching a few more atoms to one of them, thus transforming it into a purine base.

We have already cited articles in which nucleic acids were shown to self-replicate [9, 36, 40, 41] and the self-replication to be accelerated by an autocatalytic mechanism [10]. This should lead to an increase in nucleic acid concentration in the primary soup under favorable conditions. An increase in the concentration to a certain critical level resulted in cell formation in which replication and division processes were generally similar to those in the cells of present-day organisms. Evolution selected those cells containing several nucleic acids in which replication phases were in resonance with each other. Cell division was initially similar to that in prokaryotes (the simplest unicellular organisms that lack a nucleus and have a single chromosome and primitive protein ‘stuffing’ including ribosomes). The mechanism of cell membrane formation in the organophosphorous medium, which we call supercytoplasm in analogy with cell cytoplasm, can be described as follows.

Immediately after replication, nucleic acid molecules are weakly hydrated and actively sorb water from supercytoplasm. At each given moment, individual molecules of nucleic acids are at different mitotic stages. Nevertheless, it may happen that a few (or many) molecules that just completed replication and therefore actively sorb water are simultaneously present within a limited space. A situation is conceivable where the concentration of water in supercytoplasm is low and its inflow from the outside is insufficient to meet the requirements of the cells. If other molecules of nucleic acids present nearby also sorb water, some individual molecules or their groups may find themselves in an oversaturated space in which organophosphorous membranes precipitate not far from these molecules. These are the first cells. Further replication of nucleic acids and the concomitant formation of N-bases, amino acids, nucleotides, nucleosides, and other organic substances cause the water content in supercytoplasm to decrease to a certain critical level. This triggers cell formation in the entire volume of supercytoplasm and 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 supercytoplasm. Thereafter, nucleic acids replicate inside cells and cell division occurs through the mechanism described below.

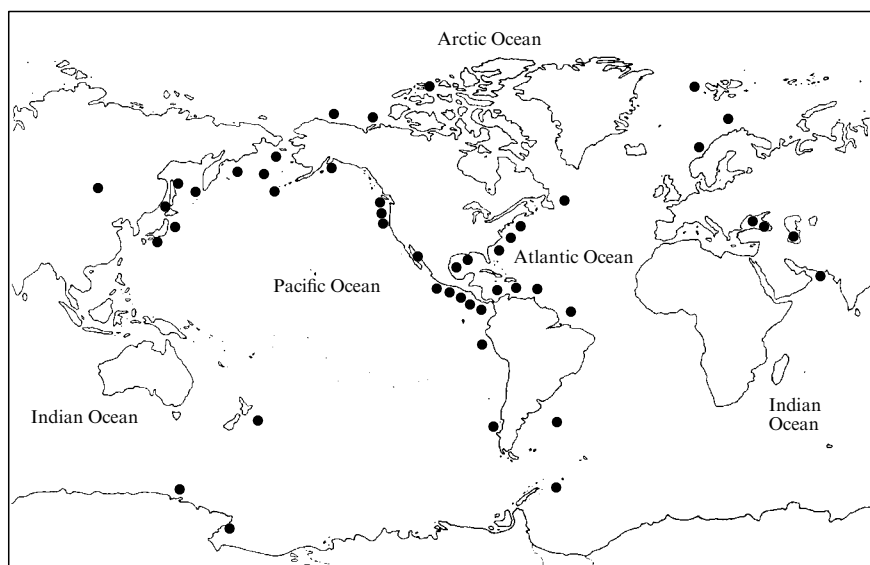
We have formulated the physico-chemical principles of the mechanisms (not chemism) of the DNA replication, double division, and mitosis for prokaryotes and eukaryotes in terms of our LOH hypothesis briefly in [12, 14, 15] and in more detail in [63, 72]. Details of these mechanisms are not discussed here. As mentioned above, we believe that the mechanism of division of primary cells in supercytoplasm was analogous to the cell division mechanism in modern prokaryotes (the so-called ‘double division’). Our understanding of this mechanism is expounded below.

Immediately after replication, sister chromosomes are pulled apart towards opposite cell poles by electrostatic repulsion forces; they actively form hydrate envelopes around DNA–DNA bonds and sorb water from the cytoplasm at a higher rate than it enters the cell through the plasma membrane. This results in a diffuse outflow of water from the cell equator towards chromosomes and the appearance of a region oversaturated with organic substances of lower density than water in the equatorial zone, leading to the formation of a cleavage furrow, the precipitation of organophosphates, the appearance of a membrane, and the division of the cell into two separate entities.

The above description of the mechanism of cell formation in supercytoplasm and the division of prokaryotic cells includes two principal propositions: (1) immediately after replication, nucleic acid molecules are poorly hydrated and therefore actively sorb water; (2) the drift of sister chromosomes apart from each other immediately after replication is a consequence of their electrostatic repulsion. In Ref. [72], these propositions logically ensue from the application of the key principles of the LOH hypothesis to the analysis of replication and double division mechanisms in prokaryotes and mitosis in eukaryotes [the 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].

There is reason to think that the functions of protein synthesis and transmission of inheritable features in the simplest living organisms very soon after their emergence from supercytoplasm were rather weak but gradually developed thereafter and were selected in the course of evolution. This inference, which necessarily ensues from our hypothesis, is supported by the following facts. First, the DNA of prokaryotes and viruses, i.e., the simplest organisms, unlike the DNA of eukaryotes, contains no protein. The cytoplasm of prokaryotic cells contains ribosomes generally regarded as ‘factory shops’ for protein production in accordance with a genetic program, but the amount of protein is generally much lower than in eukaryotes. 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, viroids, and prions are even more prone to mutation. In other words, the mechanism of trait inheritance 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 as vain to advocate as to reject it because its validity can be verified only in a direct experiment on the synthesis of the animate from the inanimate.

It can be concluded that living matter actually developed from three starting mineral substances: methane (or another simple fatty hydrocarbon), niter (sodium niter or the so-called Chile saltpeter and potassium nitrate), and apatite (or, possibly, phosphoric acid). Bearing in mind the current conditions on our planet, the most likely initial material for the formation of DNA and similar molecules was methane or ethane and propane (as shown below), niter, and apatite. As mentioned in Section 3.1, hydrates of methane and other



**Figure 5.** Submarine gas hydrates; dots show areas where suboceanic methane hydrates or signatures of their presence have been discovered (from [67, p. 15]).

simple hydrocarbons are widespread in the earth's crust; the same refers to small and large niter deposits (e.g.,  $\text{NaNO}_3$  deposits in Chile) and to phosphates of varied composition that frequently occur in nature.

In the context of our hypothesis, it is essential that deposits of hydrated hydrocarbons and niter be localized close enough to ensure diffusion of niter into the hydrate phase. Such a situation is typical today and seems to have been even more so in the past. Figure 5 borrowed from Ref. [67] schematically depicts the location of the known submarine deposits of methane hydrates (we recall that there are also mainland subterranean deposits of these materials). Specifically, the map shows a few deposits of methane hydrates along the Pacific coastline of the Americas (California, Oregon, Peru, etc.). Deposits of sodium and potassium nitrates have been discovered in elevated arid coastal areas of Chile, Bolivia, California, and other regions [75]. It is worthy of note that niter is readily dissolved in water and presently found only in dry areas. The existence of its deposits in the earth's crust more than 4.5 billion years after the formation of our planet suggests that they were much more numerous and of greater size in the past.

There is one more fact in support of our concept. It was shown in a number of studies [76–78] that gas samples taken for analysis from deposits of methane hydrates contain much nitrogen and little oxygen: 4% and 0.005%, respectively according to [76] and 11.4% and 0.2% reported in [77]. It can be seen that the  $\text{N}_2$  to  $\text{O}_2$  ratio is much higher than in the atmosphere; evidently, the samples could not have been contaminated by atmospheric nitrogen during their collection and storage. Potential sources of elemental nitrogen in the earth's crust are few. Therefore, it is quite possible that nitrogen was produced by the reduction of hydrated methane or other hydrocarbons in the reactions described in Section 4.

As regards potential sources of phosphorus, the following line of reasoning may be taken. It was mentioned in this section that apatite  $\text{Ca}_5\text{X}(\text{PO}_4)_3$ , where  $\text{X} = \text{F}, \text{Cl}$  or  $\text{OH}$ , could be a most probable 'raw material' for the synthesis of primary DNA-like molecules. Some researchers argue that certain phosphorites are the transformed products of the vital activity of colonial seabirds and the remains of dead animals

in places of their mass deaths, or the result of phosphorus accumulation by so-called phosphobacteria. But the common opinion is that apatites are of mineral origin [79]. Therefore, they could be used as a raw material for the synthesis of primary DNA. Moreover, the young earth's crust could have contained elemental phosphorus together with water vapor and metals that catalyzed the reaction  $\text{P}_4 + 16 \text{H}_2\text{O} = 4 \text{H}_3\text{PO}_4 + 10 \text{H}_2 + 1306 \text{ kJ}$  [79] yielding phosphoric acid; the reaction of phosphoric acid with N-bases and D-ribose gave DNA-like species.

The LOH hypothesis gives grounds for a totally new explanation of the chiral purity of DNA, RNA, and their derivatives. The hypothesis suggests that chiral purity of nucleic acids is a consequence of the effect of the geometric matrix in which they were first moulded in nature and continue to reproduce themselves in each newly formed cell of living matter. The fact is different enantiomers of ribose have different geometries responsible for the chiral purity of DNA and RNA. Quite possibly, the structure of hydrocarbon hydrates made ribose take the D-configuration because it would have been unable to simultaneously 'reach' both an N-base and a phosphate group in the L-configuration. It may be expected that this intriguing issue will be resolved in computer experiments. The problem of the homochirality of enzymes is related to the chemical mechanism of their formation and therefore lies beyond the scope of this review, which is not designed to consider chemism of intracellular processes. Possibly, this problem will be easier to solve after the cause of the nucleic acid homochirality is understood.

More detailed experimental and monitoring data that brought us to the proposed hypothesis are discussed in the previously cited publications. There are the following key issues to be further considered in the framework of this hypothesis. Was the formation of N-bases and D-ribose from the simplest hydrocarbons, sodium, and potassium nitrates thermodynamically feasible? (The possibility of reactions of N-bases with D-ribose and phosphates is shown in [80–83].) Were the appearance and the transformation of the elements of the simplest living matter interdependent with and interconditioned by changes in the primary atmosphere of the earth?

#### 4. Thermodynamics of the formation of the simplest elements of living matter

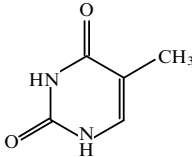
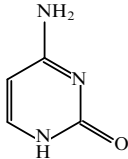
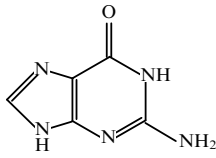
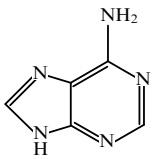
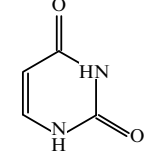
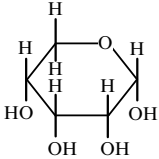
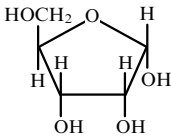
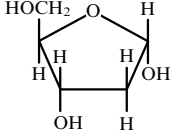
It is universally accepted that the modern vegetation cover of the earth interacts with the atmosphere and determines the equilibrium composition of the atmospheric air. According to the LOH hypothesis, transformation of the primary atmosphere of the earth and the processes conducive to the origin and 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 vegetable life 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.

In this section, we consider processes that, in accordance with our hypothesis, brought about LMSEs, show their relationship with the composition of the atmosphere and the role of hydrate structures as matrices for the formation of DNA, and demonstrate thermodynamic consistency of the hypothesis.

Thermodynamic calculations presented in this section have until recently been impossible because the necessary thermodynamic functions for N-bases and D-ribose (DR) were not available in the literature. Standard values of the enthalpy of formation  $\Delta_f H^0$  and the entropy  $S^0$  for N-bases were obtained in [84, 85].

The literature offers only standard values of the enthalpy of formation for D-ribose contained in RNA [86, 87]; complete thermodynamic data, yet unpublished, were gener-

**Table 1.** Formulas and molecular weights of compounds under consideration.

Compound	Formula	Molecular weight, g mol <sup>-1</sup>
Thymine (C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> )		126.11
Cytosine (C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O)		111.10
Guanine (C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> O)		151.13
Adenine (C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> )		135.13
Uracyl (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> )		112.09
D-ribose (C <sub>5</sub> H <sub>10</sub> O <sub>5</sub> )	 Pyranose form  Furanose form	150.11
Deoxyribose (C <sub>5</sub> H <sub>10</sub> O <sub>4</sub> )		134.11

**Table 2.** Values of the standard enthalpies of formation and absolute entropies.

Substance number ( <i>j</i> )	Substance	Formula	$\Delta_f H_j^0(T)$ , kJ mol <sup>-1</sup>	$S_j^0(T)$ , J mol <sup>-1</sup> K <sup>-1</sup>
1	Thymine (crystal)	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	-462.8 [85]	160.1 [84]
2	Cytosine (crystal)	C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O	-221.3 [85]	140.8 [84]
3	Guanine (crystal)	C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> O	-183.9 [85]	160.2 [84]
4	Adenine (crystal)	C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	96 [85]	152.0 [84]
5	Uracyl (crystal)	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>	-429.4 [85]	128.0 [84]
6	Xanthine (crystal)	C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	-379.6 [85]	160.5 [84]
7	D-ribose (crystal)	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	-1050.9 [88]	175.7 [88]
8	Water (liquid)	H <sub>2</sub> O	-285.83 [89]	69.95 [89]
9	Potassium nitrate (crystal)	KNO <sub>3</sub>	-494.0 [89]	132.9 [89]
10	Potassium hydroxide (crystal)	KOH	-424.58 [89]	78.87 [89]
11	Methane (gas)	CH <sub>4</sub>	-74.6 [89]	186.26 [89]
12	Ethane (gas)	C <sub>2</sub> H <sub>6</sub>	-84 [89]	229.06 [89]
13	Propane (gas)	C <sub>3</sub> H <sub>8</sub>	-103.89 [89]	270.0 [89]
14	Ammonia (gas)	NH <sub>3</sub>	-46.19 [89]	192.5 [89]
15	Nitrogen (gas)	N <sub>2</sub>	0 [89]	191.58 [89]
16	Oxygen (gas)	O <sub>2</sub>	0 [89]	205.04 [89]

**Table 3.** Changes in the enthalpy  $\Delta_i(\Delta_f H_j^0)$ , entropy  $\Delta_i S_j^0$ , and Gibbs free energy  $\Delta_i G^0$  for reactions of the formation of Cy, G, Ad, U, and DR from hydrocarbons and KNO<sub>3</sub>.

Reaction	$\Delta_i(\Delta_f H_j^0)$ , kJ mol <sup>-1</sup>	$\Delta_i S_j^0$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta_i G^0$ , kJ mol <sup>-1</sup>	Reaction number ( <i>i</i> )
28.2 KNO <sub>3</sub> + 38 CH <sub>4</sub> = C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> + C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O + C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> O + C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> + 4 C <sub>5</sub> H <sub>10</sub> O <sub>5</sub> + 28.2 KOH + 32.4 H <sub>2</sub> O + 6.6 N <sub>2</sub>	-9410	-3787	-8281	(3)
20.6 KNO <sub>3</sub> + 19 C <sub>2</sub> H <sub>6</sub> = C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> + C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O + C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> O + C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> + 4 C <sub>5</sub> H <sub>10</sub> O <sub>5</sub> + 20.6 KOH + 17.2 H <sub>2</sub> O + 2.8 N <sub>2</sub>	-6832	-2442	-6104	(4)
18.0(6) KNO <sub>3</sub> + 12.(6) C <sub>3</sub> H <sub>8</sub> = C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> + C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O + C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> O + C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> + 4 C <sub>5</sub> H <sub>10</sub> O <sub>5</sub> + 18.0(6) KOH + 12.1(3) H <sub>2</sub> O + 1.5(3) N <sub>2</sub>	-5840	-1970	-5253	(5)

ously provided by Boerio-Goates [88] (her enthalpy values do not differ from those in Refs [86, 87]). Thermodynamic functions for deoxyribose (DDR) present in DNA are unavailable from the literature.

Table 1 lists chemical formulas of the main constituents of DNA and RNA molecules (Cy, G, Th, Ad, U, DR, and DDR). (Nucleic acids of bacteria, plants, and animals sometimes contain 6-methyladenine, 5-methylcytosine, xanthine (2,6-dioxypurine), hypoxanthine (6-oxypurine), and other N-bases for which the general conclusions of the present review also hold, but going into detail would not answer its purposes; additional data can be found in [15].)

We analyse the thermodynamic feasibility of obtaining Cy, G, Th, Ad, U, and DR from only two mineral substances widespread in nature: one of the simplest fatty hydrocarbons and a niter. As an example, we consider interactions of methane, ethane, and propane with potassium nitrate (niter). The result are not significantly different if potassium nitrate is substituted by sodium niter.

The thermodynamic functions for DDR being unavailable, we do not calculate the thermodynamic parameters of its formation but present a qualitative estimation of the possibility of its synthesis from the above initial mineral substances.

Table 2 contains standard thermodynamic parameter values used in calculations.<sup>1</sup>

It is known that the Ad/Th and G/Cy molar ratios in DNA molecules are equal to unity. At the same time, different

forms of living matter have different (Ad + Th)/(G + Cy) ratios. They may be either larger or smaller than unity in bacteria but vary within a relatively narrow range in higher organisms. For example, they equal 1.3–1.5 in the majority of animals (human sperm contains roughly 31, 19, 31, and 19% Ad, G, Th, and Cy, respectively) and 1.1–1.7 in plants [65, p. 216].

The same is true of RNA (containing U instead of Ad). The results of calculations presented in Table 3 refer to RNA because thermodynamic data on DDR in DNA molecules are lacking in the literature (see above). We consider a hypothetical averaged situation with the molar ratio Ad/G = 1 and seek an answer to the question of whether such a situation can be realized under standard conditions in a system initially containing a saturated fatty hydrocarbon (methane, ethane, or propane) and potassium nitrate. The criterion for the possibility of the formation of the necessary set of N-bases and DR from the initial carbon and niter is a negative value of the change in the Gibbs free energy  $\Delta_i G^0$  for the reactions presented in Table 3.

In other words, we consider the thermodynamic feasibility of coupled reactions between methane (ethane or propane) and potassium nitrate under standard conditions yielding Cy, G, Ad, and U, as well as DR in equimolar ratio to the sum of these N-bases. We assume that this process gives rise to inert nitrogen that resists further transformation.

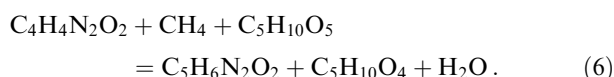
In the table,  $\Delta_i G^0 = \Delta_i(\Delta_f H_j^0) - T \Delta_i S_j^0$ , where *i* is the reaction number. This implies the possibility of forming N-bases and DR from a hydrocarbon and niter with the release of nitrogen. The larger the hydrocarbon molecular weight, the smaller the absolute decrease in the Gibbs free

<sup>1</sup> All thermodynamic calculations reported in this review are based on thermodynamic functions for the initial substances and reaction products in aggregate states corresponding to those in Table 2.

energy calculated per one set of N-bases and DR needed for the formation of four RNA nucleosides of different compositions. This finding confirms the possibility of the RNA formation under suitable natural conditions if a hydrocarbon and niter are close enough to each other. The highest ‘yield’ of the final products is feasible if methane is used as the ‘raw material’; however, RNA can just as well form from ethane and propane with the release of nitrogen. The absolute decrease in the Gibbs free energy in all the above reactions is so significant that it removes all doubt about the possibility of wide variations in relative equilibrium concentrations of Ad and G. Reaction rates are inessential for our reasoning because nature is never in a hurry.

It is worth noting that the amount of released nitrogen should be especially large when N-bases and ribose are produced from methane. If reaction (3) did give rise to the primary elements of living matter, it had to enrich the atmosphere with nitrogen.

Although the thermodynamic characteristics of DDR remain unknown, it is possible to qualitatively estimate the thermodynamic requirements for its formation in the chemical system under consideration. Here is a reaction leading to the synthesis of Th and DDR from U and DR:



We first assess the entropy change in this reaction. As the first approximation, we assume the equality of the DDR and DR entropies. According to Table 2,  $\Delta_6 S_f^0 \approx -84.21 \text{ J K}^{-1}$ ; therefore, the contribution of the entropic member to  $\Delta_6 G^0$  is negative and has the absolute value  $25.11 \text{ kJ mol}^{-1}$  ( $T\Delta_6 S_f^0 = 25.11 \text{ J K}^{-1}$ ). We further assume that  $\Delta_6 G^0 = 0$  and calculate  $\Delta_f H_f^0$  for DDR ( $\text{C}_5\text{H}_{10}\text{C}_4$ ). The result is  $-781.16 \text{ kJ mol}^{-1}$ . Taken together with the data in Table 2, this result means that for the reduction of DR by hydrogen to DDR and water  $\text{C}_5\text{H}_{10}\text{O}_5 + \text{H}_2 = \text{C}_5\text{H}_{10}\text{O}_4 + \text{H}_2\text{O}$ , the change in enthalpy is negative and equals  $-16.09 \text{ kJ mol}^{-1}$ . In reality, such reactions of reduction of organic compounds are characterized by negative changes in enthalpy that are much greater than the above magnitude. This means that the absolute value of  $\Delta_f H_f^0$  for DDR is larger than  $781.16 \text{ kJ mol}^{-1}$ . It may be concluded that an equilibrium mixture of simple hydrocarbons and niter must contain Th, Ad, G, Cy, U, DR, and DDR. The relative content of these components depends on the surrounding conditions.

It is shown below that DR can originate from the same starting substances by itself, without the concomitant formation of N-bases, with the release of nitrogen. Such a possibility is demonstrated in Table 4, where reactions with large absolute (negative) changes of the free energy are listed. All these reactions produce nitrogen.

We calculated thermodynamic parameters for reactions in which individual nitrogen bases (Th, Ad, G, Cy, and U)

are formed from potassium nitrate and various hydrocarbons in an oxygen medium. These calculations refer to the situation where the processes stop at the stage of incomplete utilization of oxygen contained in the niter. Table 5 presents the results of calculations made for reactions of potassium nitrate with methane (10)–(14), ethane (15)–(19), and propane (20)–(24).

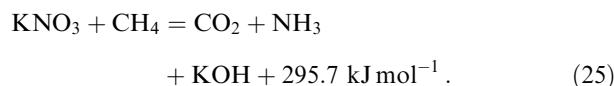
In what follows, we summarize the results for reactions (10), (11), (12), (13), and (14) leading to the formation of Th, Cy, G, Ad, and U, respectively.

All the above N-bases can exist in the atmosphere of oxygen under standard conditions. Each reaction is accompanied by a decrease in the Gibbs free energy. Oxygen is consumed in reactions leading to Th and U but released during the formation of other nitrogen bases.  $\text{O}_2$  is released when overall equilibrium corresponds to the sum of equilibria (10)–(14).

The results for reactions (15)–(19) of potassium nitrate with  $\text{C}_2\text{H}_6$  are qualitatively similar to the results of interactions between potassium nitrate and methane.

The results for reactions (20)–(24) of potassium nitrate with propane are somewhat different because the adenine synthesis cannot be realized by itself. However, all these reactions may proceed via a consecutive (coupled) mechanism because the total change in the free energy is negative.

A few peculiarities of these reactions are worth mentioning. First, the pressure of hydrocarbons over hydrates is temperature-dependent regardless of the degree of hydrocarbon conversion; stoichiometric water passes into the liquid phase. Second, gas pressure over the gas-releasing reaction zone in the subsurface of the earth or under the sea bottom is subject to self-regulation because the ground functions as a valve that releases the compressed gas into the atmosphere or seawater, either from time to time or continuously. Third, hydrates are able to sorb large amounts of nitrogen produced in the reaction with niter (the so-called accompanying gas); this process stabilizes the hydrate structure. All these peculiarities are essential for the formation of LMSEs; the first two are of greatest importance because LMSEs are products of the incomplete interaction between a hydrocarbon and niter inside the hydrocarbon hydrate phase. It is reactions of type (3)–(5) (see Table 3) in which nitrogen is reduced incompletely. Its complete reduction may lead to ammonia production:



The resulting N-bases, riboses, and molecular nitrogen are quite stable. Ammonia could hardly form in large amounts at temperatures under which hydrocarbon hydrates exist at a depth of several kilometers, or in the presence of excess hydrocarbon hydrates and the removal of nitrogen from the system. However, we cannot exclude that reaction (25) could be realized in closed systems at sufficiently high temperatures.

**Table 4.** Changes in the enthalpy  $\Delta_i (\Delta_f H_f^0)$ , entropy  $\Delta_i S_f^0$ , and Gibbs free energy  $\Delta_i G^0$  for reactions of DR formation from hydrocarbons and  $\text{KNO}_3$ .

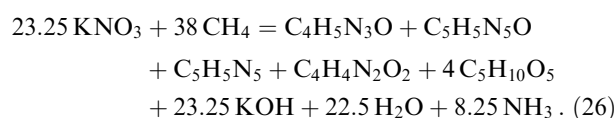
Reaction	$\Delta_i (\Delta_f H_f^0)$ , $\text{kJ mol}^{-1}$	$\Delta_i S_f^0$ , $\text{J mol}^{-1} \text{ K}^{-1}$	$\Delta_i G_f^0$ , $\text{kJ mol}^{-1}$	Reaction number (i)
$4\text{KNO}_3 + 5\text{CH}_4 = \text{C}_5\text{H}_{10}\text{O}_5 + 3\text{H}_2\text{O} + 4\text{KOH} + 2\text{N}_2$	–1258	–378.7	–1145	(7)
$3\text{KNO}_3 + 2.5\text{C}_2\text{H}_6 = \text{C}_5\text{H}_{10}\text{O}_5 + \text{H}_2\text{O} + 3\text{KON} + 1.5\text{N}_2$	–918.4	–201.7	–858.3	(8)
$2.(6)\text{KNO}_3 + 1.(6)\text{C}_3\text{H}_8 = \text{C}_5\text{H}_{10}\text{O}_5 + 0.(3)\text{H}_2\text{O} + 2.(6)\text{KOH} + 1.(3)\text{N}_2$	–787.9	–139.7	–746.2	(9)

**Table 5.** Changes of the enthalpy  $\Delta_i$  ( $\Delta_f H_f^0$ ), entropy  $\Delta_i S_f^0$ , and Gibbs free energy  $\Delta_i G^0$  for reactions of Cy, G, Ad, or U formation from hydrocarbons and  $\text{KNO}_3$ .

Reaction	$\Delta_i$ ( $\Delta_f H_f^0$ ), kJ mol <sup>-1</sup>	$\Delta_i S_f^0$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta_i G^0$ , kJ mol <sup>-1</sup>	Reaction number ( <i>i</i> )
$2 \text{KNO}_3 + 5 \text{CH}_4 + 2 \text{O}_2 = \text{C}_5\text{N}_2\text{O}_2\text{H}_6 + 6 \text{H}_2\text{O} + 2 \text{KOH}$	-1666	-869.6	-1407	(10)
$3 \text{KNO}_3 + 4 \text{CH}_4 = \text{C}_4\text{N}_3\text{OH}_5 + 4 \text{H}_2\text{O} + 3 \text{KOH} + 0.5 \text{O}_2$	-858.0	-384.0	-743.5	(11)
$5 \text{KNO}_3 + 5 \text{CH}_4 = \text{C}_5\text{N}_5\text{OH}_5 + 5 \text{H}_2\text{O} + 5 \text{KOH} + 2 \text{O}_2$	-893.0	-281.4	-809.0	(12)
$5 \text{KNO}_3 + 5 \text{CH}_4 = \text{C}_5\text{N}_5\text{H}_5 + 5 \text{H}_2\text{O} + 5 \text{KOH} + 2.5 \text{O}_2$	-613.1	-187.1	-557.3	(13)
$2 \text{KNO}_3 + 4 \text{CH}_4 + 1.5 \text{O}_2 = \text{C}_4\text{N}_2\text{O}_2\text{H}_4 + 5 \text{H}_2\text{O} + 2 \text{KOH}$	-1421	-682.9	-1218	(14)
$2 \text{KNO}_3 + 2.5 \text{C}_2\text{H}_6 + 0.75 \text{O}_2 = \text{C}_5\text{N}_2\text{O}_2\text{H}_6 + 3.5 \text{H}_2\text{O} + 2 \text{KOH}$	-1114	-429.5	-986.3	(15)
$3 \text{KNO}_3 + 2 \text{C}_2\text{H}_6 = \text{C}_4\text{N}_3\text{OH}_5 + 2 \text{H}_2\text{O} + 3 \text{KOH} + 1.5 \text{O}_2$	-416.7	-31.95	-407.2	(16)
$5 \text{KNO}_3 + 2.5 \text{C}_2\text{H}_6 = \text{C}_5\text{N}_5\text{OH}_5 + 2.5 \text{H}_2\text{O} + 5 \text{KOH} + 3.25 \text{O}_2$	-341.4	158.7	-388.7	(17)
$5 \text{KNO}_3 + 2.5 \text{C}_2\text{H}_6 = \text{C}_5\text{N}_5\text{H}_5 + 2.5 \text{H}_2\text{O} + 5 \text{KOH} + 3.75 \text{O}_2$	-61.48	253.0	-136.9	(18)
$2 \text{KNO}_3 + 2 \text{C}_2\text{H}_6 + 0.5 \text{O}_2 = \text{C}_4\text{N}_2\text{O}_2\text{H}_4 + 3 \text{H}_2\text{O} + 2 \text{KOH}$	-980.1	-330.8	-881.4	(19)
$2 \text{KNO}_3 + 1.(6) \text{C}_3\text{H}_8 + 0.(3) \text{O}_2 = \text{C}_5\text{N}_2\text{O}_2\text{H}_6 + 2.(6) \text{H}_2\text{O} + 2 \text{KOH}$	-913.1	-279.8	-829.7	(20)
$3 \text{KNO}_3 + 1.(3) \text{C}_3\text{H}_8 = \text{C}_4\text{N}_3\text{OH}_5 + 1.(3) \text{H}_2\text{O} + 3 \text{KOH} + 1.8(3) \text{O}_2$	-255.6	87.93	-281.8	(21)
$5 \text{KNO}_3 + 1.(6) \text{C}_3\text{H}_8 = \text{C}_5\text{N}_5\text{OH}_5 + 1.(6) \text{H}_2\text{O} + 5 \text{KOH} + 3.(6) \text{O}_2$	-140.0	308.4	-232.0	(22)
$5 \text{KNO}_3 + 1.(6) \text{C}_3\text{H}_8 = \text{C}_5\text{N}_5\text{H}_5 + 1.(6) \text{H}_2\text{O} + 5 \text{KOH} + 4.1(6) \text{O}_2$	139.9	402.7	19.79	(23)
$2 \text{KNO}_3 + 1.(3) \text{C}_3\text{H}_8 + 0.1(6) \text{O}_2 = \text{C}_4\text{N}_2\text{O}_2\text{H}_4 + 2.(3) \text{H}_2\text{O} + 2 \text{KOH}$	-819.0	-374.9	-707.2	(24)

Inhibition of niter/hydrocarbon interaction at the stage of LMSE and nitrogen formation was promoted by the fact that reactions (3)–(5) produce nitrogen, while those listed in Table 5 release oxygen. Gas pressure over the hydrate phase increases to the threshold level determined by the depth of the reaction zone, the temperature of the hydrate phase, and the density of the ground layer overlying the hydrate layer; thereafter, the gas is released into the atmosphere or seawater. The methane pressure is thus maintained at the initial level as part of the released nitrogen and/or oxygen is removed from the reaction zone. This hampers complete oxidation of carbon and facilitates stabilization of the LMSEs being formed. In other words, the interaction between a hydrocarbon and niter under suitable conditions has the form of oscillations about the equilibrium state corresponding to LMSE synthesis.

In a closed system, i.e., under conditions where nitrogen is not removed from the reaction zone during the interaction of a hydrocarbon with niter and the temperature is too low for further carbon oxidation and molecular nitrogen reduction, this reaction proceeds via the state of the system that can be described as an equilibrium between the initial compounds (niter and a hydrocarbon) and the products such as N-bases, riboses, and ammonia. For example, for the reaction of  $\text{CH}_4$  with  $\text{KNO}_3$ , we have



In this case,  $\Delta_{26}G^0 = -6146 \text{ kJ mol}^{-1}$ . It follows that a complete set of LMSEs can be obtained under standard conditions from methane and niter with the release of ammonia. For reactions of this type with ethane or propane,  $\Delta_i G^0$  is also negative,  $-5198$  and  $-4757 \text{ kJ mol}^{-1}$ , respectively.

We believe that 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 xanthine and ammonia yielding guanine. It is clear that equilibrium in the reaction system suggests equilibrium between all its components, in agreement with the detailed equilibrium principle; this allows elucidating whether xanthine ( $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$ ) can exist in a system containing guanine and ammonia.

For the reaction



the relevant values are  $\Delta_{27}(\Delta_f H_f^0) = -43.94 \text{ kJ mol}^{-1}$ ,  $\Delta_{27}S_f^0 = -122.9 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $\Delta_{27}G^0 = -7.31 \text{ kJ mol}^{-1}$ . The free energy of this reaction decreases, which means that the equilibrium in (27) is shifted to the right and xanthine formation is thermodynamically disadvantageous. The absolute change of the free energy is small; therefore, nucleic acids may contain xanthine under certain conditions differing from standard ones. Indeed, xanthine is sometimes found in natural nucleic acids.

The majority of the above equilibria 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  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{NH}_3$ , and  $\text{CO}_2$ . For our purposes, it is inessential whether equilibria are actually achieved; the possibility of reactions leading to LMSE formation is of much greater importance. Negative values of the standard Gibbs free energy changes suggest that the relevant reactions could occur in the earth's depths at temperatures that were probably maintained there for a long time.

Moreover, we demonstrated that the free-energy loss during the formation of LMSEs from hydrocarbons and

niter may be significant; in other words, these starting substances in contact with each other actively ‘seek’ to turn into LMSEs. Certainly, the loss of the free energy when LMSEs are formed from precursors simpler than methane and niter (i.e., chemical elements) at the interface between the earth’s surface and atmosphere must be even greater. But a selective interaction of a large number of single gaseous and dissolved molecules with a growing precursor is much less probable than the interaction between only two phases and the subsequent interaction with one more phase in the interior of the earth.

Besides, it is clear that the conditions in the subterranean ‘incubator’ are much more stable than in a medium bordering the atmosphere; therefore, they facilitate the ordering of elements in time if the system’s free energy decreases. We emphasized above that all talk about the antientropic character of biological evolution makes no sense. Moreover, the values of any thermodynamic functions for any given substance alone say nothing about the possibility of the formation of this substance from other substances, because the direction of a chemical process is determined by the total change in the Gibbs free energy in the course of the process. The accumulation and transmission of information, as well as the generation of new properties with a growing degree of molecular ordering, are also intrinsic in some systems other than biologically active compounds. For example, a solid surface can ‘impart’ its properties to a thin film layered over it and the ordered structure of crystalline quartz shows the properties of birefringence and optical activity lacking in isolated molecules or melted silicon dioxide. Certainly, the rapid multifunctional response to external stimuli and abstract thinking are inherent only in living creatures, but they can be a direct result of the growing complexity of living matter.

## 5. Relationship between transformations of the earth’s atmosphere and processes responsible for the formation of the primary elements of living matter

Modern natural sciences are based on quasi-consensus with regard to the origin of the sun and the planets of our solar system from a gas–dust nebula. This quasi-consensus is underlain by the hypotheses of Kant [90] and Laplace [91] supplemented by the concept of internal unity of matter and energy, which were used to explain (Hoyle, Cameron, Schatzman) the nontrivial momentum distribution between the sun and the planets [92], and the concept of gradual condensation and internal self-heating of protoplanets [93] under the effects of compression, tidal forces, magnetism, and radiochemical reactions, in conjunction with external warming by solar radiation initiated by the energy of the thermonuclear synthesis of helium from hydrogen in the sun’s nucleus (Weizsäcker, Bethe). Opinions differ over whether the protoplanetary cloud was initially hot or cold. This problem is apparently unimportant for the general understanding of the planetary formation process because calculations indicate that it took planets two or three orders of magnitude more time to accumulate matter than the cloud needed to cool [94].

Many problems still await solution despite a long history of forwarding hypotheses, their refutation, the return to rejected hypotheses, and their updating [95–97]. However, the problems of the creation of the universe are beyond the scope of this review. In what follows, we confine ourselves to

the formulation and discussion of our views concerning transformation of the earth’s atmosphere in the context of the proposed hypothesis of the origin of simplest living-matter elements.

The quasi-consensus with regard to the common origin of the sun and the planets of the solar system gave birth to a widespread opinion that the primary atmosphere of the planets, like the present-day photosphere of the sun, almost exclusively consisted of hydrogen and helium, i.e., the lightest gases most difficult to condensate. The putative processes of transforming this atmosphere into the atmospheres of modern planets, including the earth, are widely discussed in the literature (see, e.g., [98–104]), but no definitive solution has yet been proposed. An additional difficulty is posed by the faint young sun problem arising from the fact that the sun of the Archean (2.5–3.8 billion years ago) is believed to have been only 75% as bright as it is today. It was insufficient for the presence of liquid water on the earth. On the other hand, geological surveys indicate that the earth had a constant temperature during this period and the subsequent proterozoic era. A few models have been proposed to resolve this paradox. The simplest one is to the effect that the Archean atmosphere contained large amounts of greenhouse CO<sub>2</sub> that resulted from bedrock decomposition and prevented cooling of the planet [100, 101]. Our hypothesis of atmospheric transformations incorporates this proposition.

We propose the following scheme for the formation of the earth and transformation of its atmosphere. The primary atmosphere of the young earth consisted of the lightest gases, hydrogen and helium. Agglomeration and compaction of the protoplanet were accompanied by its heating, decomposition of carbonates, and release of CO<sub>2</sub>. Hydrogen and helium dispersed through the earth’s atmosphere much faster than through the atmospheres of the cool planets formed farther from the sun, where the kinetic energy of hydrogen and helium was lower. At the same time, this process proceeded more slowly than in the atmospheres of Mercury, Venus, and Mars, having a smaller mass and heated more strongly (Mercury and Venus) than Earth (Table 6).

Particles of protoplanetary dust were coated with a layer of absorbed dissociated hydrogen that was able, due to the peculiar electron structure of H atoms, to differently polarize the surface of solid particles, depending on its chemical nature. Surprisingly, this well-known property of hydrogen, which might have important implications, has thus far been disregarded in the consideration of planetary history. Differences in the electrostatic potential of dust particles conditioned by hydrogen adsorption had to stimulate their ‘adhesion’ to one another and to conglomerates. Adsorption resulted in the occlusion of large amounts of hydrogen inside the developing planet, which was later forced by high pressure to fill closed hollows and aluminosilicate cellular structures. Gradual heating of the earth’s mass promoted by its compaction stimulated the decomposition of carbonates and release of CO<sub>2</sub> not only into the atmosphere, as was thought before [100, 101], but also into the hydrogen-filled cavities and cellular structures. In this way, conditions for the very first reaction shown in Table 7 were created.

The standard change in the Gibbs free energy for reaction (28) is negative and its absolute value is so large that the reaction in closed hollows could proceed very slowly until one of the initial gases was almost completely exhausted. Cooling created conditions for the formation of



**Table 6.** Characteristics of the Sun and the planets (the data are borrowed from Wikipedia [last updated: 21 November 2005]).

Celestial body	Mass relative to Earth's mass	Equatorial acceleration of gravity, $m^2 s^{-2}$	Gas tension *, kPa	Composition of the atmosphere (photosphere for the Sun), %	Mean surface temperature **, K
Sun	332,950	273.95		H (73.5), He (24.9), O (0.77), C (0.29), Fe (0.16), N (0.09), Si, Mg, S	5780
Mercury	0.055	3.701	Следы	K (31.7), Na (25), O (9.5), O <sub>2</sub> (5.6), He (5.9), N <sub>2</sub> (5.2), CO <sub>2</sub> (3.6), H <sub>2</sub> O (3.4), H <sub>2</sub> (3.2)	440 (503)
Venus	0.815	8.87	9300	CO <sub>2</sub> (96.4), N <sub>2</sub> (3.5), H <sub>2</sub> O (0.002), He (0.0012), SO <sub>2</sub>	737 (229)
Earth	1.00	9.780	100	N <sub>2</sub> (77), O <sub>2</sub> (21), CO <sub>2</sub> (0.038), H <sub>2</sub> O, Ar, He	287 (250)
Mars	0.107	3.69	0.8	CO <sub>2</sub> (95.3), N <sub>2</sub> (2.7), O <sub>2</sub> (0.13), H <sub>2</sub> O (0.03), CH <sub>4</sub> , He, CO, NO	210 (216)
Jupiter	317.8	23.12	70	H <sub>2</sub> (86), He (14), CH <sub>4</sub> (0.1), H <sub>2</sub> O (0.1), NH <sub>3</sub> (0.02), PH <sub>3</sub> , ...	152 (113)
Saturn	95	8.96	140	H <sub>2</sub> (> 93), He (> 5), CH <sub>4</sub> (0.2), H <sub>2</sub> O (0.1), NH <sub>3</sub> (0.01), PH <sub>3</sub> , ...	143 (83)
Uranus	14.54	8.69	120	H <sub>2</sub> (83), He (15), CH <sub>4</sub> (2), H <sub>2</sub> O (0.1), NH <sub>3</sub> (0.01), C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>2</sub>	68 (63)
Neptune	17.15	11.15	≥ 100	H <sub>2</sub> (80), He (19), CH <sub>4</sub> (1.5), HD	53 (53)
Pluto	0.0021	0.58	0.30	N <sub>2</sub> , CH <sub>4</sub>	44 (43)

\* Gas tension coincides with the real atmospheric pressure close to the planet surface only for Earth; the real pressure for other planets can be obtained by multiplying relevant table values by the respective ratios of the acceleration of gravity to the acceleration of gravity on Earth.

\*\* Numbers in parentheses are 'equilibrium' temperatures [105] calculated from solar radiation (surface temperature in the absence of planetary heat sources).

**Table 7.** Changes in the enthalpy  $\Delta_i(\Delta_f H_f^0)$ , entropy  $\Delta_i S_f^0$ , and Gibbs free energy  $\Delta_i G^0$  for reactions of hydrocarbon formation from hydrogen and carbon dioxide.

Reaction	$\Delta_i(\Delta_f H_f^0)$ , kJ mol <sup>-1</sup>	$\Delta_i S_f^0$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta_i G^0$ , kJ mol <sup>-1</sup>	Reaction number ( <i>i</i> )
4 H <sub>2</sub> + CO <sub>2</sub> = CH <sub>4</sub> + 2 H <sub>2</sub> O	-252.8	-409.8	-130.6	(28)
7 H <sub>2</sub> + 2 CO <sub>2</sub> = C <sub>2</sub> H <sub>6</sub> + 4 H <sub>2</sub> O	-440.3	-832.5	-192.1	(29)
10 H <sub>2</sub> + 3 CO <sub>2</sub> = C <sub>3</sub> H <sub>8</sub> + 6 H <sub>2</sub> O	-638.3	-1257	-263.6	(30)
6 H <sub>2</sub> + 2 CO <sub>2</sub> = C <sub>2</sub> H <sub>4</sub> + 4 H <sub>2</sub> O	-303.9	-711.8	-91.68	(31)
8 H <sub>2</sub> + 3 CO <sub>2</sub> = C <sub>3</sub> H <sub>6</sub> + 6 H <sub>2</sub> O	-514.0	-998.9	-216.2	(32)
19 H <sub>2</sub> + 6 CO <sub>2</sub> = C <sub>6</sub> H <sub>14</sub> + 12 H <sub>2</sub> O	-1236	-2537	-479.9	(33)

underground 'storehouses' of methane hydrate. Probably, oxides of iron, copper, nickel, and other metals played a role as catalysts in reaction (28). (The importance of catalytic processes for the formation of the mineral composition of the earth's crust (with reference to carbohydrates) was emphasized in earlier publications (see, e.g., [106, 107]).) The concept of large hydrogen reserves enclosed in the interior of the earth sheds a new light on the hypothesis by Mendeleev about the mineral origin of oil because hydrocarbon molecules could grow in size in reactions (29)–(33), etc.

As the earth's crust actively formed in the Archean period, the compressed gas not infrequently escaped from underground storehouses and enriched the atmosphere in carbon dioxide and methane as described in [108]. The presence of H and CO<sub>2</sub> promoted reaction (28) in the lower layers of the atmosphere, the water being formed was added to the water remaining in the unsealed storehouses, and together they gave rise to the oceans. Reaction (28) in the atmosphere most likely had a photochemical component and its rate was determined by diffusion, i.e., atmospheric hydrodynamics (see [99]). Thus, H<sub>2</sub> was used up in a wide range of changing conditions and the earth's atmosphere was enriched in greenhouse gases, first CO<sub>2</sub>, then methane and H<sub>2</sub>O vapor. Greenhouse gases promoted heat accumulation by the earth while the Sun was faint; in addition, its surface was heated by subcrust processes

and reaction (28). The concentration of CO<sub>2</sub> in the atmosphere gradually decreased, methane decomposed under the effect of solar radiation in the reverse reaction of (28) in the upper atmospheric layers, and the lightest gases, H<sub>2</sub> and He, dispersed through the earth's atmosphere.

In the meantime, the faint sun period was coming to an end and solar radiation increased. The processes described in Section 4 then began to develop, producing nitrogen and oxygen, which entered the atmosphere. We emphasize that according to our hypothesis, the atmosphere was enriched in oxygen before living matter appeared as a result of methane oxidation by niter; that is, plants were not the sole source of oxygen on the earth.

The available data about today's conditions on the planets of the solar system confirm the postulated transformations of the earth's atmosphere and do not contradict them at least. The atmospheres of the cool giant planets (Jupiter, Saturn, Uranus, Neptune) are largely composed of hydrogen and helium, like the solar photosphere and the primary atmospheres of the planets orbiting closer to Earth (Pluto is very small and has virtually no atmosphere) (see Table 7). Atmospheres of the cool Jupiter, Saturn, Uranus, and Neptune contain no carbon dioxide, which was either completely absent there or totally reacted with hydrogen in reaction (28) (see Table 7). The atmospheres of the remaining

planets contain carbon dioxide together with very small amounts of residual helium, but have no hydrogen (the percentage of hydrogen and helium content in Mercury's atmosphere is rather high but the absolute quantities of either gas are negligible due to the very low atmospheric pressure). The atmosphere of this planet is highly rarified and practically devoid of gaseous components because its mass is 18 times smaller than that of Earth (hence, its weak gravity and significantly higher temperature of the atmosphere). The atmosphere of Venus is heated much more strongly than that of Earth and its hydrogen had most likely dispersed before it reacted with carbon dioxide. Had methane and water ever formed on Venus, they would have evaporated from its hot atmosphere (methane and water molecules are approximately 2.5 times lighter than  $\text{CO}_2$ ) and methane hydrate could not be synthesized at the planet surface with its very high temperature. None of the facts listed in this paragraph is in conflict with the proposed hypothesis of the formation of Earth's atmosphere.

Only Mars of all the planets close to Earth may contain methane hydrate in its crust formed from  $\text{CO}_2$  and hydrogen in the past (all residual hydrogen later evaporated from Mars's atmosphere). The presence of small amounts of nitrogen and oxygen in the atmosphere of this planet is probably due to reactions similar to those described in the preceding section that occurred (and may even continue) in its crust. However, Mars appears to have always been cooler than Earth. Therefore, if such a reaction had indeed occurred in its crust, the subsequent process of complicated chemical transformations from their products to the emergence of the first cellular organisms would have lasted much longer than on Earth; hence, the probability of its interruption at an intermediate stage was significantly higher. In our opinion, any primitive life that may possibly exist on Mars should not be regarded as traces of a highly organized past life; it simply did not reach the level of life that thrives on Earth.

## 6. Conclusion

It is generally accepted that living matter in the form of simple invertebrate organisms emerged on the earth during the upper Archean period some 1.2–2.7 billion years ago, although their remains are practically unknown (the oldest unicellular algae found in ancient rocks of the Issua region, Greenland, have the estimated age 3.9 billion years [109]). The appearance of unicellular and multicellular organisms had to be preceded by the formation of N-bases and D-ribose, their interaction with phosphoric acid residues, the synthesis of DNA-like species, and the 'selection of viable' molecules capable of self-reproduction due to the consumption of nutrients from the environment. The lower Archean, starting from the origin of the earth and the Moon (4.57 and 4.53 billion years ago, respectively), was the time when the main geological formations came into being, the primary gaseous atmosphere underwent transformation, and large water masses accumulated in the crust and on the earth's surface.

This review develops the hydrate hypothesis of the origin of the simplest living matter elements and considers putative changes in the earth's atmosphere associated with processes that ended in the synthesis of N-bases, ribose, and DNA and RNA-like products of their interaction with phosphates, as well as processes that contributed to the formation of hydrocarbons in the crust. The proposed hypothesis was prompted by the results of calorimetric, kinetic, and stoichiometric studies of the interactions of liquid water and its vapors with polymer and monomer organic substances containing  $\text{H}_2\text{N}$ -,  $\text{O}=\text{}$ , and other functional groups.

Another source of the hypothesis was the results of the analysis of published data concerning thermodynamic and stoichiometric aspects of the interaction of water with DNA and DNA-like molecules, certain phenomenological problems of mitosis, formation and decomposition of gas hydrates, and structural characteristics of  $\text{H}_2\text{O}$ - and  $\text{O}=\text{}$  groups in various chemical compounds.

The gas hydrate hypothesis, together with our experiments on hydration and dehydration of various functional polymers and monomers, provided an explanation of certain phenomena described in the literature, such as the fact that water molecules located close to guanine in DNA- $\text{H}_2\text{O}$  systems are desorbed more easily than those near other N-bases [110, 111], while water molecules around N-bases are more readily desorbed than those around phosphate groups [112]. The same hypotheses allowed proposing [14, 15, 72] an original physico-chemical explanation of the mechanism underlying processes leading to DNA replication, double cell division in prokaryotes, and mitosis in eukaryotes.

The data and their discussion presented in this review indicate that DNA- and RNA-like molecules most probably formed in nature (and may continue to form at present) from only three mineral substances widespread in the earth's crust: methane hydrate (or other simple carbohydrates), niter (sodium or potassium nitrates), and phosphate in the methane hydrate phase or other simplest hydrocarbon in the interior of the earth or in near-bottom or sub-bottom layers of the ocean. It was shown in Section 4 that N-bases and ribose can arise from only two minerals, methane and niter, that are not only widespread in nature but also can be found in close proximity to each other in the earth's crust. It may be conjectured that subterranean or submarine natural biolaboratories still exist in our time in some coastal areas of southeast Eurasia, along great Chinese rivers, or elsewhere. One can hardly guarantee that newly appearing varieties of viruses that from time to time manifest themselves in nature arise as a result of mutations alone.

In this review, we tried to integrate the known concepts of chemism and the mechanisms of hypothetical natural processes responsible for the formation of the simplest elements of living matter and transformation of the earth's atmosphere and to substantiate their thermodynamic feasibility. The main hypothetical stages of the formation of the simplest living matter elements and the concomitant atmospheric changes during the Archean period are listed in Table 8.

We considered an original hypothesis of coupling between the processes that preceded the origin of life and those involved in atmospheric transformations. On the one hand, hydrogen of the primary atmosphere (together with carbon dioxide released from the earth crust) facilitated the formation of hydrated methane and other hydrocarbons in the interior of the earth (which formed the environment and became starting substances for the formation of living matter elements). On the other hand, processes that immediately preceded the synthesis of DNA (and RNA) resulted, in the course of time, in the appearance of oxygen and nitrogen in the atmosphere prior to the emergence of life.

An important feature of the proposed hypothesis is the possibility of its experimental verification. This requires creating proper methane pressure over water and niter in an

**Table 8.** Hypothetical sequence of the appearance of simplest living matter elements and the concomitant changes in the earth's atmosphere.

Period number	Events of the periods	
I *	Self-compaction of the gas-dust nebula	
II *	Atmosphere:	the amount of H <sub>2</sub> and He gradually increases
	Terrestrial globe:	porous hydrogen-saturated hardening mass
III *	Atmosphere:	H <sub>2</sub> /He/CO <sub>2</sub> /CH <sub>4</sub> /H <sub>2</sub> O; H <sub>2</sub> and He gradually evaporate and reaction CO <sub>2</sub> + 4H <sub>4</sub> = CH <sub>4</sub> + 2H <sub>2</sub> O occurs
	Terrestrial globe:	solid mass undergoing compaction with the release of heat; formation of hydrogen-filled cavities; carbonate decomposition and CO <sub>2</sub> release into these cavities and the atmosphere; methane synthesis inside the cavities in reaction CO <sub>2</sub> + 4H <sub>2</sub> = CH <sub>4</sub> + 2H <sub>2</sub> O and formation of more complex hydrocarbons
IV *	Atmosphere:	CO <sub>2</sub> /CH <sub>4</sub> (some H <sub>2</sub> O); methane decomposition in upper layers in reaction CH <sub>4</sub> + 2H <sub>2</sub> O = CO <sub>2</sub> + 4H <sub>2</sub> ; CO <sub>2</sub> mineralization
	Terrestrial globe:	formation of solid earth crust, cooling, and synthesis of methane hydrate; formation of oceans
V **	Atmosphere:	N <sub>2</sub> /O <sub>2</sub> (with an admixture of CO <sub>2</sub> and H <sub>2</sub> O)
	Terrestrial globe:	reactions of the (3), (7), and (10)–(14) type between CH <sub>4</sub> and niter in the methane hydrate phase with the formation of N-bases and ribose and the release of water
VI ***	Atmosphere:	N <sub>2</sub> /O <sub>2</sub> (with an admixture of CO <sub>2</sub> and H <sub>2</sub> O)
	Terrestrial globe:	interactions between nitrous bases, ribose, and phosphates yielding DNA- and RNA-like molecules; development of cellular living matter
* Faint young sun period.		
** Termination of the faint young sun period.		
*** Onset of the mature sun period.		

abiotic autoclave at a temperature slightly above 273 K; the autoclave must have a pressure release valve and equipment for repeated chemical analyses. Then, the experimenters should arm themselves with patience. Certainly, many technical problems must be solved before the experiment is undertaken, such as the creation and long-term maintenance of abiotic conditions, and the development of analytical methods, but the game is worth the candle.

We emphasize that such an experiment is in principle different from the well-known experiment described by Miller and Urey in 1953 based on the assumption that living matter appeared on the earth surface as a result of one or several stochastic events initiated by electric discharges in the atmosphere. Over the last 50 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 but inevitable transformations of concrete simple mineral substances governed by thermodynamic laws. Observation of processes leading to the formation of DNA in the proposed experiment could give evidence that the emergence of living matter is a natural phenomenon intrinsic in the atomistic world during a certain period of its development and that life has originated on the earth many times since the planet accumulated large masses of water and may be originating in our time.

It was mentioned that the LOH hypothesis opens up new prospects for the explanation of the monochirality of nucleic acids. Such an explanation may be sought in a computer experiment on the compatibility of DNA and gas hydrate structures.

A recent publication (see Ref. [113]) reports the discovery of huge colonies of prokaryotes 400 m under the seabed (deeper drilling was not performed) at water depths from 427 to 5,086 m in open areas of the Pacific Ocean and along the coastline of Central America. The concentration of living organisms in these colonies varies from a few thousand to several million per cubic centimeter and does not decrease with drilling depth. Submarine ground harboring bacteria contains methane hydrate. It is noteworthy that the bacteria are found near the American continent with its large niter

deposits (see Section 3.2). The authors of [113] believe that living and dead bacteria release methane and serve as a source of methane hydrate deposits. But another, equally verisimilar suggestion is in order. It may be supposed that the presence of bacteria in close proximity to methane hydrate and niter deposits under the sea bottom resulted in the formation of nitrous bases and D-ribose that later interacted with phosphates (widespread in the earth crust) and gave rise to DNA, etc. In this case, the discovery of the simplest bacteria under the sea bottom confirms our hypothesis. Temperatures of 274–299 K measured by the authors of [113] in the ground layers containing active prokaryotes require a separate explanation. Normally, the seabed temperature at a depth of more than 400 m is about 274 K and increases by 3 K per each 100 m of vertical drilling. Therefore, the temperature 400 m below the sea bottom must be only 286 K. It is unlikely that the metabolism of prokaryotes would result in a substantial increase in ambient temperature. One of the possible explanations of the unusually high temperature in the zone of prokaryote activity is the production of heat during the formation of DNA from mineral substrates.

It is worthwhile to mention that we predicted the formation of living matter in the past and at present at a depth of dozens and hundreds of meters under the sea bottom long before the publication of Ref. [113]. We suggested that one region where such formation is possible would be in the Pacific along the coastline of America, where a combination of inorganic and simplest organic substances creates favorable conditions for the synthesis of living cell components, while both temperature and pressure are conducive to the formation of hydrate structures. A similar conclusion was made in our paper [15]. Conditions in which the prokaryotes discovered in [113] exist are reminiscent of the conditions for the appearance of living matter described in our earlier publications.

To summarize, the LOH hypothesis comprises the hypothesis of the origin of living matter and sub-hypotheses concerning the nature of certain processes that contributed to the transformation of the earth's primary atmosphere and the formation of hydrated hydrocarbon deposits and perhaps

liquid hydrocarbons. We demonstrated that basic postulates of the LOH hypothesis may be helpful in the discussion of mechanisms of DNA replication and mitosis in the cells of living organisms. The main purpose of the hypothesis is to try to elucidate the enigmatic mechanisms of life origin and the functioning of living matter. This review is focused on the first of these puzzles posed by nature.

The LOH hypothesis has developed from experiments and from the discovery of a correspondence between the size of N-bases and other DNA components on the one hand and the size of the cavities in gas hydrate structures on the other hand. It may seem that these experiments are unrelated to the problems discussed in this review. Nevertheless, they motivated us to analyze modern concepts of natural phenomena with which it is concerned; taken together with the just mentioned geometric correspondence, they brought us step by step to the formulation of our hypothesis.

This hypothesis is original in terms of both physical essence (because it suggests that living matter originated in a certain geometric matrix) and concrete content (because it considers the ability of water to form structured gas hydrates as necessary and sufficient for the emergence of the simplest living matter under conditions that existed on the young earth). Also, the hypothesis is original in that for the first time it draws attention to the role of nebular hydrogen in all these processes. The LOH hypothesis provides a new approach to the solution to the problem of monochirality of nucleic acids. It comprises the following key postulates that distinguish it from the majority of other hypotheses of the origin of living matter.

(1) The LOH hypothesis interprets the process as the appearance of many essentially similar but slightly different polymer molecules arising from the interaction of two solid phases and their subsequent reaction with the third solid phase, as opposed to the process of the formation of separate polymeric molecules as a result of multiple collisions between gas molecules or dissolved molecules and a precursor.

(2) The LOH hypothesis postulates that primitive life originated on the earth many times and in different places (it probably continues to originate at present) and that the complete series of reactions from initial mineral substances to cellular organisms was completed within a single location.

(3) The proposed hypothesis specifies both the composition of the simplest substances that built up the simplest elements of living matter, nucleic acids, and divisible cells and the conditions under which the relevant processes proceeded.

(4) An important advantage of the hypothesis is the possibility of its experimental verification.

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