




From Minerals to Simplest Living Matter: Life Origination Hydrate Theory

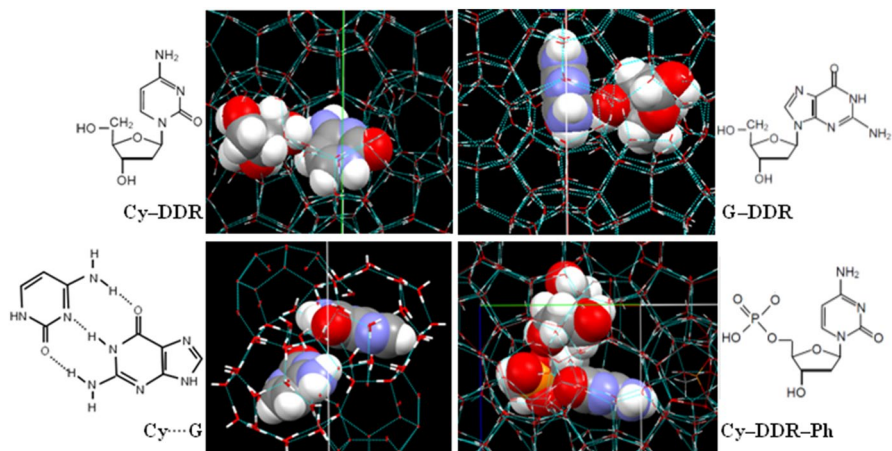
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Abstract

Long since, people tried to solve the mystery of the way that led to the appearance and propagation of living entities. However, no harmonious understanding of this mystery existed, because neither the scientifically grounded source minerals nor the ambient conditions were proposed and because it was groundlessly taken that the process of living matter origination is endothermal. The Life Origination Hydrate Theory (LOH-Theory) first suggests the chemical way capable of leading from the specified abundant natural minerals to origination of multitudes of multitudes of simplest living entities and gives an original explanation for the phenomena of chirality and racemization delay. The LOH-Theory covers the period up to origination of the genetic code. The LOH-Theory is grounded on the following three discoveries based on the available information and on the results of our experimental works performed using original instrumentation and computer simulations. (1) There is the only one triad of natural minerals applicable for exothermal thermodynamically possible chemical syntheses of simplest living-matter components. (2) N-base, ribose, and phosphdiester radicals and nucleic acids as whole are size-compatible with structural gas-hydrate cavities. (3) The gas-hydrate structure arises around amido-groups in cooled undisturbed systems consisting of water and highly-concentrated functional polymers with amido-groups. The natural conditions and historic periods favorable for simplest living matter origination are revealed. The LOH-Theory is supported by results of observations, biophysical and biochemical experiments, and wide application of original three-dimensional and two-dimensional computer simulations of biochemical structures within gas-hydrate matrix. The instrumentation and procedures for experimental verification of the LOH-Theory are suggested. If future experiments are successful, they, possibly, could be the first step on the way to industrial synthesis of food from minerals, i.e., to execution of the work that is performed by plants.

Graphical Abstract



Keywords Gas-hydrate structure in organisms · Methane hydrate as chemical synthesis medium · DNA natural synthesis · Genetic code prerequisite origin · Chirality phenomenon natural formation · Biological substances formation thermodynamics

Abbreviations

AA	Amino-acid
Ad	Adenine
Cy	Cytosine
DDR	Deoxy-D-ribose
DNA	Deoxy-ribonucleic acid
DR	D-ribose
G	Guanine
LMSEs	Living matter simplest elements (N-bases, DDR, DR, Ph, nucleosides, and nucleotides)
LOH-Theory	Life Origination Hydrate Theory
N-base	Nitrogen base
PAA	Polyacrylamide
Ph	Phosphodiester radical
Pu	Purine
Py	Pyrimidine
RNA	Ribonucleic acid
Th	Thymine
U	Uracil
X	Xanthine

*An honest man, armed with all the knowledge available to us now, could only state that, in some sense, the origin of life appears at the moment to be almost a miracle. So many are the conditions which would have had to have been satisfied to get it going. But this should not be taken to imply that there are good reasons to believe that it could not have started on the earth by a perfectly reasonable sequence of fairly ordinary chemical reactions. (Francis Crick, *Life Itself: Its Origin and Nature*, Simon and Schuster, 1981, p. 88.).*

1 Introduction: Origin of Life as a Tangle of Mysteries

At present, multitudes of diverse simplest unicellular bacteria, viruses, and simplest multi-cellular entities and of remains of long-extinct microorganisms are detectable underground and underseabed at different depths in various regions of the Earth. The species diversity of these entities is rather great and poorly explored. Their total mass is enormous and, according to some estimates, can exceed the total living-matter mass that occurs on the Earth surface and in ocean water. Among these living entities, there can be those who “eat” minerals to develop and propagate and, therefore, should be ranked with plants and those who “eat” plants or self-like entities and, therefore, should be ranked with animals. At present, it is known that underground and underseabed there are also viruses, which are incapable of propagating in ambient mineral medium but propagate through the colonization of other entities and utilization of their cellular material for spreading. We have no information on detection of coronaviruses either underground or underseabed.

These primitive underground entities play a significant role in human life; their remains make up the deposits of the so-called kerogen, which is widely used as the source of hydrocarbon fuel and as the feedstock for chemical and pharmaceutical industries. Some of the underground entities, when emitted to the Earth’s surface, can cause different diseases in plants, animals, or humans.

It is important to know, how the underground entities originate, evolve, and propagate and what benefit and what harm may be done by these entities and by the products of their metabolism to man and to the Earth’s flora and fauna. All these knowledges are important to development of effective and safe technologies for exploration and production of the underground and underseabed mineral sources of energy and feed stock.

But none of the questions about an evolution event dating back millions of years could be adequately answered being considered by itself in isolation from the related questions. This rule propagates deep into the millenniums and leads to the necessity of considering a multitude of the events that occurred in the past rearward to the origin of the subject under consideration. The memory of the origins is concealed in any natural phenomenon and only knowledge of the origins can give the key to the adequate understanding of its essentiality. A non-apprehended or misapprehended essentiality of a phenomenon leads almost necessarily to mistaken answers to the questions relating to its evolution.

Therefore, the problem of origination of the bacterial communities in the Earth’s crust upper layers is one of the problems of the temporal transformation of the young Earth mineral composition. In line with this, each unicellular bacterium contains a

DNA, which determines its development and vertical transmission of hereditary features, i.e., it is substantially similar to the cells of any highly developed living organism. And thus, origination of nucleic acids and bacteria can be considered as origination of the simplest life.

From times immemorial, people tried to identify the ways of appearance and propagation of living entities over the Earth and their own place in the world hierarchy. However, only in the past century, against the background of unprecedented development of science and engineering, researchers began to search answers to old questions on the basis of modern understanding in different fields of knowledge. The discussion of the problem of life origination and propagation has a thousand-year history. The extant systematization of the approaches to this problem and accumulation of the observations, investigations, and conclusions related to it started in the days of Georges Cuvier in the eighteenth century and continued by Jean Lamarck, Charles Darwin, and their contemporaries and successors. In the twentieth century, the public interest to the problems of the mechanisms of living matter origination, development, and propagation was intensified in connection with the broadening of the popular schooling and development of the means of communication. The causes and mechanisms of life origination, mass extinctions, Earth's glaciations, repeated astounding growths of Earth's flora and fauna with the onset of a great number of new species, and the possibilities of the appearance of hazardous natural phenomena in the future are discussed widely in the literature by biologists, paleontologists, biophysicists, cosmologists, and biochemists (e.g., Sole and Newman 2002; Alvarez et al. 1980; Schwartz 1999; Ostrovskii and Kadyshevich 2014a, 2017).

In 1993, it was reported (Schopf 1993) on the basis of paleontological studies that prokaryotic microorganisms existed on the Earth as early as at least about 3465 Mya; according to these studies, these entities emitted oxygen into environment. In 1996, the period of the bacterial life appearance at the Earth was shifted to earlier time by no less than by 350 Myr; the remains of the ancient living entities found in the Isua supracrustal belt, West Greenland, and at the nearby Akilia island were dated by the period no later than 3850 Mya (Mojzsis et al. 1996). It was reported that these remains were sampled in a carbonaceous medium within apatite grains.

Several hypotheses, authors and followers of which have tried to understand and explain somehow or other the sources, mechanisms, and moving forces of the living matter origination and propagation, were proposed and spread over the world. Some of them have received a wide acceptance.

Early in the century, Oparin (1924) proposed a repeatedly republished life-origination hypothesis. It was formulated before the revelation of nucleic acids as the transmitters of hereditary characters for living organisms and was based on the notion that just protein-like substances were the precursors of the emergence of entities at the Earth; Oparin thought that the external energy of electric discharges, hydrothermal sources, etc. was necessary for living-matter origination, that H₂O, NH₃, and CO₂, bubbles of which were discovered within ancient minerals, represent the remains of the Archean atmosphere, and that just these gases determined the synthesis of precursors of entities. For tens of years, Miller, (1953), Miller and Urey, (1959) tried to confirm experimentally Oparin's theory but scored no decisive

success. A critical consideration of this hypothesis is available in (Ostrovskii and Kadyshevich 2007a, 2007b, 2012a).

Another widely distributed hypothesis is the so-called Panspermia, idea of which reached us from the depth of centuries, was renewed in our days owing to numerous reports about findings of different organic substances and even DNAs in high atmospheric layers and within meteorites (Hoyle and Wickramasinghe 1981). According to it, life precursors or microorganisms had formed no one knows where and how, precipitated to the Earth, and transformed then into entities by a mysterious mechanisms. Panspermia bears on reports about findings of some amino-acids and even nucleic acids in the composition of meteorites and in the upper atmosphere. This hypothesis discusses where life was born but not how it began.

One more distributed hypothesis, the so-called RNA World, is based on the assumption that just RNA, but not DNA, played a key role in the process of the heritage vertical transmission (Kimoto and Hirao 2014; Lazcano 2014). Probably, it should be noted that Darwin thought that the first entities or several ones originated accidentally from molecules of minerals. This specification by no means exhausts all opinions on the appearance of living matter on the Earth.

Meanwhile, the extended scientific hypotheses contain no scientifically proved information on the ambient conditions promoting and preventing the living matter and nucleic acids origination processes, on the mechanisms of such processes and their thermodynamics, on the mineral substances from which the first entities originated, on the causes of the species diversity, and on the causes and mechanisms of chirality formation and racemization delay.

We developed the Life Origination Hydrate Theory (LOH-Theory), which considers and clarifies the phenomena and processes listed in the previous paragraph and some other, such as the conditions of the life occurrence at other celestial objects and the future dangers for the Earth's living matter from the Sun (Ostrovskii and Kadyshevich 2006, 2007a, 2007b, 2011, 2012a, 2012b, 2014b; Kadyshevich and Ostrovskii 2007, 2009, 2011a, 2015, 2016, 2017; Kadyshevich et al. 2013).

This theory considers the living matter origination and development line that had passed at its initial steps through formation of DNA and RNA nucleic acids, DNA double helixes, etc., as was discovered in the epochal works performed earlier in the mid-twentieth century. Most of the present eukaryotic species and a portion of prokaryotic species represent the extension and diversification of just this line of the living-matter development. In different time periods and in different environments, the kinetics of living matter origination on the basis of the DNA- and RNA-like entities could vary, the primary entities could receive various admixtures in their compositions, and all these could lead to formation of dissimilar primary species. According to (Madigan et al. 2019), the biological factors governing the metabolism of some living-matter species and even of entire domains, especially prokaryotic ones, can differ significantly in their chemical composition and structure from the Watson–Crick nucleic acids. The possibility of such a phenomenon and the mechanisms of origination and transformation of such entities are out of our general consideration.

In (Ostrovskii and Kadyshevich 2012b), we wrote the following: “In our opinion, living matter resulted from thermodynamically conditioned, natural, and inevitable

chemical transformations governed by universal physical and chemical laws, and such an approach underlies the LOH-hypothesis; Nature went step by step by its way from minerals to living matter and decreased gradually the Gibbs free energy at each step. Just as a result of the directedness of natural phenomena, researchers are principally capable of mental doubling back the course of Nature and, thus, of revealing the main milestones in Nature's progression. A naturalist must search for a "hook" in the environment in order to catch onto it and, having the thermodynamic laws as a guiding thread, to guess the logics used by Nature in its development." When writing "Nature", we keep in mind all phenomena that occur without the participation of people, irregardless what forces initiate these phenomena.

Shapiro (2000), Abel and Trevors (2006), Trevors and Abel (2004) noted fairly that a sum of random events is never capable of leading to an efficient result. If N-bases settle randomly along the polymer chains of the DNA and RNA molecules, these molecules carry no meaning and can produce no definite thing but a noise. We wrote in (Kadyshevich and Ostrovskii 2009) that the arrangement of DNAs and their constituents within the medium, in which living matter originated according to our theory, is not random. In this paper, we present the proofs of this statement. In this connection, we also clarify three more rather intimate questions, the last of which represents one of the most mysterious scientific problems.

These questions are as follows.

- How had it happened that the sequences of N-bases in DNA molecules are not random?
- Why neither the Cy–Ad bond nor the Th–G bond is realizable in the DNA double helixes?
- Why neither the Cy–Th bond nor the Ad–G bond is realizable in the DNA double helixes?
- What is the mechanism of origination of the DNA's prerequisites providing the capacity of DNAs to participate in the vertical transmission of principal species characters inherent in entities and thus to realize the genetic (biological) codes?

To answer these questions, we should formulate the LOH-Theory (Ostrovskii and Kadyshevich 2006, 2007a, 2007b, 2011, 2012a, 2012b, 2014a; Kadyshevich and Ostrovskii 2007, 2009, 2011a, 2015, 2016, 2017; Kadyshevich et al. 2013), substantiate it, and present the discoveries underlying it.

The question, of what minerals the simplest living entities could be first formed from, had been put by Eschenmoser (2007) in paper titled "The search for the chemistry of life's origin". However, these minerals were not revealed there.

Meanwhile, this question was answered by us earlier in (Ostrovskii and Kadyshevich 2006) and, repeatedly, in (Ostrovskii and Kadyshevich 2007a, 2007b, 2011, 2012a; Kadyshevich and Ostrovskii 2007, 2009). We specified the unique triad of the minerals capable of forming living entities and, all the more, revealed the conditions under which these processes could be realized and showed that the processes of living-matter formation proceeded with the heat emission rather than with the heat absorption as was assumed by researchers earlier.

Krishnamurthy (2012), an Eschenmoser's younger colleague, reasoned that "water, by far, would have had the most influence in determining the physicochemical properties of the molecules and in beginnings of chemical self-organization toward life's origin."

Meanwhile, six years before the paper just mentioned, it was showed that not liquid water but a solid gas-hydrate mineral matrix structure could be the maternal medium for LMSEs and simplest living matter formation as will be shown below.

The LOH-Theory is formulated on the basis of three important scientific discoveries and is the first to clarify, from what minerals, under what ambient conditions, in what medium, and by what mechanism the primary living matter was formed, its chirality and DNA's prerequisites for genetic code appeared, and the species diversity was stimulated.

The problem of the life beginnings at the Earth is, in our opinion, a biophysicochemical problem to a greater extent than a biological one. Indeed, the principal chemical components of nucleic acids and of proteins as well as the simplest living entities were generated by Nature from minerals on the basis of the natural physicochemical laws that govern chemical transformations of these minerals. Therefore, we consider the problem of simplest living matter origination in line with the scientific laws fixed for transformations of mineral substances and take that the chemical transformations of substances are regulated by the laws of thermodynamics and kinetics and can be influenced by steric effects and diffusion limitations.

A number of the principal statements of the LOH-Theory are obtained on the basis of simulation. While our earlier publications contained the two-dimensional graphic simulation only, this review paper presents widely the three-dimensional physicomathematical graphic simulation of polyatomic organic biomolecules and polymerized poly-radical fragments of nucleic acids within the matrix gas-hydrate structure. The three-dimensional simulation allows for the measurements of the degree of compatibility of the guest fragments with the host structure through the comparison of the equilibrium inter-radical bond lengths in the guest fragments with the corresponding bond lengths measured by the X-ray method in available works (see Table 1). The three-dimensional simulation is used in this paper at the step of the LOH-Theory foundation and at the step of its application for explanation of the observed phenomena.

The LOH-Theory development led us to formulation of the Mitosis and Replication Hydrate Theory (MRH-Theory) (Ostrovskii and Kadyshevich 2011, 2012b; Kadyshevich and Ostrovskii 2007) and Ageing, Optimal Nutrition, and Life-Prolongation Theory (Ostrovskii and Kadyshevich 2014c).

2 Three Discoveries: The Methodological Basis for Formulation of the LOH-Theory

2.1 First Discovery

In undisturbed highly-concentrated semi-liquid water/polymer systems, such as H₂O/DNA, the matrix gas-hydrate structure II forms at rather low temperatures around side functional polyatomic groups.

This discovery was first described and substantiated in (Ostrovskii and Kadyshevich 2000, 2002) on the basis of our adsorption, kinetic, and calorimetric studies of interactions in the PAA/water system (Ostrovskii et al. 2001). Investigation of this system allows for clarifying the water effect just on the Pu–Py bond in the DNA double helixes because of elimination of water interactions with phosphodiester and ribose radicals and because the bonds between amido-groups in the DNA–DNA double helixes are similar to the bonds between amido-groups in PAA–PAA dimers.

Such structures are honeycomb and include cavities, which are limited in their size by H-bonded water “host” molecules and most of which are occupied with “guest” molecules or atomic groups. Gas-hydrate structure II (Chaplin last updated July 2020) consists of large (0.56–0.69 nm in diameter) and small (0.36–0.48 nm in diameter) cavities; the diameter of the cavities can vary within the limits of no less than $\pm 15\%$ as dictated by the convenience of the situation, i.e., the lengths of H-bonds and, consequently, their energy can vary in rather wide limits. This important finding shows that the situations when some cavities of hydrate structure can be somewhat increased with decreasing of the adjacent cavities without destruction of the common structure are possible. The guests form no chemical bonds with matrix, are connected with it by Van-der-Waals forces only, and are capable of diffusing inside the structure.

This discovery is the preamble to the Second Discovery that proves the correctness of the first one.

2.2 Second Discovery

DNA molecules are structurally compatible with matrix gas-hydrate structure II: (1) the sizes of the N-base radicals entering into DNA composition conform to the sizes of the large cavities; (2) the sizes of ribose- and phosphodiester-radicals entering into DNA composition conform to the sizes of the small cavities; and (3) the lengths of the bonds connecting these radicals in DNA molecules housed within gas-hydrate structure II are equal to the lengths of the corresponding bonds measured by the X-ray method in DNA crystals.

We don't cast doubt on the occurrence of chemical bonds between the N-base radicals, ribose radicals, and phosphodiester radicals in the DNA strands, on the lengths of chemical inter-atomic bonds, and on the mode of H-bonding between DNA strands in the double helixes stated in the works by Crick, Franklin, Watson, Wilkins and their colleagues. The novelty is that the DNA double-helix conformation, defined by the angles of the single-valence bonds connecting the N-base radicals, ribose radicals, and phosphodiester radicals into the common structure, has been imposed in highly-concentrated water solutions (such as sperm) by the surrounding gas-hydrate matrix structure.

This discovery was verified by us on the basis of a two-dimensional consideration (Ostrovskii and Kadyshevich 2000, 2002, 2006, 2007a, 2007b) and confirmed by using three-dimensional schemes (Kadyshevich et al. 2013, 2014; Dzyabchenko and Kadyshevich 2013; Ostrovskii et al. 2014). For the calculations, we used a program

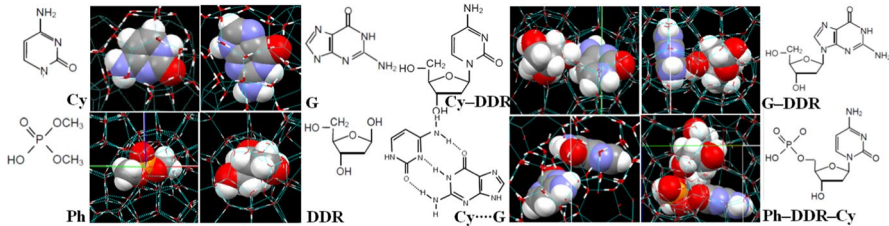


Fig. 1 Scaled arrangement of the DNA fragments in gas-hydrate structure II: cytosine (Cy) and guanine (G) in large cavities, deoxy-D-ribose (DDR) and phosphodiester radical (Ph) in small cavities; Cy in a large cavity—DDR in a small cavity; G in a large cavity—DDR in a small cavity; Cy...G pair in two adjacent large cavities; Ph in a small cavity—DDR in a small cavity—Cy in a large cavity. The spheres are the atoms of H (white), O (red), C (gray), N (blue), and P (yellow), the ideal matrix cavities are bounded with H₂O molecules. (color figure online)

developed by Dzyabchenko (2008), repeatedly tested by calculations of the structures of various organic substances by Reilly et al. (2016), and modified in (Dzyabchenko and Kadyshevich 2013). The structural characteristics of chemicals are taken from the Cambridge Structures Database (Allen 2002). The computer 3D descriptions of crystal structures and measurements of interatomic distances and angles between bonds were performed by using the Mercury program (Macrae et al. 2008).

Figure 1 demonstrates the scaled arrangements of cytosine (Cy) and guanine (G) in large cavities, deoxy-D-ribose (DDR) and phosphodiester radical (Ph) in small cavities, DNA fragments Cy-DDR, G-DDR, and Cy-G in two corresponding neighboring cavities, and Ph-DDR-Cy in three corresponding neighboring cavities within the gas-hydrate structure II.

We also modeled a number of other DNA fragments inside the corresponding cavities, namely, four-radical fragment Cy-DDR(-Ph1)-Ph2, five-radical fragment G-DDR1-Ph-DDR2-Cy, and seven-radical fragment Ph1-DDR1(-G)-Ph2-DDR2(-Cy)-Ph3.

From the Table 1, it is seen that the DNA fragments can be housed within this matrix with a striking accuracy of representation of the real lengths inherent in the inter-radical chemical bonds and inter-strand H-bonds. These results are, in our opinion, rather forcible.

The lengths of the interatomic bonds, obtained as a result of simulation under the condition of minimum energy of the corresponding fragments, were measured and were compared with those earlier measured by other researchers on the basis of the X-ray method. It was confirmed that the lengths of all bonds, modeled by us, coincide with those previously obtained by the X-ray method for DNA crystals within the limits of the measurement accuracy of the latter. Obviously, these results are sufficient to confirm the Second Discovery and the First Discovery.

No activation of the nucleotides is required under the natural conditions and within the methane-hydrate matrix. The methane-hydrate matrix and thermodynamics allow each radical located within the corresponding structural cavity in the neighborhood to a cavity occupied by another radical to form a chemical bond and, thus, to minimize its energy. Formation of such a chemical bond, i.e., the realization

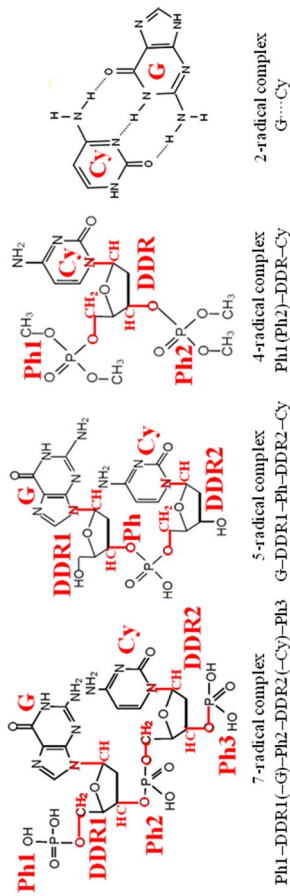
Table 1 Comparison of the lengths of the modeled inter-radical chemical and purine-pyrimidine H-bonds in some DNA fragments with those measured by the X-ray method

Substance (see the structures under the Table*)	Bond	Bond length (nm)			
		Our modeling	X-ray data, according to different sources		
7-radical DNA-fragment Ph1-DDR1(-G)-Ph2- -DDR2(-Cy)-Ph3	O(Ph1)-C(DDR1)	(First published)	Takusagama et al. (1982)	(Nucleic acid database)	Pauling (1960)
	C(DDR1)-N(G)	0.143	-	0.143	-
	C(DDR1)-O(Ph2)	0.145	0.155	0.146	0.153
	O(Ph2)- C(DDR2)	0.158	-	0.161	0.156
	C(DDR2)-O(Ph3)	0.141	0.142	0.144	-
	C(DDR2)-N(Cy)	0.141	-	0.143	-
5-radical DNA-fragment G-DDR1-Ph-DDR2-Cy	N(G)-C(DDR1)	Kadyshovich et al. (2014)	Takusagama et al. (1982)	(Nucleic acid database)	Pauling (1960)
	C(DDR1)-O(Ph)	0.145	0.151	0.147	0.153
	O(Ph)-C(DDR2)	0.143	0.142	0.143	-
	C(DDR2)-N(Cy)	0.141	0.142	0.144	-
		0.146	0.145	0.147	0.153
		Ostrovskii and Kadyshovich (2014a); Ostrovskii et al. (2014)	Sundaralingam and Jensen (1965)	(Nucleic acid database)	Pauling (1960)
4-radical DNA-fragment Ph1(Ph2)-DDR-Cy	O(Ph1)-C(DDR)	0.142	-	-	-
	O(Ph2)-C(DDR)	0.143	0.143	0.143	-
	C(DDR)-N(Cy)	0.147	0.147	0.147	0.153
2-radical DNA-fragment G-Cy	N(G)...O(Cy)	Ostrovskii and Kadyshovich (2014a); Kadyshovich et al. (2013)	White et al. (1978)	Ycas (1969)	
	N(G)...N(Cy)	0.287	0.293	0.284	
	O(G)...N(Cy)	0.295	0.296	0.292	
		0.288	0.293	0.284	

Table 1 (continued)

Substance (see the structures under the Table*)	Bond	Bond length (nm)	X-ray data, according to different sources
2-radical DNA-fragment G-DDR	N(G)-C(DDR)	Our modeling	X-ray data, according to different sources
		Ostrovskii and Kadyshevich (2014a); Dzyabchenko, Kadyshevich et al. (2013)	Takusagama et al. (1982)
		0.148	0.151

*Structures to the Table



of the thermodynamically favorable position, is achievable as a result of the mutual oscillations of the radicals capable of chemical bonding with each other.

2.3 Third Discovery

The unique triad of natural minerals, namely, CH₄-hydrate (possibly, also C₂H₆- or C₃H₈-hydrate) and NO₃⁻- and PO₄³⁻-ions (most probably, potassium or sodium niter and apatite), represents the triple source material necessary and sufficient for syntheses of all principal living-matter constituents, such as different DNAs, RNAs, AAs, polysaccharides, proteins, etc., with no external energy.

No biophysically and biochemically grounded and verifiable way of the DNA natural synthesis was earlier proposed. Meanwhile, we ascertained in the context of the second discovery the following.

First, no medium other than a mineral matrix could be used by Nature for the DNA syntheses and subsequent replications.

Second, no pair of different molecules or different minerals is known that could be capable of producing all living-matter constituents.

Third, no quartet (all the more, quintet or sextet) of different molecules or different minerals could practically multiply meet together for reproducible chemical reactions resulted in formation of any the same product.

These three points taken together mean that it is necessary to reveal a triad of minerals capable of chemically producing simplest living entities and a mineral matrix, within which this process could be executed.

Finally, we arrived at the conclusion that only one mineral matrix, satisfying Second Discovery, i.e., corresponding by its space structure and sizes of structural cavities to the DNA and RNA molecular sizes and structure, exists in nature. This unique matrix is the gas-hydrate structure II.

This Third Discovery was the generalizing one and was justified on the basis of thermodynamic approach, i.e., through approximate calculations of the changes in the Gibbs free energy during the chemical reactions that could lead to different DNAs, AAs, and proteins within gas-hydrate structures.

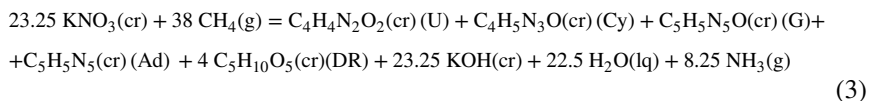
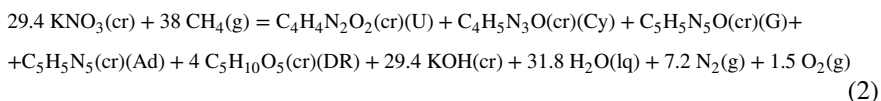
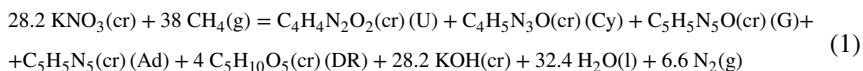
Besides the thermodynamic analysis, we also analyzed, as effectively as it can be done billions of years after the determinative events, the kinetics and mechanisms of the processes that, in our judgment, had underlain the simplest living matter formation.

Meanwhile, we used the data indicating that Nature had formed primordially, before living matter origination, underground and underseabed matrix hydrate structures and had filled them with methane and some other low-molecular normal saturated hydrocarbons. These data are detailed in the recent paper (Kadyshevich and Ostrovskii 2020) and in the papers cited there. In our opinion, just the availability of these mineral structured matrix deposits was and remains the prime condition implementing the possibility of repeated encounters of the CH₄, NO₃⁻, and

PO_4^{3-} particles together within bounded very small cavities and of their interaction up to formation of simplest living entities.

As for the thermodynamic grounds of the living matter origination process, they were considered in the papers (Ostrovskii and Kadyshevich 2006, 2007a, 2007b; Kadyshevich and Ostrovskii 2009, 2015) and in some other ones published, generally, in the special thermodynamic journals. The approximate calculations of the free energy change were performed for more than 90 simple chemical reactions included in the process of living matter formation from CH_4 , NO_3^- , and PO_4^{3-} . It was stated that the process of living matter origination from these minerals could be realized by Nature with a decrease in the free energy. Below, some principal results of these calculations are presented.

The processes of formation of DNAs, RNAs, and proteins from N-bases, DR, DDR, and AAs represent poly-condensation, which is usually thermodynamically possible (a decrease in the Gibbs free energy for the protein formation through poly-condensation of AAs is proved by us (Kadyshevich and Ostrovskii 2015)). Therefore, just the thermodynamic possibility of synthesizing of the full set of precursors (N-bases, DR, DDR, and AAs), which are necessary for living-matter origination from source minerals, determines the thermodynamic possibility of DNAs, RNAs, and proteins formation. Keeping in mind this statement, we calculated the $\Delta(\Delta H^0)$, ΔS^0 , and ΔG^0 values for three following conventional reactions, which represent three possible directions, each leading to formation of the full set of N-bases and DRs necessary and sufficient for synthesis of four RNA nucleosides with $(\text{Ad}/\text{G}) = (\text{U}/\text{Cy}) = 1$ (Ostrovskii and Kadyshevich 2006, 2007a, 2007b, 2014a; Kadyshevich and Ostrovskii 2009). Practically, all these reactions can simultaneously proceed in some relationship in the volume of any CH_4 -hydrate localization.



For reactions (1), (2), and (3), ΔG^0 (kJ/mol) = -8281 , -8121 , and -6146 , respectively. This means that all these directions of transformation of the source substances are thermodynamically possible and the relative contributions of these reactions into the common current conversion of source substances are determined by kinetic factors and depend on ambient conditions.

Each of these reactions represents the sum of the simple special reactions that lead to syntheses of the individual substances specified in the right side of the corresponding equation. The thermodynamic functions for all special reactions are presented in thermodynamic journals (Ostrovskii and Kadyshevich 2006; Kadyshevich

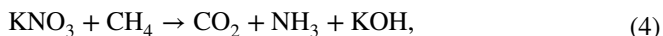
and Ostrovskii 2009), where the possibility of all these reactions was originally stated.

As applied to reaction (1), we calculated the ΔG^0 values for the conditions when $(Ad/G)=(U/Cy)=0.0625, 0.25, 4.00,$ and 16.0 ; the corresponding values of ΔG^0 (kJ/mol) = $-8227, -8244, -8318,$ and $-8336,$ respectively. It is seen that the decrease in the Gibbs free energy depends on the (Ad/G) ratio only slightly.

Thus, the natural syntheses of RNAs from CH_4 and NO_3^- -ions are thermodynamically possible within a very wide range of the (Ad/G) ratios. It should be noted that the processes under consideration can proceed in different appropriate periods of the Earth's history and, in each such a period, are capable of proceeding in different CH_4 -hydrate localizations, thus providing the species diversity (see, Ostrovskii and Kadyshevich 2014a).

When this work was being performed, the values of thermodynamic parameters for DDR were not available. However, the syntheses of DNA and RNA are very similar and the principal results of such calculations for these two nucleic acids should be the same.

In the periods, when the temperature increases, the side reaction



which leads to CH_4 oxidation up to CO_2 , proceeds. Carbon dioxide can be also produced as a result of oxidation of the living-matter components or remains. Therefore, the gas mixture over the methane-hydrate can contain CO_2 . Meanwhile, in the time periods favorable for the living-matter origination, reaction (4) is inhibited. The causes of its inhibition and of preferable formation of nucleosides through reactions (1)–(3) are considered in detail in (Ostrovskii and Kadyshevich 2012a, 2012b, 2014a). In short, they are as follows: (1) low temperature and, as a consequence, the thermodynamic front, i.e., slow steady-state C (–4) oxidation by N (+5); (2) DNA kinetic stability (the DNAs of the frozen mammoths are available even today); (3) elimination of N_2 (produced at the step of DNA formation) from the reaction zone. These features summed with the occurrence of excessive CH_4 -hydrate provide the stability of nucleosides.

We also considered the thermodynamic possibility for formation of the proteino-geneous AAs, i.e., those entering into the protein compositions, from natural gas and niter. The results are detailed in (Kadyshevich and Ostrovskii 2015). The ΔG^0 values for the reactions of formation of 14 AAs out of their total quantity of 20 were estimated. For six AAs, the calculations are impossible because the thermodynamic characteristics of the AAs either are not available or vary from one publication to another so significantly that specification of the correct values is problematic. The calculations for alanine and leucine were performed for L, D, and DL and for L and DL optical modifications, respectively. Thus, totally, the ΔG^0 values were calculated for 17 modifications of AAs. The ΔG^0 values are negative for 15 AAs and are positive for L-tyrosine and L-lysine. It was concluded that the entire set of the considered AAs can be produced by the associate mechanism with no external energy.

It was shown by us (Kadyshevich and Ostrovskii 2015) that the primary proteins could be produced together with AAs and DNAs from natural gas and niter and

the process of the primary protein formation could proceed with a decrease in the Gibbs free energy, i.e., with no external energy sources, within the cavities of the gas-hydrate matrix in the intra-cellular protoplasm as a result of poly-condensation of AAs. Apparently, proteins and cellular protoplasm with AAs synthesized in it as a result of interaction between CH_4 and NO_3^- -ions were in dynamic equilibrium dependent on the temperature and concentrations of the intra-cellular components. Such a state is similar to the equilibrium in the present living organisms, where proteins are able to hydrolyze with separation of AAs or with joining AAs, depending on the water concentration.

The conclusion that the possibility of protein formation from AAs, i.e., formation of peptide bonds, could be called in enquiry, because works by Dobry et al. (1952), Borsook (1953), and Flegmann and Tattersall (1979), although they present near-zero values for the free-energy changes in these reactions, give, all the same, no clear answer relative to the possibility of such reactions. However, the studies of these authors were performed in diluted aqueous solutions, where concentrations of substrate were of the order of 0.1 M and lower. Meanwhile, according to the LOH-Theory, the processes of living matter origination proceeded in the semi-liquid medium, where substrate/water molar ratios were significantly higher. Besides, the intra-cellular processes proceeded under the prebiotic conditions around 273 K without enzymes at a very low rate, while the authors of the works just cited used enzymes for acceleration of the reactions and these enzymes could change the reaction mechanism. In addition, the methane-hydrate localizations are usually associated with deposits of silica, which, according to McKee et al. (2018), is capable of accelerating the peptide-bond formation. Therefore, there are no grounds to think that the results obtained by Dobry et al. (1952), Borsook (1953), and Flegmann and Tattersall (1979), contradict our conclusion on the protein formation from AAs.

It may seem unexpected that the molecular oxygen is not required for the process of living matter origination and that the removal of the molecular oxygen emitted in the course of the first entities origination promotes this process in spite of the fact that all entities considered by us contain oxygen. However, that is really so and it is because the lower is the O_2 concentration, the lower is the rate of CO_2 formation and the higher is the relative rate of the living matter precursors synthesis from NO_3^- -ions; the advantage of the NO_3^- -ions results from the fact that the reactions that lead to the living matter precursors are the redox ones and the valences of the source substances should be coordinated. In addition, the use of O_2 and of any substance as the source of nitrogen could disturb the condition of the occurrence of triad of source substances and could make the process of living matter formation practically impossible.

Notice that just the N^{5+} and O^{2-} rather than source nitrogen and oxygen of any other initial valences should be included into the triad of the minerals (CH_4 -hydrate, NO_3^- and PO_4^{3-} ions) necessary and sufficient for the reactions of living-matter formation, because these reactions are the redox ones and the valences of the source substances should be coordinated.

It is known after the works by M. Kononov (1892, 1893a, 1893b) that alkanes are capable of reacting with NO_3^- -ions and of producing nitroalkanes as the primary

detected products (Konovalov's reaction). Sukhorukov (2023) With CH_4 , Konovalov's reaction proceeds slowly on the scale of usual laboratory experiments. Meanwhile, just low reaction rate is necessary for living matter origination, because the reaction steps should proceed slowly one after another in the direction of the gradual decreasing in the free energy of the reacting system.

Konovalov (1892, 1893a, 1893b), being experienced on the basis of his own pioneering studies of nitration of different normal saturated hydrocarbons, wrote in the paper (Konovalov 1893a): "...nitric acid is able of direct nitrating any saturated hydrocarbon; it nitrates paraffins, hexahydrobenzenes, and fatty chains of aromatic hydrocarbons... The difference is only in the following: how much time, what concentration, what temperature, etc. are needed for the desirable nitrating effect of nitric acid. In short, the difference is determined by the conditions only."

However, Konovalov didn't study the methane-nitration process. His above-cited works contain no data on CH_4 nitration; among normal saturated hydrocarbons, he studied hexane, octane (Konovalov 1892), and heptane (Konovalov 1893a). But the following studies had confirmed the generalization made by Konovalov. Moreover, the reaction of CH_4 nitration by nitric acid up to CH_3NO_2 formation was practically realized in production quantities.

This synthesis was described in details near 90 years ago in the work by Hass et al. (1936) and was repeatedly reviewed, for example, in the books by Fieser and Fieser (1961) and by Carey and Sundberg (2004, 2007).

Hass et al., summing up the results obtained in their laboratory, conclude in the paper of 1936: "The results obtained in this laboratory during several years of study of the vapor phase nitration of paraffins are reviewed. Nitromethane, nitro-ethane, both nitropropanes, and all four nitrobutanes are readily obtainable".

Fieser and Fieser in their book "Advanced organic chemistry", when citing the results obtained by Hass and his coauthors, write as follows: "When a gaseous mixture of two moles of hydrocarbon and one mole of nitric acid vapor is passed through a narrow reactor tube at 420° (760 mm. pressure), ethane, propane, and n-butane react rapidly. Methane is attacked only slowly at this temperature, but at 475° some 13% of the material is converted in each pass through the reactor into nitromethane, and the recovered hydrocarbon can be recycled."

Thus, there are no doubts that methane can be nitrated by nitric acid in a gas-phase flow reactor at 475°C with a so high reaction rate that it is sufficient for commercialization of this process. Meanwhile, for a reaction that proceeds as a result of intermolecular collisions, the reaction rate r can be written as $r = A \exp(-E/RT)$, where E is the so-called activation energy and A is the frequency of pair collisions of the molecules of reacting substances. This frequency is dependent on the temperature only slightly; namely, it is proportional to the absolute temperature. The rate of such a reaction decreases as the temperature goes down to the temperature range favorable for origination and metabolism of living entities. However, the reaction rate can't go down to zero.

The interaction of NO_3 -ions with alkanes was recently studied in the context of removal of nitrate-ions from air in the regions affected by oil/gas extraction activity (Zhou et al. 2019). These authors had corroborated Konovalov's data on the ability of NO_3 -ions to interact with alkanes. On the basis of kinetic experiments performed at about 298 K, they concluded that the reactions of NO_3 -ions with some alkanes

can contribute to the removal of alkanes from the atmosphere in the regions with high alkane concentrations. As an example, Zhou et al. consider the regions affected by oil/gas extraction activities. The rate of reaction of nitrate-ions with methane is rather low, however it not null is.

Thus, there are no doubts that the reaction of nitromethane formation from methane and nitrate ions is principally possible.

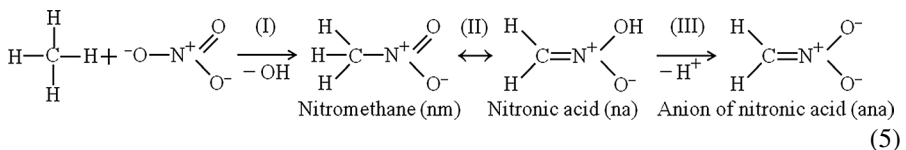
Under the conditions that exist within the methane-hydrate structure, the rate of this reaction is not limited by its kinetics. It is limited by the rate of diffusion of NO_3^- -ions into the external layers of the methane-hydrate structures. The rate of NO_3^- diffusion into methane-hydrate structures is, in turn, dependent on the concentration of NO_3^- -ions in the humid ground adjacent to these methane-hydrate deposits, ground composition, temperature, moisture.

In any event, the rate of this reaction can't go down to zero at the temperatures when the ground is defrosted and the repeated collisions between methane and nitrate molecules occur. All the more, such a reaction can't go down to zero between CH_4 molecules and nitrate-ions under the conditions of ion-molecular collisions. And this reaction should proceed in the direction of nitromethane formation, because this direction is thermodynamically caused and because the reaction of molecular mating is the simplest one in this system.

Under the conditions considered in this paper, the reaction mechanism differs principally from the mechanism of gas-phase interaction between CH_4 and nitric acid. The rate of nitromethane formation within methane-hydrate matrix structures is limited by diffusion of nitrate-ions into the gas-hydrate cavities rather than by the rate of the reaction between the pairs of CH_4 and NO_3^- particles within the cavities. However, the process within the cavities should proceed integrally in the same direction because it is thermodynamically caused. These two particles, being within a structural cavity, very quickly become transformed into nitromethane molecule.

The process of nitromethane formation within gas-hydrate structures is slow, as is written above. Meanwhile, just the slowness of the reaction steps stimulates the unidirectionality of the reaction directed to the steady decrease in the free energy of the reacting system.

Equation (5) illustrates our notion of the mechanism of reactions occurring at the initial steps of interaction between methane and nitrate-ions within the gas-hydrate structure at low temperatures, when the interactions are directed to origination of living entities and at elevated temperatures, when gas-hydrate structure doesn't exist, the living-matter precursors don't form, and the reaction process is directed to formation of aldehydes, ketones, and other substances that bear no relation to the living matter formation process.



This line of chemical equations allows explanation of our notion of the mechanisms inherent in the low-temperature reactions between methane and nitrate-ions

in the direction leading to formation of living matter precursors within CH_4 -hydrate localizations; particularly, this line of equations explains the cyclization of nitromethane molecules leading to formation of N-bases (see Fig. 2). Indeed, numerous extended colonies of different simple living entities were discovered repeatedly underground and underseabed within CH_4 -hydrate localizations, as it will be shown below in this paper. Apparently, the ancestry of these living entities could appear there by no other way except being formed from the minerals as it follows from the Third Discovery.

The mechanisms postulated by this line of chemical equations include also the available conception (Fieser and Fieser 1961; Carey and Sundberg 2004, 2007; Wikipedia 2022) of formation of aldehydes, ketones, and other products from the same pair of source substances at elevated temperatures, at which hydrocarbon-hydrates don't exist and, therefore, living-matter precursors can't be formed.

According to (5), the nitrate-ions react with CH_4 in the form $\text{O}^-\text{N}^+(\text{=O})(\text{O}^-)$ with formation of nitromethane (step I), and just this reaction step is the limiting one among the steps included into this reaction. Nitromethane (nm) is capable of reacting in two equilibrium temperature-dependent forms, $\text{H}_3\text{C}-\text{N}^+(\text{=O})(\text{O}^-)$ and $\text{H}_2\text{C}=\text{N}^+(\text{OH})(\text{O}^-)$, the equilibrium between which is shifted to the right at high temperatures, and in the form of nitronate substance $\text{H}_2\text{C}=\text{N}^+(\text{O}^-)(\text{O}^-)$.

The form $\text{H}_3\text{C}-\text{N}^+(\text{=O})(\text{O}^-)$ prevails under low temperatures.

Just this form initiates, as will be shown below in Fig. 2, the reactions directed to formation of living matter precursors.

The form $\text{H}_2\text{C}=\text{N}^+(\text{OH})(\text{O}^-)$ is termed nitronic (azinic) acid (na). Its molecules are capable of dissociating with formation of the anions of nitronic acid $\text{H}_2\text{C}=\text{N}^+(\text{O}^-)(\text{O}^-)$ (ana). This is nitronate substance, because it contains nitronate group $=\text{N}^+(\text{O}^-)(\text{O}^-)$.

We somewhat widen the available notion of nitronate, considering that R_1 and R_2 in their abundant form $(\text{R}_1)(\text{R}_2)=\text{N}^+(\text{O}^-)(\text{O}^-)$ can be hydrogen ions but not exclusively hydrocarbon radicals.

The high-temperature na and ana initiate formation of aldehydes, ketones, and of other substances detected by different authors earlier. Apparently, this direction of chemical reactions has no connection with the low-temperature direction of chemical reactions, which are directed to formation of living entities.

It is possible to show that N-bases can be obtained from nitromethane as a result of rather simple addition reactions (Fig. 2). The Ad and G molecules are formed from nitromethane molecules only and the Cy, Th, U, X, and Hx molecules are formed from nitromethane molecules and methane molecules, i.e., there are no N-bases whose molecules contain more N atoms than C atoms; the excessive H and O atoms form water, O_2 , H_2 , or transmit as ions into the so-called auxiliary gas within the CH_4 -hydrate structure and can participate in the subsequent reactions inside gas-hydrate matrix or outside it. Figure 2 illustrates the possible mechanism of Ad, G, Cy, and Th formation.

Figure 2 illustrates the possible mechanisms of formation of different N-bases. As it was noted above, their synthesis can be performed, in our opinion, on the basis of the nitromethane form $\text{H}_3\text{C}-\text{N}^+(\text{=O})(\text{O}^-)$. Line (1a) shows that it is possible to expect that ana can reveal itself in different forms during next reactions.

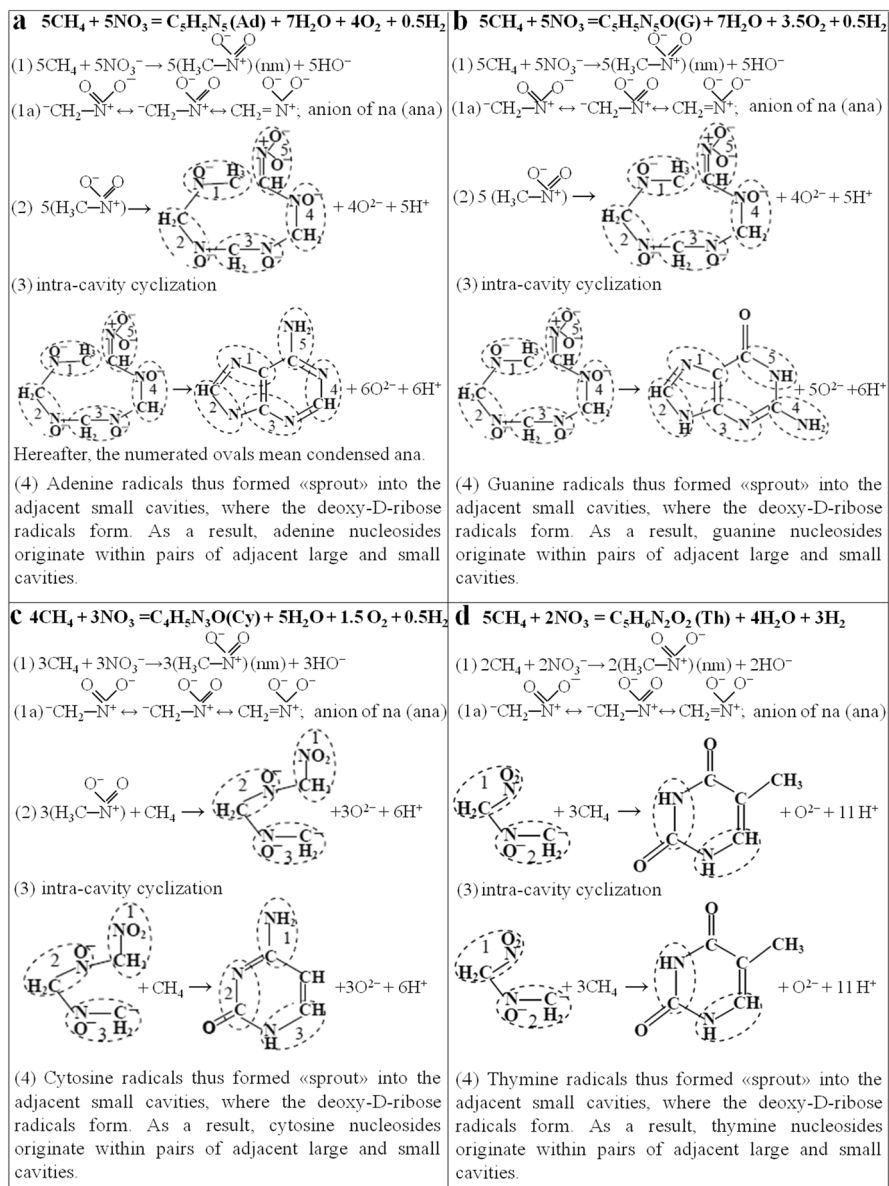


Fig. 2 Illustration of the stepwise chemical transformation of nitromethane and methane with formation of Ad (a), G (b), Cy (c), and Th (d) in methane-hydrate structure

The mechanisms of chemical reactions that lead to formation of different N-bases have some common features.

The addition reactions are characteristic, in our opinion, for natural syntheses of each of the necessary N-bases; namely, nitromethane molecules, being in their

active form, i.e., having free negative and positive valences at O and N atoms, respectively, found one another within some large structural cavities and get bonded there chemically with each other. The nitromethane radicals, incorporated into molecules obtained as a result of addition reaction, are outlined in Fig. 2 by dashed ellipses. Along with the nitromethane radicals, the CH_4 molecules, diffusing within the gas-hydrate structure, also can be enclosed into the growing intracavity molecules in the form of methyl radicals. The mechanism of formation of such molecules looks like the mechanism of catalytic polymerization of gaseous monomers with no solvent (see, e.g., Ostrovskii and Khodzhemirov 2001, 2002, 2003) but has some important distinctions.

To describe the similarity and difference of these two processes, we give just below an account of the mechanism of catalytic polymerization.

Each first adsorbed monomer molecule, capable of originating polymer chain, joins chemically by one its end with a catalyst. Therewith, a free valence at another end of this molecule forms. The next monomer molecules join one after another to the first adsorbed monomer molecule with formation of a polymer chain. In this process, the free valence migrates along the growing chain from the penultimate molecule to the last one. Just the occurrence of the free valence at the polymer chain end provides elongation of the chain. A variety of polymer molecules grows up simultaneously from a variety of the surface catalytic centers located in immediate proximity to one another. The chains become elongated to a certain length in the line out of the catalyst surface and bear one another owing to H-bonds that arise between them.

Formation of each N-base from nitromethane and methane proceeds as a result of a number of consistent addition reactions, similarly to the polymerization processes. However, the process of formation of N-bases has two principal distinctions.

The first one consists in the absence of any catalyst and in the self-initiation of the start of the reaction.

Nitromethane molecules are capable of reacting in the form of nitronic acid, and, thus, the nitromethane molecules can join together with formation of chains. The first immobilized nitromethane molecule has a free valence, and this free valence provides the joining of other molecules up to full admission of the structural cavity. Therewith, the free valence moves along the chain similarly to that in other polymerization reactions.

The second distinction consists in the cyclization of the growing polymer chains early in their development. The cyclization proceeds as a result of formation of each N-base within a structural cavity of a limited and rather small size. When a cavity is fully filled with the polymer, the last has potentially free valences of opposite signs at its ends. The chain is capable of forming cyclic molecule as a result of multitude of oscillations within the cavity. The cyclization proceeds in the moment when the distance between the ends of the molecule turns out to be about the length of the chemical bond between the end atoms. The sequence of diffusion of the nitromethane and methane molecules into different large cavities is not the same and the free valences are capable of migrating along the nitromethane molecules. Therefore, the nitromethane molecules can join to each other and to CH_4 -molecules in different ways and the filled large cavities can contain N-base molecules formed from

different numbers and differently joined nitromethane and methane molecules. As a result, the chemical composition of the N-bases is unequal.

According to Fig. 2, adenine and guanine are formed from five interconnected nitromethane molecules, but the way of their connection in G differs from that in Ad. Methane molecules have no time or have no possibility to enter into some cavities before nitromethane molecules. This figure also shows that each Cy molecule is formed from three nitromethane molecules and one CH_4 molecule and each Th molecule is formed from two nitromethane molecules and three CH_4 molecules.

Thus, our studies show that the first step of the methane reaction within the gas-hydrate matrix is its interaction with nitrate ions. This reaction leads to nitromethane formation. The subsequent nitromethane transformation “stands on the railing” conducive to formation of nucleic acids and simplest living entities. All reactions within the gas-hydrate matrix proceed very slowly as a result of low temperatures. Therefore, the reactions proceed from step to step in the direction of the gradational decreasing in the free energy of the system and stop at the full filling of the gas-hydrate structure cavities and formation of the bonds between the DNA components and after formation of the simplest DNA double strands.

The question can arise of why just NO_3^- and PO_4^{3-} -ions rather than some other ones diffuse into the CH_4 -hydrate structure. The point is that only those processes, during which the free energy of the system decreases, proceed in nature. Meanwhile, the CH_4 molecules are rather stable under the conditions about 273 K when methane-hydrate can exist. Factually, they are capable of reacting with NO_3^- -ions only. Therefore, being in immediate proximity to the methane-hydrate structures, these ions can be absorbed into the external layers of the methane-hydrate structure and can react with methane within structural cavities. Diffusion of the molecules of any other composition into the methane-hydrate structures is stimulated by nothing; by and atour, such a process would be thermodynamically unfavorable due to entropy decreasing. Diffusion of the polyatomic molecules into methane hydrate structures is limited by the sizes of the inter-cavity windows.

3 The Life Origination Hydrate Theory (LOH-Theory)

3.1 Basic Content

The LOH-Theory is presented below in its logical development. The description not always coincides with the sequence of publications.

- (1) In a number of scientific works performed in our group, PAA/water systems are considered as the model ones for understanding the water interaction with N-bases entering into the composition of nucleic acids. The results of our calorimetric and adsorption–desorption studies of highly concentrated water systems of polymers with side amido-groups showed that the matrix structure similar to the methane-hydrate structure II forms around these functional groups (Ostrovskii et al. 2000, 2001).

- (2) Detailed studies of this phenomenon allowed us to assume that the living-matter precursors, nucleosides and nucleotides, nucleic acids, amino acids, primary proteins, and protocells could be formed within the gas-hydrate structure (Ostrovskii and Kadyshevich 2000, 2007a, 2007b, 2012a, 2012b; Kadyshevich and Ostrovskii 2007).
- (3) The unique triad of minerals, namely, CH_4 and NO_3^- and PO_4^- ions, which are capable of forming the living-matter precursors, nucleic acids, AAs, poly-saccharides, proteins, and other components of primary living matter, was revealed. These minerals were chosen on the basis of studies of the available geological literature and keeping in mind that molecules of no more than three different minerals could repeatedly meet in one localization and that the living-matter-forming molecules react selectively, i.e., they react among themselves rather than with other molecules.
- (4) It was shown that the stoichiometric equation of the chemical reaction between the set of four nucleosides, namely, of U, Cy, G, and Ad nucleosides and the set of N-bases, four DRs, and carbon-free molecules can be written and balanced.

The results of the logic sequence (1)–(4) allow the conclusion that the nucleic acids were formed by Nature within underground and underseabed CH_4 -hydrate structures. Realizing that the set of three molecules of different substances but not the set of four or, all the more, of five ones could meet together repeatedly in some one place with a sufficient probability to interact chemically with formation of a sequence of intermediate substances directed to the production of simplest living entities, we tested various simple nitrogen-containing minerals as “sparring partners” for the methane molecules housed within large methane-hydrate cavities. We concluded that only N^{+5} particles are applicable for performance of necessary redox reactions with subsequent reactions with methane and phosphate ions to obtain living-matter precursors. The formation of nitromethane molecules proceeded, apparently, as a result of oscillations of pairs of these particles up to the state allowing the chemical-bond formation. The above-considered mechanism represents a possible kinetics of the first step directed to the formation of living entities from mineral molecules. After that, phosphate ions diffused from outside through methane-hydrate cavities to nitromethane molecules, reacted with these molecules, and so on.

It remained to understand in which direction such a reaction would proceed with a decrease in free energy.

To make clear the place of these equations in the history of formulation of the LOH-Theory, we should present our understanding of the principal kinetic and thermodynamic content of the complicated natural processes that proceed for some long-continued but limited historic periods underground or underseabed at limited depths.

It is well known that the living matter development was influenced by some external processes of the explosion type, in the course of which mass extinctions proceeded, and, after each of them, a new cycle of the conditions favorable for the life development started, new living matter, including new simplest living matter, had appeared again, and new flora and fauna had developed. The processes that influenced the Earth’s living matter so severely could be of the Earth or Solar origin.

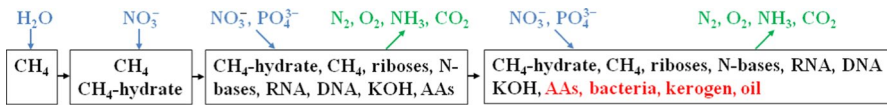


Fig. 3 The living-matter origination history compressed at most

Different opinions about their sources are available, and we don't consider this problem here.

On the basis of the above-described logic analysis, we arrived at the conclusion that the stoichiometric equation indicating the chemical possibility of the complete carbon transfer from the presumed set of methane and nitrate molecules into the predetermined set of the N-bases and riboses necessary and sufficient for the synthesis of four typical nucleosides would be an illustration of the possibility of the full chemical transformation of the proposed mineral source substances into the desirable products.

However, the stoichiometric correspondence between these two sets of the substances doesn't determine the direction of the chemical reactions that could proceed between them according to the thermodynamic law of a decrease in the Gibbs free energy of the system in the course of the chemical reactions proceeding with no external energy sources.

Therefore, in addition to the above-described statement of the stoichiometric correspondence, we also performed the detailed thermodynamic calculations to clarify the direction of the chemical process proceeding with a decrease in the Gibbs free energy in the reacting system composed from the source methane and nitrate and the resulted set of U, Cy, G, and Ad nucleosides.

We analyzed the direction of the reaction in this system (see Eqs. (1, 2, 3)) and in different other systems included into the integral process of living-matter formation not only on the basis of nitrate and methane but also ethane, propane, ethylene, or propylene (Ostrovskii and Kadyshevich 2006, 2007a, 2007b) to N-bases and riboses. We also calculated the approximate changes in the Gibbs free energy for the subsequent steps of living-matter formation, including AAs and simplest proteins formation on the basis of the same source substances; more than 70 such reactions with the results of the corresponding calculations are presented in the papers (Ostrovskii and Kadyshevich 2006, 2007a, 2007b, 2011, 2012a, 2012b, 2014a; Kadyshevich and Ostrovskii 2009, 2015).

It is possible to assert that the full process of living-matter formation, including its individual phases, undoubtedly proceeds on the basis of nitrate-ions and methane or ethane, undoubtedly, and ethylene, probably, with a decrease in the Gibbs free energy.

According to the LOH-Theory, the principal presumable sequence of the natural processes foregoing to formation of DNAs and cells from minerals can be described by Fig. 3.

In the post-glaciation periods of the Earth's history, when the temperature was slightly above 273 K and the intra-soil diffusion was already defrosted, the LMSEs could originate repeatedly in the underground CH_4 -hydrate localizations located not far from the Earth's surface (Ostrovskii and Kadyshevich 2014a). The occurrence of nitrate and phosphate salts, along with the occurrence of CH_4 -hydrate, in the near-surface layer

of the planet is the necessary condition for development of the living-matter origination processes on the Earth's surface. This conclusion has something in common with the opinion of Planavsky et al. (2010) who analyzed the Earth's phosphate distribution in time. They concluded that "an enhanced postglacial phosphate flux would have caused high rates of primary productivity and organic carbon burial and a transition to more oxidizing conditions in the ocean and atmosphere."

According to the Theory, methane and NO_3^- and PO_4^- ions were used by Nature for formation of living-matter precursors and subsequent synthesis of simplest living entities on the basis of thermodynamically grounded chemical processes without use of external energy. This doesn't mean that external energy could not be used in the processes of obtaining the components of the source mineral triad.

As the sources of nitrate-ions, Nature used planetesimals and interplanetary dust (Shmidt OYu 1958; Safronov 1969; Ostrovskii and Kadyshevich 2007a, 2007b, 2014a, 2014b, 2014c, 2014d, 2015; Kadyshevich and Ostrovskii 2010, 2011b, 2020) and also the nitrogen-containing atmospheric minor particles and ions obtained as a result of the lightning-like atmospheric discharges (Kasting and Siefert 2001; Wong et al. 2017) after oxidation of their nitrogen under the earthy conditions up to +5-valent state. Therewith, the local powerful deposits of nitrogen-containing salts could be formed by planetesimals at early stages of our planet formation. Meanwhile, the nitrogen-containing particles dispersed over the Earth's near-surface layer, apparently, were produced to a considerable degree by atmospheric electric discharges over a rather prolonged period. For the living-matter formation in the near-surface layer, the nitrate-ions obtained as a result of atmospheric discharges and dispersed over the surface layer from the local powerful deposits were used by Nature.

As for the phosphate-ions, they appeared in the Earth's surface layer, apparently, as a result of the planetesimal collisions with the Earth and cosmic dust precipitation (Shmidt OYu 1958; Ostrovskii and Kadyshevich 2007a, 2007b). According to the work by Hao et al. (2020), the phosphate distribution over the Earth surface layer was influenced to a considerable degree by the weathering of the phosphate localizations and the following propagation of the phosphate dust by water.

The NO_3^- and PO_4^{3-} ions diffused in moist soil into the CH_4 -hydrate localizations from saltpeter and apatite deposits. Such processes proceeded in buried solid or semi-liquid CH_4 -hydrate localizations not subjected to variations in the ambient conditions.

Because the processes of living-matter origination proceeded in the post-glaciation periods of defrosting of the Earth's surface, the temperature of the underground layers was at an approximately constant level and the methane partial pressure over any CH_4 -hydrate localization was almost constant. The gas pressure over the reaction zone was self-regulating. Namely, the stratum layer, if a gas-hydrate localization was underground, or the sum of the stratum layer and water column, if a gas-hydrate localization was under the bottom of a water basin, operated as a pressure valve and periodically threw off to the atmosphere the excessive N_2 and O_2 evolved in the course of the living-matter formation reactions (see reactions (1)–(3)) presented above; as a result of complete oxidation of a portion of CH_4 by NO_3^- ions, CO_2 evolved (Ostrovskii and Kadyshevich 2007a, 2007b).

Even in our days, there are regions where CH_4 deposits are rather close to the surface and methane emits out of the ground. In the nineteenth–twentieth centuries, the CH_4 -jets in Azerbaijan were so concentrated that they could be ignitable by flames. In addition, it is well-known after the Cassini–Huygens experiment that the Solar System objects can contain great amounts of hydrocarbons in their atmospheres and surface layers. On this basis, we state that CH_4 -hydrate localizations came into existence on the Earth in the periods of its cooling and some of them were slowly unfreezing in the periods of warming.

The Earth's CH_4 -hydrate, at least a portion of it, had formed at the Earth in the period of formation of the Solar System planets, before origination of the first entities at the Earth (Ostrovskii and Kadyshevich 2007a, 2007b; Kadyshevich and Ostrovskii 2009); this portion of CH_4 could form by two mechanisms: on the way to the Earth, similarly to formation of CH_4 discovered on Titan, Europa, and other Solar-System cold objects, and in the Earth's underground layers as a result of interaction between H_2 and CO_2 , as was considered in (Ostrovskii and Kadyshevich 2014a). At present, the CH_4 -hydrate deposits are widely distributed over almost all regions of the globe.

The questions on the occurrence of the closely-located CH_4 -hydrate deposits and sources of NO_3^- - and PO_4^{3-} -ions in the Earth's sub-surface layers are detailed in (Ostrovskii and Kadyshevich 2014a). It is impossible to say anything about the Earth's crust state of 4000 Mya. However, in our days, such regions occur. For example, several CH_4 -hydrate localizations occur along the shelf of California, Oregon, Peru, etc., sodium and potassium niters occur over the coastal continental heights of Chile, Bolivia, and California, and apatite deposits are in Northern Chile, Brazil, and Mexico.

There was an opinion that NaNO_3 of Atacama Desert resulted from decomposition of the bird metabolism products. However, the rookeries couldn't occur without water and water should eluate very-soluble niters rather than poorly-soluble phosphates from the bird metabolism products; meanwhile, the saltpeter ore of this region contains no phosphate. Therefore, there are no objective grounds to affirm that these saltpeter ores are of biogenic origin.

As is mentioned repeatedly in this paper, living matter had originated more than once at the Earth, when the appropriate conditions allowed its appearance. The distribution of the minerals in the Earth's near-surface layer varied with time. Its variations could be associated with the acceptance by the Earth of the interplanetary bodies and dust (Lankford 1997; Ostrovskii and Kadyshevich 2007a, 2007b) and single molecules and ions, the last obtained through atmospheric electric discharges (Kasting and Siefert 2001; Wong et al. 2017). Thus accepted elements, including nitrogen and phosphorus, could be oxidized in the close sub-surface layer and introduce a contribution to the processes of the living matter formation.

In the works (Canfield et al. 2010; Thomazo and Papineau 2013), it is noted that, in the Precambrian period of the Earth history, the nitrogen content in Earth's near-surface layer was controlled by the atmospheric and geological processes and the biosphere appearance and development coincided with the protracted oxygenation of the atmosphere.

As for the localizations of phosphates, they exist everywhere over the globe. It is commonly accepted that apatite $\text{Ca}_5\text{Y}(\text{PO}_4)_3$ ($\text{Y} = \text{F}, \text{Cl}, \text{or OH}$) is of mineral origin. In addition, phosphate-ions are dissolvable in different water sources. They could be transported to the Earth during and just after the period of the Earth formation, or phosphor-containing compounds could be oxidized in the period of cooling of the young planet. It cannot be also excluded that the Earth's surface had contained elemental phosphorus, which had formed H_3PO_4 solution through hydrolysis (Ostrovskii and Kadyshevich 2014a).

According to the LOH-Theory, nitrate-ions diffused into the external layers of methane-hydrate structures from the humid neighboring Earth's ground at 273 K and slightly higher temperatures, i.e., at the temperatures when the CH_4 -hydrate deposits exist, reacted with the CH_4 -molecules within the methane-hydrate structural cavities, produced there nitromethane, and thus gave start for subsequent organic reactions that led step by step to synthesizing of living entities.

The reactions proceeded slowly. Just low rates of the reaction steps stimulated the process that led gradually to formation of living matter precursors and, then, to formation of simplest living entities.

The processes that lead to living matter formation are governed by the mutable-in-time diffusion processes dependent significantly on the temperature and on the composition of the neighboring mineral bedrocks and their water saturation. Such processes cannot be characterized by any definite time-constant kinetics. The notions of the kinetic peculiarities for these processes under different concrete conditions could be obtained only after detailed experiments performed in autoclaves in different mineral mediums and at different constant temperatures.

The rate of nitromethane formation within any methane-hydrate localization is regulated, in general, by the nitrate concentration and temperature distribution over this localization and in its vicinities. For any concrete localization, these parameters are specific and their variations with time are different.

Any opinions about quantitative characteristics for such parameters in distant past and about their variations are untestable and are free for different fantasies. However, some factors influencing the temperature within and in the vicinities of CH_4 -hydrate localizations and, consequently, influencing the nitromethane formation rate, can be disclosed in terms of numbers. It is made below, and the results are used for a qualitative comparison of the rates of the reaction under consideration under the real conditions underground and underseabed with the rates of this reaction studied by Zhou et al. (2019).

It is known that the CH_4 -hydrate liquation temperature is under equilibrium with the pressure of the over-hydrate gaseous methane. The higher is the methane pressure, the higher is the gas-hydrate liquation temperature (Carroll 2009). According to our works (Ostrovskii et al. 2000, 2001), the hydrate structure, which is necessary for simplest living matter formation from minerals, survives in the semiliquid hydrate at a temperature somewhat higher than that characteristic for the start of the hydrate liquation process.

The maximum methane pressure over CH_4 -hydrate is determined by the counter-pressure of the overlying ground-column.

The greater is the depth of the burial for an underground or underseabed CH_4 -hydrate localization, the higher is the maximum temperature at which the CH_4 -hydrate localization maintains its gas-hydrate structure.

Meanwhile, according to the LOH-Theory, simplest living entities could be synthesized by Nature from minerals within the CH_4 -hydrate structures and nowhere but within them.

The higher is the temperature, the higher is the reaction rate.

The depth of the CH_4 -hydrate location can be 5000 m and more. For example, the extensive bacterial colonies were disclosed underground in western Siberia at as deep level as 6820 m; therewith, the colonies of living bacteria were associated with methane-hydrate deposits (Oborin and Khmurchik 2008). Usually, at the depths of more than 400 m, the temperature increases by at least $5\text{--}10^\circ$ per each 1000 m. This means that the temperature of this Siberian CH_4 -hydrate localization is at least 310–340 K and, most likely, even higher.

Because the reaction rate increases exponentially with the temperature, the aforesaid means that the nitromethane formation rate in the underground CH_4 -localizations can be rather high and, at least, significantly higher than the rate of similar process measured by Zhou et al. (2019) in their model experiments.

Therefore, the possibility of the underground and underseabed interaction of CH_4 with nitrate-ions is, apparently, beyond question. In any event, neither our studies of the available literature nor numerous peer reviews of our papers give grounds for justified apprehension in the possibility of such reaction under the conditions of CH_4 -hydrate existence.

Incidentally, it is also known that nitrate-ions decrease the methane production in ruminal culture (Liu et al. 2017).

The mechanism of this process is discussed, and different its interpretations are available. However, the most simple and consistent its interpretation is, apparently, that a portion of escaping methane interacts with nitrate-ions. As is written above, just nitromethane should be primary product of such a reaction.

Being based on the Newton's aphorism "Nature is simple and doesn't luxuriate in excesses", it is possible to think that this simplest mechanism proposed by us is the most plausible one and that the work (Liu et al. 2017) also counts in favor of the possibility of CH_4 slow interaction with nitrate-ions under low temperatures.

Note that we don't insist on the evidential force of the data of Liu et al. (2017) for the additional confirmation of the possibility of underground and underseabed slow interaction of CH_4 with nitrate-ions. We think that this interaction is proved by the data given above. We demonstrate the possibility of explanation of the phenomenon described by Liu et al. (2017) as the methane interaction with nitrate.

In the course of the breakup periods, the conditions favorable for simplest living matter formation were not at a great depth under the Earth surface.

In these periods, on the one hand, the temperature on the Earth surface should be sufficiently low for the CH_4 -hydrate to be not at a great depth under the Earth surface and not to dissociate up to water and gaseous methane and, on the other hand, the temperature should be somewhat higher than 273 K, for underground diffusion in the vicinities of CH_4 -hydrate localization to be defrosted and proceed being a slow process.

According to the LOH-Theory, just in the course of the breakup periods, when the temperature within the recently thawed CH₄-hydrate localizations and in their vicinities was only little more than 273 K, the conditions were most favorable for the start and development of the processes that resulted in the origination of simplest living matter on the Earth's surface. Such a temperature regime provides the condition of slow stepwise proceeding of the reactions in the direction of a gradual decrease in the Gibbs free energy over the entire volume of methane-hydrate localizations.

The primary living matter formation was initiated by diffusion of NO₃⁻ and PO₄³⁻ -ions into the CH₄-hydrate localizations. These processes led to formation of very different DNAs in each of these localizations. Reactions (1)–(3) and polycondensation led to liquation of these systems and formation of the super-cytoplasm (prebiotic soup). Therewith, the matrix gas-hydrate structure wasn't broken because of the sufficiently low temperature, high concentration of the biologically-active substances, and absence of agitation (see First Discovery). After liquation of CH₄-hydrate, subsequent development of the chemical reactions proceeded in the semi-liquid super-cytoplasm, which maintained the matrix structure, and led to subsequent formation of DNA and RNA molecules, AAs, first proteins, and proto-cells and their agglomerates and to development of the processes of DNA replication, mitosis, and separation of the unicellular entities into plants and animals.

Notice that, according to our terminology introduced and justified in (Ostrovskii and Kadyshevich 2007a, 2007b) and applied below in this paper, we term DNA and RNA molecules the simplest forms of the pre-cellular living matter. Therewith, we keep in mind that DNAs and RNAs represent individual entities, which are capable of fulfilling different functions in the processes that lead to formation and reproduction of living organisms. Such qualities as the chirality and ability of replicating originate at the step of appearance of the pre-cellular living matter. Just at the step of the natural synthesis of pre-cellular living matter, Nature forms DNA's prerequisites for creation of genetic codes. The LOH-Theory considers the physicochemical grounds of the transformation of inanimate mineral substances into the pre-cellular living matter possessing the above-mentioned qualities, including the prerequisites for creation of genetic codes and the mechanisms of the appearance of each of these qualities will be specified below.

The main factors that determined the evolutionary transformation of inanimate to animate are generally presented in descriptions of the First, Second, and Third Discoveries and detailed in (Ostrovskii and Kadyshevich 2006, 2007a, 2007b, 2012a, 2014a) (some points were advanced as the LOH-Theory had been unfolded); some special questions of formation of AAs and proteins are considered in (Kadyshevich and Ostrovskii 2015). The living-matter sources are specified in description of Third Discovery and are illustrated by Fig. 2.

The thermodynamics, in line with the geometry of the gas-hydrate matrix, participates in the specification of the composition of the N-bases incorporated into nucleic acids. This statement is confirmed by the reaction of hydrolysis of G. It proceeds in the closed system and without subsequent transformation by the reaction



In a medium, where G and NH_3 exist, equilibrium is shifted to the left (Ostrovskii and Kadyshovich 2012a, 2012b; Kadyshovich and Ostrovskii 2009), $\Delta G^0 = 7.32 \text{ kJ mol}^{-1}$. Meanwhile, the ΔG^0 magnitude is rather small and it is the cause of the occurrence of X in the compositions of some DNAs.

The primary DNA mono-strands had contained different and random nucleotide sequences in their compositions, because these sequences were not determined by any biological, physical, or chemical law or regulation, and the lengths of these mono-strands were determined only by the duration of the reactions of their natural syntheses and the ambient conditions.

In the semi-liquid super-cytoplasm, syntheses of new DNAs and their replication and syntheses of RNAs continued under conditions of diffusion of the NO_3^- and PO_4^{3-} ions from the environment. Under appropriate ambient conditions, this led to an increase in the concentrations of nucleic acids and of side organophosphorous substances within the reaction system up to a certain critical level, to precipitation of phosphor-containing membranes around DNAs, and, thus, to origination of primary proto-cells. AAs and primary proteins were synthesized in cells after their formation in the super-cytoplasm, through interaction between CH_4 , nitrate-ions, and S^{2-} -containing substances (H_2S , COS, and CH_4S), which are usually included into the CH_4 -hydrate localizations as admixtures; thermodynamics allows formation of the entire set of the proteinogeneous AAs and their poly-condensation with formation of the peptide bonds (Kadyshovich and Ostrovskii 2015).

Thus, just the underground and underseabed basins of super-cytoplasm were the first “crèches” for the incipient living matter. DNA molecules are capable of conserving their individual features for a long time outside the medium necessary for the life processes and under rather low temperatures, for example, in Antarctic ices, ancient remains, etc.

3.2 Food Revolution and Differentiation of Unicellular Entities into Plants and Animals

Usually, when thinking about origin of life, researchers of this problem don't subdivide this process into origination of plants and animals. Indeed, it is known after one of the top-ranked discoveries of the last century (Crick and Watson 1954) that DNAs of all species consist generally of the same five elements, H, C, O, N, and P, and are rather conformable and, therefore, it would seem that they could originate by the same mechanism.

And, indeed, according to the LOH-Theory and, apparently, in reality, living matter originated and existed in the most remote period of its development as the simple uniform phenomenon undivided into plants and animals and propagated through absorption of the minerals. The DNAs have come into being in those ancient times about 3,900 Mya or, may be, even earlier, because the minerals necessary for their creation appeared at the Earth much earlier.

At present, both these branches of living matter have DNAs of the same structure and of the same elemental set and these DNAs differ by the nucleotide sequences only. Each of the DNAs inherent in these both living-matter branches is aimed at

synthesis of a living organism. Therewith, the source material used by the DNAs of plants for their work differs principally from that used by the DNAs of animals for their work and the mechanisms used by the DNAs of plants for their work differ from those used by the DNAs of animals for their work, because the contents of these works are different and their final results are different as well. The first destination of each plant DNA consists in synthesizing of a plant parent-like DNA from minerals, while the first destination of each animal DNA consists in synthesizing of an animal parent-like DNA from the nucleotides that enter into the composition of the food.

The sole evident distinctive feature of the DNAs that determines not only the attachment of a DNA to such and such living-matter branch but also the species to which DNA relates is their nucleotide sequence. This fact illustrates the laconism of Nature, which managed to provide the existence of the millions of multitudes of so multiform entities through only one characteristic of some chemical substance.

Meanwhile, though both these branches of living matter have DNAs, which contain the plan of development of each individual organism, of the same structure and elemental set, they use not quite the same simplest sources for their formation, and all other component parts of the plants and of the animals are constructed on the basis of not quite the same primary sources. Namely, although the today progenies of the currently existing plants and animals in more or less early period of their development all receive just maternal nutrition through seeds, fruits, bellies, ova, grains of roe, or eggs, the posterior nutrition of the entities of these two living-matter branches differ principally in the methods and contents. Indeed, though the plants use minerals from the environments, while animals use, substantially, organic products formed within plant and animal bodies. Even so, the DNAs of animals differentiate principally from those of plants by nothing but the sequences and relative proportions of the nitrogen bases, i.e., by the same characteristics that discriminate DNAs of different animals.

This feature gave us an important hint; owing to it, we understood that the vegetable DNAs originate underground from minerals, while the animal DNAs originate from the vegetable ones, not only underground but on the Earth surface and in water basins as well, because animal DNAs come into being just through transpositions of plant nucleotides rather than in some more complicated way. This, maybe, could proceed even with the DNAs of lifeless plants as a result of the millenniums-old variations under the natural conditions in the course of the glacial and post-glacial periods.

Apparently, the separation of living organisms into plants and animals began at the stage of unicellular entities in the unfavorable periods when the diffusion of the nutrition, PO_4^{3-} - and NO_3^- -ions, into the CH_4 -hydrate localizations was insufficient. Due to the lack of nutrition, some unicellular entities could begin to “feed on” other ones that were dissipated in the super-cytoplasm soup. The “entities-killers” destroyed DNAs of the “entities-victims” up to nucleotides and used this material for their own extended reproduction. They were the first animals. Other entities, i.e., plants, continued to use the mineral food.

Thus, just the “food revolution” separated the primary simple uniform phenomenon of living-matter origination into two different branches of plant and animals.

Apparently, at the first step of the “food revolution”, some plant organisms kept the ability of using two forms of feeding, the mineral and plant ones, for their metabolism. With time and in the course of evolution, the “mineral-eating” and “flesh-eating” entities turned out to be more viable than the “pitcher plants”, may be, as a result of a more complicated constitution of their organisms. Today, only about 600 species of the pitcher plants, which populate the places with lack of mineral food, are known.

The “food revolution” increased the rate of extended reproduction of the animal species; their DNAs originated more frequently, because, instead of the syntheses of original nucleotides from mineral “bricks” (CH_4 , NO_3 , and PO_4), animals used ready “structural panels” (nutritional nucleotides) and, thus, accelerated their reproduction and formation of new species as a result of mutations and species splitting.

Multitudes of different plant and animal organisms arose within the CH_4 -hydrate localizations and in their nearest vicinities where DNAs and primary cells were carried out by water or gas flows. The “food revolution” had initiated the present almost-fivefold dominance of the animal species over the plant species.

According to Zhang (2013), the number of animal species was in 2013 about 1,660,000 (about 134,000 fossil ones) in 40 phyla, including vertebrates about 85,000 (among these, about 36,000 “fishes” and 20,000 fossil ones). As for the plants, different publications give from 250,000 to 350,000 species. It is seen that, at present, the number of the animal species exceeds the number of the plant species by a factor of 5–6.5.

Thus, the increased reproduction rate of the animal species in comparison with the reproduction rate of the plant species and the present dominance of the animal species over the plant ones resulted from the difference in the reproduction mechanisms of these two living-matter branches initiated by the “food revolution”.

3.3 Chirality and Racemization Delay Nature and Origination Mechanism

The LOH-Theory allows solution of the two-century-old mystery of why all principal natural biologically-active organic substances are mono-chiral.

As this paper is intended for a wide variety of researchers, and the interrelated phenomena of chirality and racemization delay in general and as applied to living matter are rather specific and complicated not only for general public but even for naturalists, we consider necessary to describe as briefly as possible the biophysical essence and principal regularities of these phenomena and the content of the terms that will be used below. When considering the subject matter relating to living matter origination and development, it is impossible to skirt these two phenomena, because they relate so closely to this subject matter that the aphorism “There is no life without chirality” is rather popular in the scientific literature.

A molecule is termed chiral if the space positions of all atoms and atomic groups entering into its composition don't allow for their overlapping on their reflections in

an ideal plain mirror at any rotation or displacement of this molecule in the three-dimensional space.

Chirality phenomenon can be defined as the ability of molecules, falling into some symmetry groups and characterized by a definite common chemical composition and by a definite chemical composition of each of the atomic groups included into them but differing in the spatial arrangement of some of their atoms or atomic groups, to reveal not the same biological, physical, and chemical properties; therewith, such properties of multitudes of chiral molecules of any one composition as the boiling and melting points and NMR, IR, and UV spectra are the same independently of the ratio of the molecules characterized by different arrangement of the atoms or atomic groups in these multitudes.

Thus, chirality is a geometric property, and the chirality property inherence in the molecules of a definite composition is determined by the type of their symmetry. Therefore, the chiral molecules can be revealed among the molecules of different geometry through their attribution to definite symmetry groups. The necessary but not unique chirality sign peculiar to a molecule is the occurrence of no symmetry in its structure (e.g., Kadyshevich et al. 1976). The existence of one or several so-called chiral centers in the composition of a molecule is an important but not determining sign of its chirality. As the chiral centers, the sp^3 -hybridized tetrahedral carbon or some other atoms chemically connected with four different atoms or atomic groups are most meaningful. Two mirror-like tetrahedral arrangements of substituents around such an atom are possible. In other words, chirality of a molecule is determined by the definite peculiarities in the symmetry of the arrangement of its atoms. The structure of such molecules can be so complicated that the ascertainment of the character of symmetry of atoms entering into it is a difficult task. A special procedure for the recognition of chiral molecules on the basis of analyses of molecular structures was proposed by F. Cotton (see Polavarapu 2018).

Chirality is one of the principal features of DNAs, amino-acids, proteins, and almost all other living-matter components; the plants synthesize chiral substances in their bodies from the terrestrial minerals and atmospheric carbon dioxide, and the animals take the chiral substances synthesized by the plants as the nutrition to live and to propagate over the Earth. It is impossible to understand the mechanism of living-matter origination without understanding of the chirality phenomenon origination mechanism. The understanding of the importance of chirality of the food substances and of the mechanism of their synthesis from minerals is the problem of prime importance for population, because this understanding is necessary for production of artificial nutrition and medicinal substances.

Chiral molecules are capable of rotating the light polarization plane. This feature is termed optical activity, and the molecules that reveal it are termed optically active. Optically active molecules of any one chemical composition can exist in nature in the form of optical antipodes, which, being under the same conditions, are counter-rotating the light polarization plane by an equal angle. Thus, such molecules represent optical isomers. They are termed enantiomers as opposed to other isomers, which also have equal chemical compositions and differ in some their properties. The history of medicine of the last decades knows a number of examples that show

positive and negative therapeutic effectiveness of the substances of the same chemical composition but inverse chirality. The type of chirality and the ratio of enantiomers are also important in examination of the quality of articles of food and in other fields.

The optically active substances counter-rotating the light polarization plane are conventionally subdivided into the dextrorotatory and levorotatory ones. The direction of rotation is determined from the observer's point of view; therewith, the substances rotating the light polarization plane clockwise are termed dextrorotatory and the other ones are termed levorotatory. The dextrorotatory and levorotatory substances are specified as the D- and L-substances, respectively.

It is known that the chiral organic molecules, i.e., those not identical to their own mirror images, are always optically active, but the molecules with chiral centers are, as a rule but not always, optically active. Just the absence of any symmetry rather than the occurrence of chiral centers is the precondition for chirality (Bruice 2007). The molecules of the so-called meso-compounds contain one or several tetravalent carbon atoms connected with different substituents, i.e., contain chiral centers and, with it, are identical to their own mirror images; therewith, they are characterized by the internal symmetry and, therefore, they are achiral and, thus, are optically inactive. As an example of such molecules, the meso-tartaric acid can be named.

The mixtures of equal quantities of enantiomers of the same chemical composition are optically inactive, because the oppositely directed and equal in value chiral effects cancel out. Such mixtures are termed racemic mixtures or racemates. In the liquid phase, the non-optical properties of racemates are usually identical to those of pure enantiomers; in solid state, such properties of racemates as the melting temperature and heat and the solubility differ from those inherent in pure enantiomers.

Thermodynamically, L- and D-enantiomers are practically equivalent. Therefore, it would seem that L- and D-enantiomers of the natural biologically-active substances should be formed in equal quantities, giving racemic, non-chiral substances. However, L- and D- enantiomers are produced in nature in different quantities and biologically-active substances are usually chiral; therewith, a majority of the chiral natural substances, such as nucleic acids, amino-acids, monosaccharide, proteins, etc. occur in the forms of one enantiomer. The cause of this situation was up to now one of the mysteries of the living-matter origination and propagation process.

To solve this mystery, we consider the mechanism of the chirality appearance by the examples of AAs and DNAs. Some aspects of the chirality problem were considered in (Ostrovskii and Kadyshevich 2014a; Kadyshevich and Ostrovskii 2016).

The chirality of AA molecules is, in our opinion, the consequence of the origination of tetrahedral C-atoms at one of the first steps of natural synthesis of these molecules and of the subsequent formation of different quantities of enantiomeric molecules characterized by different symmetries of atomic groups in the vertexes of the tetrahedron around this C-atom. Below, we describe the sequence of the corresponding reactions.

Consider a multi-component reactive system, where the molecules of one of the components are capable of forming a chiral molecular mixture as a result of chemical interactions with the molecules of other nature. We term the molecules of this component "source molecules". As one of the conditions, each source molecule

should have a tetrahedral C-atom in its composition or should obtain such an atom as a result of the first steps of chemical interactions in this reactive system. This tetrahedral C-atom should be bonded with two radicals (radicals 1 and 2) of different chemical nature and with two other chemically-identical radicals (3 and 3'). Radicals 1 and 2 should be located in such a way in the molecular composition of the source molecule that the approaching of any potential reagent to radical 3 requires overcoming energetic or mass hindrances which are stronger than those preventing the approaching of an analogous reagent to radical 3'. In other words, the chemical reaction of some substance with radical 3' proceeds easier and, as a corollary fact, more frequently than the reaction with radical 3. Therefore, the rate of the reaction with the radical 3 is higher. When the molecules of component 4 of this system enter into a substitution reaction with the source molecules and, as a result of this reaction, radicals 4 (atoms or atomic groups) replace radicals 3 and 3' in the source molecules of this system, it is obvious that the rate of substitution of 3' is higher than the rate of substitution of 3. Therefore, the quantity of the newly-formed molecules, in which the sequence of the radicals in the vertexes of the tetrahedrons formed by the substituents located around the central C-atoms is 1, 2, 3, 4, exceeds the quantity of the molecules, in which the alternative sequence is 1, 2, 4, 3'. Meanwhile, it is known that just the occurrence in a molecule of a C-atom bonded with four different radicals makes this molecule chiral and that the sequence of the arrangement of these radicals in the vertexes of the tetrahedral surroundings of this C-atom determines the type of chirality. This means that the reaction mechanism described above is capable of forming chiral substances, in which chirality results from the occurrence of tetrahedral C-atoms surrounded by different radicals. Just such molecular structure causes the chiral structure of AAs and proteins. In the sequel, the addition of new atoms or atomic groups to radicals 4 will aggravate the differences between the molecules containing the sequence 1, 2, 3, 4 and molecules containing the sequence 1, 2, 4, 3' and will hamper the racemization. Somewhat below, the dependence of the type of chirality on the sequence of the substituents around the chiral C-atom will be illustrated by the example of alanine.

The above consideration shows that the appearance of the property of chirality in a molecule can be caused by the kinetic factor, namely, by the diffusion delay in the attachment of an atom or atomic group to a precursor of this molecule into one of two possible positions due to steric hindrances.

Thus, the steric peculiarities, inherent in the molecules of some substances with included tetrahedron carbon-atom, are capable of leading to chirality of the products resulted from some chemical reactions of these substances with definite other substances.

Apparently, just the above-described mechanism of such a type is used by Nature for synthesizing AAs from methane and niter.

As for the DNA (RNA) structural features providing chirality of these molecules, they are considered in (Ostrovskii and Kadyshevich 2014a), and we do not detail this subject here due to the briefness of the paper. The consideration in (Ostrovskii and Kadyshevich 2014a) is given in the context of the LOH-Theory.

The DNA optical activity, as such, surprises nobody, because the DNA molecules include asymmetric four-substituted C-atoms and form double helixes and because

the plane-polarized light rotation phenomenon is inherent in different organic molecules which are asymmetric or have topological chemical bonds.

Meanwhile, the cause of the monochirality of the biologically-active substances and the mechanism of appearance of this amazing property has represented an unsolvable mystery from the time of the Pasteur's discovery. It became more stirring from the mid-twentieth century when the studies of the determining role of the dextrorotatory DNAs and levorotatory amino-acids and proteins in the processes of the living matter development had got a powerful pulse in their development as a result of the DNA structure discovery and the subsequent achievements in biology. A great number of unexpected in their courage and originality hypotheses on the sources of monochirality of biologically-active molecules were published. As no realistic chemical understanding of this phenomenon was proposed, the physicists went to bat for chemists and biologists. Among the assumptions, such ideas as the inscrutable effects of the fundamental universe asymmetry and weak interactions responsible for the atomic beta-decay (Ulbricht and Vester 1962), hypothetical intensification of the minor differences in the reaction ability of different mirror isomers by large-scale systems (Kondepudi and Nelson 1985), asymmetric biota as the result of "struggle for survival" between two branches of antipodal life (Frank 1953; Avetisov and Goldanskii 1996), and others were proposed with no concrete justifications. These assumptions had been discussed in (Ostrovskii and Kadyshevich 2007a, 2007b). As opposed to (Ulbricht and Vester 1962; Kondepudi and Nelson 1985; Frank 1953; Avetisov and Goldanskii 1996), a simple physicochemical mechanism based on the occurrence of steric hindrances in the course of some chemical reactions was proposed in (Ostrovskii and Kadyshevich 2014a). This mechanism is developed in this review.

The chirality phenomenon is known not only in organic chemistry but it is also known as applied to some inorganic materials. For example, quartz is chiral.

Up to the LOH-Theory development, an opinion existed that such living-matter components as N-bases, phosphates, and riboses originated independently and met then together at any one point through some mysterious mechanism. Meanwhile, the possibility of such a mechanism gave birth to a number of puzzling questions relative to the chirality of the living matter components. First, the mechanism of the natural synthesis of each of the substances necessary for the living-matter origination was incomprehensible; second, the process of separation of chiral enantiomers from the mixtures of the thermodynamically equivalent enantiomers seemed impossible; and, third, the meeting and reacting of necessary substances in any one point seemed to be of extremely low probability. The mysteriousness of the process was multiplied, because the combination of the source natural minerals necessary and sufficient for living matter origination was unknown and the natural conditions that could provide the synthesis of chiral nucleic acids of so specific composition and structure seemed impossible. Moreover, any thinking researcher could understand that the beginning of the process of living matter propagation over the Earth could not be provided by mysterious act of the birth of any one entity with included chiral components and that similar acts should had been proceeding multiply and not far away from each other and,

thus, the same chiral components must be formed in different localizations and in similar combinations.

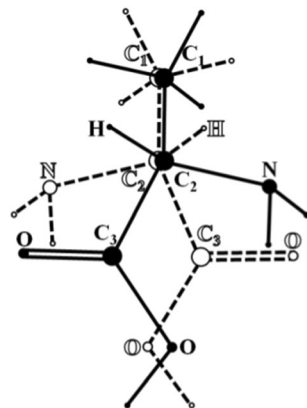
The LOH-Theory gives a principally new elucidation of all these puzzling questions. Its answers are unexpected and, within the framework of this theory, are natural. It turns out that there was no necessity to join D-ribose with N-bases; indeed, there was no necessity to separate D-ribose from L-ribose; and, more than that, there was no necessity to produce D-ribose. It turns out that the chiral nucleosides were synthesized by Nature in the appropriate periods of the Earth's history within a number of localizations and a lot of different but similar DNAs originated in any one localization. As was assumed by Bonner (1988), the chirality of the living matter components is credited with the living matter origination process. According to the LOH-Theory, no ribose as such forms when DNAs are being produced from CH_4 and nitrate- and phosphate-ions inside the hydrate structure. The N-base radicals, after their formation from CH_4 and nitrate-ions within the large gas-hydrate cavities, "sprout" into the neighboring small structural cavities and step-by-step synthesize the nucleoside radicals. The spatial structure of these radicals is determined by the stereochemistry of the intra-matrix reactions. Then, obeying the thermodynamic front and kinetic regulations, the ribose-like "tails" become the three-leg junctions between the N-base radicals and the pairs of phosphodiester radicals. These junctions are similar in their chemical composition to the deoxy-D-ribose radicals but they have never been the deoxy-D-ribose molecules and they are not identical to them in their three-dimensional structure. Namely, their pentameric rings are somewhat twisted (Ostrovskii and Kadyshevich 2014a; Ostrovskii et al. 2014; Sundaralingam and Jensen 1965) as compared to the ribose rings and the geometry of their side HOCH_2 -groups somewhat differ from those of deoxy-ribose.

Thus, according to the LOH-Theory, the DNA origination process does not require the deoxy-D-ribose selection from the mixtures of enantiomers and the DNA's chirality has the natural explanation.

The LOH-Theory allows for revealing the cause of the absence of the subsequent fast racemization of thus produced chiral substances. The fact is that, according to this theory, each polyatomic natural biologically-active molecule is synthesized individually within a separate gas-hydrate cavity or within two adjacent cavities. This process proceeds with no agitation and under a rather low temperature, when the newly-formed large molecules localized within corresponding gas-hydrate cavities are incapable of diffusing within the matrix structure and do not meet each other. Meanwhile, this matrix structure is traversable for the small particles, which are the precursors for the newly formed large polyatomic molecules. If the process under consideration were proceeding in an agitated solution, the molecules would collide with each other, exchange by their polyatomic groups when colliding, and equalize their L- and D-isomers.

Thus, the cause of chirality of the above-considered natural biologically-active molecules consists in their formation in gas-hydrate matrix. As these molecules increase in size due to intra-matrix chemical reactions, their movability reduces gradually to zero.

Fig. 4 Scaled scheme of superposition of alanine D and L enantiomer molecules: D and L schemes are given by solid and dashed lines, respectively; C₁–C₂ bond projections of the structures on the drawing plane are superposed (H atoms, not used in this consideration, are not labeled); the geometry of the molecules is scaled; C₁, C₃, H, and N atoms are the vertexes of the tetrahedron with the central C₂ atom



The laboratory experiments proceed in solutions, in the N_2/O_2 atmosphere and with mixing; to increase the reaction rate, chemists, on frequent occasions, perform the reactions on heating. Under such ambient conditions, the gas-hydrate structure doesn't form and the steric difficulties don't arise. Therefore, under the laboratory conditions, molecules collide with each other and racemization takes place. In nature, the processes of syntheses of entities from minerals and the processes of DNA replication and mitosis proceed under the methane pressure and at the temperature when the methane-hydrate structure exists. They proceed rather slowly, but Nature has nowhere to hurry.

The chirality of AAs and some other similar organic substances can be explained as follows. Each such molecule is synthesized individually and doesn't contact other molecules of the same chemical composition; therefore, the way of formation of these molecules is determined by a kinetic preference of formation of one optical isomer independently of the thermodynamic identity of L- and D-isomers (Kadyshевич and Ostrovskii 2016). Being synthesized, chiral molecules don't collide with each other and, therefore, the change of their type of chirality is greatly hampered. Indeed, racemization proceeds very slowly because the reconstruction of the type of chirality of each molecule requires hardly probable resonance interchanges of the positions of several atomic groups in it. Such reconstruction is highly improbable (Kadyshевич and Ostrovskii 2016). It can be illustrated by the example of alanine on the basis of Fig. 4.

We wrote above that the type of chirality depends on the sequence of the substituents around the chiral C-atom. Figure 4 testifies to the correctness of this statement. It presents the scaled scheme of superposition of alanine D and L enantiomer molecules represented by solid and dashed lines, respectively; C₁–C₂ bond projections of the structures on the drawing plane are superposed (H atoms not used in this consideration, are not labeled). In the figure, C₁, C₃, H, and N atoms are the vertexes of the tetrahedron with the central C₂ atom. It is seen that the L- and D-forms of the alanine molecule differ in the sequence of radicals located in the vertexes of the chiral C₂-atom.

The rearrangement of the alanine L-structure to the alanine D-structure represents a complicated process, which consists of the interchanges of the $-\text{NH}_2$ group and $-\text{C}(\text{O})\text{OH}$ group positions relative to the molecule axis and, therefore, should have a rather high temperature coefficient. To understand the mechanism of such a process, it should be taken into account that each atom or an atomic group included into a molecule oscillates around its central position with a frequency of about 10^{13} s^{-1} (the usual frequency of atomic oscillations) and with a temperature-dependent amplitude. If there are two possible positions in a molecule for this included particle and if the energetically preferable position or the position of the same energy is free, this particle can pass to the new position and occupy it as a result of any oscillation in which it finds itself nearer to the new position than to the position earlier occupied by it. For the L-to-D transformation of an alanine molecule, the $-\text{NH}_2$ or $-\text{C}(\text{O})\text{OH}$ group jumping is insufficient. In the case of this molecule, a resonance coincidence between the $-\text{NH}_2$ and $-\text{C}(\text{O})\text{OH}$ oscillations, which are sufficient for jumping of each of these groups, is necessary and, in addition, the $-\text{CH}_3$ group should turn and the equilibrium H-atom position labeled in Fig. 4 should change. It is important that no intermediate state is chemically possible and, therefore, the resonance of oscillations is necessary. The above-specified features can result in multiple deceleration of the L–D equilibration. Low rates of racemization of AAs allow their use for specific action of the age of different antiquities, in particular, of biological nature. The difficulties that arise in the course of such measurements are caused by the dependence of the racemization rate on the temperature, humidity, and AA structure.

The analogous peculiarities are inherent in L-to-D transformation of biologically-active AA molecules and of AA radicals incorporated in a protein.

As the temporal coincidence of such a set of the rearrangement events is improbable, no wonder that racemization of either AAs or proteins usually occurs. Low temperatures of the observations aggravate this result: when temperature increases, the AAs and proteins decompose before the temperature of their racemization is achieved. However, exceptions occur and the best known of them is racemization of aspartic acid, the rate of which is observable, but it is as low as 0.1% per year (Helfman and Bada 1975). Apparently, it is now clear why the AAs produced as levorotatory ones are incapable of transforming to the thermodynamically caused racemic ratio of their optical isomers for usual observation periods.

With respect to nucleic acids, their racemization is impossible because of their complexity.

In a few words, we consider that the chirality phenomenon, which is characteristic for biologically active substances and for tissues of living organisms, results from thermodynamic equilibrium disturbances in the process of natural syntheses of the corresponding chemical structures and from low rates of liquidation of these disturbances. Therewith, both these features are caused by the steric peculiarities of the structures characteristic for the complex organic substances, step-wise character of the reactions of syntheses of organic substances, and low temperatures inherent in metabolism of living populations.

Other opinions are also available (Francis 2015; Han da et al. 2010; Hein and Blackmond 2012), and each reader can decide what opinion is more plausible. In

our opinion, the experiments are capable to solve this problem and the discussion of this problem before experiments has no sense.

It was shown in (Kadyshevich and Ostrovskii 2016) that some two- (or more) step chemical reactions can come to a stop just before the step that could lead to thermodynamic equilibrium or can proceed at this last step slower than at the previous step. The causes of such phenomena can be various and can lead to different peculiarities of reacting systems. The chirality phenomenon is caused by the situation, at which an atom or an atomic group formed as an intermediate in the course of a reaction, when entering in the chemical bond with one of the atoms of the newly forming molecule, should occupy one of two space positions near it and choose that of them which meets smaller obstacles from other adjacent atoms of this molecule. Therewith, the final system contains the resulted molecules characterized by the same chemical composition, by the same chemical composition of the atomic groups belonging to these molecules, by the same chemical interatomic bonds, but by different spatial arrangements of their atoms and, as the result of the last, by different optical features.

The existence of optical isomers demonstrates that, in the general case, the processes of syntheses of substances and the processes of establishing of chemical equilibriums in reacting systems can proceed by different mechanisms and obey different kinetic laws.

This conclusion is important for the natural science, because it casts doubt on some widely-distributed physicochemical theories.

Below, basing on the LOH-Theory, we consider the mechanism of origination of DNA's prerequisites that provide the capacity of DNAs to participate in the vertical transmission of principal species differences inherent in living entities.

3.4 Prerequisites for Genetic Codes: Clarification of Occurrence

At the end of sub-Sect. 3.2, it was shown that, at present, the number of the animal species is about 1,660,000 and the number of the animal species exceeds the number of the plant ones that is 250,000–350,000. These data characterize the species diversity and the possibilities of variations of DNAs that determine the principal species differences through variations in the nucleotide sequences.

The history-making scientific works of the mid-twentieth century (Crick and Watson 1954; Franklin and Gosling 1953; Meselson and Stahl 1958; Wilkins 1961; Pauling 1970) had led to the conclusion that just the DNAs and, more specifically, the sequences of combinations of N-bases in their structure determine the species differences of entities and some individual features of organisms. However, the mechanisms of origination of millions of species of entities and millions of the so-called genetic codes not subjected to principal hereditary changes through a multiplicity of generations and determining the transmissions of the principal species characters through generations remain subjects of discussions. The LOH-Theory and MRH-Theory are aimed at clarification of the physicochemical mechanisms of origination of the primary DNAs and primary living matter (e.g., Ostrovskii and Kadyshevich 2006, 2011) and of the mechanisms

of origination of the species diversity (Ostrovskii and Kadyshevich 2014a, 2017; Kadyshevich and Ostrovskii 2007, 2009). In our opinion, solutions of some of these problems are hidden in the peculiarities of the gas-hydrate matrix, within which DNAs, capable of replicating through generations, originated, and in the peculiarities of the historic variations in the natural conditions.

According to the widely-accepted terminology, the genetic code includes a set of rules (considered, e.g., in (Griffiths et al. 2000; Turanov et al. 2009), following which the nucleotide sequences in the DNAs of living cells are translated into the amino-acid sequences in the corresponding proteins. The real existence of such a connection is experimentally stated and is widely used in the practical biology. This means that the genetic code of an organism is determined by a definite sequence of the DNA nucleotides (or N-bases) inherent in this organism. Therefore, to provide the transmission of the principal species characters from a maternal organism to the daughter one, the transmission of the DNA nucleotide sequence through generations is necessary and sufficient.

Chargaff et al. (1952) first stated that the molar G/Cy and Ad/Th ratios in the DNA double helixes are equal to unity. Then, Crick and Watson (1954) used this discovery when formulating the DNA double-helix structure. Some years later, Meselson and Stahl (1958) stated experimentally that the DNA replication proceeds through the unwinding of the DNA double helixes with formation of two copies of each double helix, each copy consisting of one maternal DNA strand and one new daughter DNA strand synthesized on the maternal strand as on a matrix. Apparently, it was the first introduction of the notion of a matrix into the explanation of the processes underlying the DNA replication phenomenon. The MRH-Theory (Kadyshevich and Ostrovskii 2007; Ostrovskii and Kadyshevich 2011, 2012b) continues and expands the concept of the need for natural matrixes for the living-matter appearance and development in line with the discoveries made in (Chargaff et al. 1952; Meselson and Stahl 1958).

The question of why only the G–Cy and Th–Ad H-bonds rather than the G–Th, Cy–Ad, G–Ad, and Cy–Th H-bonds are realized in DNA double helixes remained unanswered.

Note that, thirty years ago, Szathmáry (1991) assumed that other pairs of N-bases, possibly, could also exist in the context of the RNA-hypothesis of living matter origination in the case of fulfillment of some conditions, whose reality was never established in practice. However, even if this is possible in the context of the RNA hypothesis, which as such is by no means proved, this doesn't mean that the same is possible in the processes of synthesis of the today organisms, which contain no RNAs as the translators of the heritage.

Below, this mystery will be solved. Meanwhile, to perform a so delicate function as the transmission of the DNA nucleotide sequence through generations, the chemical and structural characteristics of the DNA strands, apparently, should be observed rather strictly. Particularly, the DNA–DNA bonding through the G–Cy and Th–Ad H-bonds is one of the critical features, the observance of which is necessary for the performance of the DNA double-helix functions. The occurrence of only two possibilities for bonding DNA strands in the double helixes is one of the necessary prerequisites for the ability of DNAs to regulate the formation and subsequent

cooperation of different functional parts of complicated living organisms, i.e., is one of the prerequisites for the genetic codes controlling the corresponding organisms.

Shapiro (2000) and Abel and Trevors (2006) noted that convincing formulation of the mechanism for reproduction of hereditary characters is an important requirement placed upon any life-origination theory. The problem formulated in these works consists in the necessity of revealing the mechanism of transformation of a multitude of randomnesses into directednesses, i.e., transformation of a random noise into definite ordered events, processes, or phenomena capable of repeating through generations as a result of monodirectional natural processes. Really, this requirement relates to both, the species characters and DNA characters, because the invariability of the last in replications is one of the conditions of the infallible vertical transmission of hereditary characters by living entities.

When creating the DNA double helixes in CH_4 -hydrate localizations, Nature solved this problem.

In this Section, we consider the means used by Nature for this aim, i.e., the mechanism of transformation of the multitudes of randomnesses that are the multitudes of natural syntheses of primary DNA strands with random sequences of N-bases into the multitudes of directednesses that are the natural syntheses of multitudes of DNA double-strands capable of vertical transmitting their N-base sequences.

As a result of diffusion of NO_3^- -ions into such localizations, a multitude of different chiral nucleosides, which included different randomly chosen N-bases, were formed within adjacent large/small cavity pairs; the PO_4^{3-} -ions, diffusing along the small cavities of the matrix structure, bonded the pairs of the ribose-like “tails” of nucleosides through phosphodiester bridges as a result of the poly-condensation reaction. The subsequent chemical attachments of next nucleosides to the first nucleoside pairs resulted in formation of primary strands with different random sequences of nucleosides. Simultaneously, the nucleosides, which were produced within the cavities adjacent to the growing DNA strands or diffused into the cavities located against them, combined with these strands through H-bonds that connected the N-bases of the growing strands with the N-bases of the attached nucleosides. Steadily, the attached nucleosides had covered the primary DNA strands and the PO_4^{3-} -ions had joined them to each other through phosphodiester bridges. As a result of these reactions, the DNA double helixes composed of two complementary mono-strands, still imperfect, had formed within the gas-hydrate matrix structure.

Their elongation and perfection with formation of DNA double helixes capable of replicating and transmitting their N-base sequences through generations had proceeded in the super-cytoplasm after liquation of the gas-hydrate matrix. Thus, in a CH_4 -hydrate localization, as a result of diffusion of NO_3^- and PO_4^{3-} -ions into it, lots and lots of different primary DNA double strands, characterized by restrictedly-random sequences of the Pu–Py H-bonds between them, had formed. Such a not complete randomness of the Pu–Py sequences in the double helixes is caused by the natural limitation in the possibilities of the inter-strand bonding in the DNA double helixes; indeed, only Cy–G or Th–Ad H-bonds connect DNA strands in the DNA double helixes and neither Pu–Pu or Py–Py nor such Pu–Py bonds as Cy–Ad or Th–G connect DNA strands in helixes. It seems that, if this limitation didn’t exist, the DNA double strands couldn’t transmit their nucleotide sequences and the living

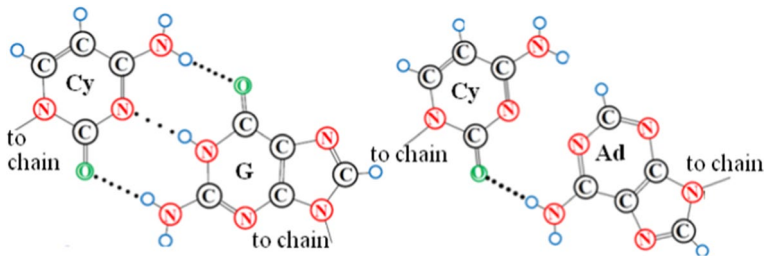


Fig. 5 Illustration of the cause of unrealizability of the Cy–Ad bonds in DNA double helices

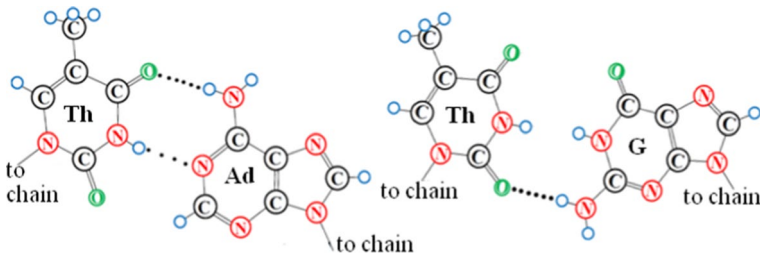


Fig. 6 Illustration of the cause of unrealizability of the Th–G bonds in DNA double helices

matter couldn't originate. The explanation of the origin of this limitation is given below.

The features considered above allow the conclusion that the gas-hydrate matrix not only represents the medium for origination of primary LMSEs but also provides transformation of primary random noise-like ensembles of definite source substances into the ordered DNA double-strands which result from replication of the primary double strands and possess a set of hereditary characters such as the nucleotide sequence and length.

It is known (Meselson and Stahl 1958; Kadyshevich and Ostrovskii 2007; Ostrovskii and Kadyshevich 2011) that the process of replication of DNA double helices proceeds through their gradual unwinding and formation of a complementary daughter DNA mono-strand on each of the DNA mono-strands; it is also known that the DNA mono-strands in double helices are bonded by H-bonds and that each such a bond links Pu of one strand to Py of its paired strand. Therewith, only pairs Cy–G and Th–Ad provide formation of complementary daughter DNA mono-strands, while no other pairing of N-bases in the process of DNA replication is possible.

The formal occurrence of these peculiarities was considered in many journal papers and books; however, their physicochemical causes weren't discovered. This mystery will be clarified below in the context of the LOH-Theory, and it will be shown that its solution is explainable by the mechanism of living-matter origination and development.

To solve this mystery, it is necessary to answer the following questions:

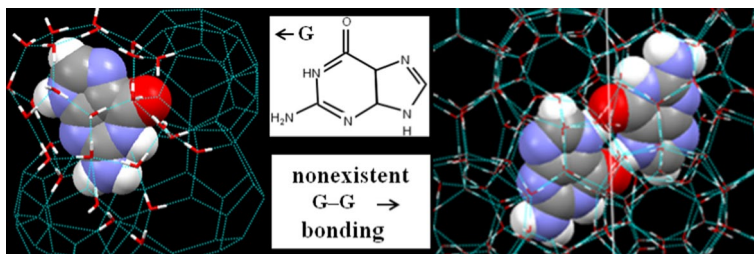


Fig. 7 Illustration of the cause of unrealizability of the Pu–Pu bonding in DNA double helices (by the example of G); left figure: guanine in a large cavity, right figure: nonexistent G–G dimer going beyond two adjacent large cavities. The Mercury program shows that too many G atoms in the right figure are beyond the large cavity (see the top piece of the right figure)

- (i) Why does Nature choose only the Cy–G and Th–Ad pairs from four seemingly possible Pu–Py pairs, namely, from the Cy–G, Th–Ad, Cy–Ad, and Th–G pairs, i.e., why are the Cy–Ad and Th–G pairs ignored?
- (ii) Why is the G–Ad pair, i.e., the Pu–Pu pair, ignored?
- (iii) Why is the Cy–Th pair, i.e., the Py–Py pair, ignored?

Figures 5 and 6 allow the answer to question (i).

From Fig. 5, it is seen that the Cy–G bonding is provided by two O···H H-bonds and one N···H H-bond and that the Cy–Ad bonding is provided by one O···H H-bond only, i.e., the energy of Cy–G bonding is higher than the energy of Cy–Ad bonding.

As is seen from Fig. 6, the Th–Ad bonding is provided by one O···H H-bond and one N···H H-bond and that the Th–G bonding is provided by one O···H H-bond only, i.e., the energy of Th–Ad bonding is higher than the energy of Th–G bonding.

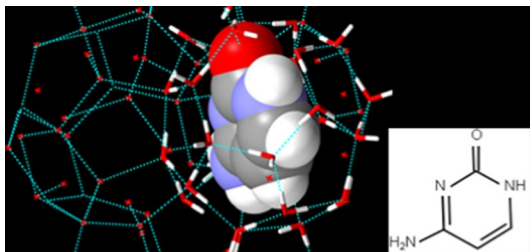
According to Fig. 5, the Cy(Py)–G(Pu) bonding is thermodynamically more preferable than the Cy(Py)–Ad(Pu) bonding. This means that, in the course of replication of any DNA double helix, a Cy–DDR–Ph nucleotide (hereafter, Ph is phosphodiester radical, see abbreviations), when diffusing along one of the replicating DNA strands, forms the H-bond with G rather than with Ad of this strand; then, its Ph forms the chemical bond with the adjacent DDR of the newly forming strand.

According to Fig. 6, the Th(Py)–Ad(Pu) bonding is thermodynamically more preferable than the Th(Py)–G(Pu) bonding. This means that, in the course of replication of any DNA double helix, a Th–DDR–Ph nucleotide, when diffusing along one of the replicating DNA strands, forms the H-bond with Ad rather than with G of this strand; then, its Ph forms the chemical bond with the adjacent DDR of the newly forming strand.

Figure 7 allows the answer to question (ii).

It allows understanding why no G–Ad bridges, i.e., no Pu–Pu ones, occur in the DNA double helices. The G–Ad bonds are not realized in the DNA double helices, because two adjacent large cavities are too small for the arrangement of two H-bonded purines within them. One of the projections of G and Ad juts out into the adjacent large-cavity by about 15%. According to Chaplin (last updated

Fig. 8 Illustration of the cause of unrealizability of the Py–Py bonding in DNA double helixes (by the example of Cy)



July 2020), the gas-hydrate structures endure such excesses of guest-molecule sizes over the ideal cavity size. However, there are no doubts that the occurrence of two so large guest particles within adjacent large cavities would be inadmissible for gas-hydrate structure II and could lead to its destruction.

Figure 8 allows the answer to question (iii).

It allows understanding why no Cy–Th bridges, i.e., no Py–Py ones, occur in the DNA double helixes. The Cy–Th bond is not realized in the DNA double helixes, because two adjacent large cavities are too roomy for the arrangement of two pyrimidines within them. To understand why the DNA strands cannot be H-bonded in the gas-hydrate structure through Py–Py bridges, it is necessary to take into account that, first, each Py should be chemically bonded with a DNA strand and, second, the large gas-hydrate cavities are rather roomy for pyrimidines. Just therefore, the Py–Py H-bonds couldn't be realized in such a structure; indeed, the large cavities are too roomy for the simultaneous H-bonding of two Py radicals and chemical bonding of one of them with DDR, whose position is fixed by the size of its two chemical bonds with the neighboring Ph radicals. In other words, the Py–Py H-bonds between two DNA strands cannot be realized within gas-hydrate structure II because of too long inter-Py distances imposed on the DNA strands by the gas-hydrate structure.

It is seen that the notion of structuring of waters in highly-concentrated solutions of biologically-active substances allows clarification of the mysterious choice by Nature of only two modes of DNA-strands H-bonding in double helixes out of six seemingly possible ones. It is made in the context of the LOH-Theory (Ostrovskii and Kadyshevich 2006, 2007a, 2007b, 2014a) and MRH-Theory (Kadyshevich and Ostrovskii 2007; Ostrovskii and Kadyshevich 2011, 2012b), according to which the processes of living matter origination and living matter development, including DNA replication and cellular mitosis, are thermodynamically caused and governed by the processes of formation and destruction of gas-hydrate structures.

Figures 5, 6, 7, 8 show that the occurrence of the Cy(Py)–G(Pu) and Th(Py)–Ad(Pu) pairs and the absence of the Cy(Py)–Ad(Pu) and Th(Py)–G(Pu) pairs in DNA double helixes are explainable by thermodynamic causes and that the absence of the G(Pu)–Ad(Pu) and Cy(Py)–Th(Py) pairs in DNA double helixes is explainable by geometric causes. Thus, the occurrence of only Cy(Py)–G(Pu) and Th(Py)–Ad(Pu) pairs in DNA double helixes is explained by the combined effect of the thermodynamics and of the geometry of gas-hydrate matrix.

The analysis of the above-presented figures leads us to the conclusion that the selective bonding of the DNA strands in the DNA double helixes is caused by the matrix gas-hydrate structure of the reaction medium and by the thermodynamic preferences.

This important result allows us to consider that we managed to clarify the physicochemical grounds of principal processes launched by Nature on the way of transformation of inanimate mineral substances into multitudes of the simplest forms of the pre-cellular and unicellular living matter capable of vertical transmitting their hereditary characters and possessing all prerequisites for the next step of evolution that is formation of genetic codes, i.e., of the ability of translating their own nucleotide sequences into the functional properties and structures of complicated organisms.

4 Discussion: Hindsight and Prospecction

In this paper, we generalize our two-decade studies aimed at clarification of the biophysicochemical mechanisms used by Nature for transformation of inanimate minerals into multitudes of DNA double helixes characterized by the following features:

- each of these multitudes consists of identical DNA acids;
- the DNA acids of different multitudes are different, namely, they contain different nucleotide sequences;
- each carboxylic acid is capable of vertical transmitting its hereditary characters and possesses all prerequisites for the next step of evolution that is the appearance of biological (genetic) code.

We perform our consideration by the example of the DNA-world. The followers of the primary origination of the RNA-world are free to formulate a parallel theory.

The LOH-Theory is based on three discoveries made by us. The first discovery results from the original adsorption, kinetic, and calorimetric studies. The second discovery follows from the three-dimensional simulation of DNA fragments within gas-hydrate structure II and from the comparison of the simulated lengths of the chemical and H-bonds with those measured by the X-ray method (see the Table). The third one follows from the chemical compositions of the minerals entering into the unique mineral triad revealed by us among the minerals available at the Earth crust upper layer.

It was stated that the primary living matter formed repeatedly in the post-glaciation periods of the Earth's history within the underground solid and semi-liquid CH₄-hydrate localizations from CH₄ and from NO₃⁻ and PO₄³⁻ ions diffusing in moist soil into the honeycomb CH₄-hydrate super-cytoplasm from saltpetrer and apatite deposits. The primary DNA double-strands contained different vertically transmittable nucleotide sequences, and their lengths and nucleotide compositions were determined by the ambient conditions and duration of their natural syntheses. Thus,

it is shown that the underground and underseabed super-cytoplasm basins of gas-hydrate structure were the first “crèches” for the incipient living matter.

There is no life without chirality, and this feature is inherent in each living entity! The LOH-Theory allows first solution of the two-century-old mystery of why all principal natural biologically-active organic substances are mono-chiral.

The phenomena of chirality and racemization delay result from thermodynamic equilibrium disturbances in the natural syntheses of the corresponding chemical structures and from low rates of liquidation of these disturbances; both these peculiarities are caused by the steric specialities of the structures of complex organic substances, step-wise character of the reactions of syntheses of organic substances, and low temperatures of syntheses and existence of biologically active substances and living organisms.

It is shown (Kadyshevich and Ostrovskii 2016) that chemical reactions and establishment of chemical equilibriums can proceed by different kinetic laws and can come to an end in the course of different time periods in the reactions when the product of a definite chemical composition and with definite interatomic chemical bonds can have different structures, forming, for example, different enantiomers.

We considered the differences in the origin of plants and animals and the causes capable of explaining an almost fivefold excess of the animal species number over the plant one. These differences were mysterious, especially because there are no distinctions either in the elements, of which the base substances of these two living-matter branches consist, or in the elemental composition and structure of their DNAs, which differ only by the N-base sequences. The branching process is termed by us the “food revolution”. Some individual entities had a feature that allowed them, in the periods of a deficiency of mineral nutrition, to “eat” other entities, and thus, as a result of the subsequent mutations, such entities formed more or less stable organisms that became the progenitors of new animal species. The animals destructed the DNAs of plants to nucleotides and used them to construct their own DNA structures. Thus, instead of the syntheses of original nucleotides from mineral “bricks” (CH_4 , NO_3 , and PO_4), they used ready “structural panels” and, thus, accelerated their reproduction and formation of new species as a result of mutations and species splitting.

At present, one more mystery of the DNA coupling is left in abeyance; this paper reveals the causes of the mysterious phenomenon, which should attend the DNA double helix formation and whose occurrence until now seemed unknowable. After the work by Chargaff et al. (1952), it is known that the G/Cy and Ad/Th molar ratios in the DNA double helixes are equal to unity. Somewhat later, it was experimentally found by Meselson and Stahl (1958) that the DNA replication proceeds through the DNA double helixes unwinding with formation of two copies of each double helix, each copy consisting of one maternal DNA strand and one new daughter DNA strand synthesized on the maternal strand as on a matrix. However the causes and mechanisms of these features were unknown.

The physicochemical explanation of the DNA replication phenomenon was given by us in (Kadyshevich and Ostrovskii 2007; Ostrovskii and Kadyshevich 2011, 2012b, 2014a) on the basis of the notion of the living-matter originations

and replications in the gas-hydrate medium. However, the causes of the occurrence of relations $(G/Cy) = 1$ and $(Ad/Th) = 1$ remained mysterious.

Above, this mystery was originally solved. We explained why only the G–Cy and Th–Ad H-bonds rather than the G–Th, Cy–Ad, G–Ad, and Cy–Th H-bonds are realized in DNA double helixes and, thus, explained why G/Cy and Ad/Th are equal to unity. The selective bonding of the DNA strands in the DNA double helixes is caused by the geometry of the matrix gas-hydrate structure II where DNAs originate and replicate and by the thermodynamic preferences characteristic for these processes.

Such a rather specific feature of the DNA–DNA double strands, apparently, couldn't be explained by any other way, and the possibility of its explanation by the effect of the gas-hydrate matrix confirms reliably the LOH-Theory.

The whole set of the important results summarized above in this Section allows us to consider that we, apparently, managed to clarify the physicochemical grounds of the principal processes launched by Nature on the way of evolution. These processes include transformation of inanimate mineral substances into multitudes of the simplest forms of pre-cellular and unicellular living matter. Our consideration is brought to the next step of evolution when the primary-originated living entities became capable of vertical transmitting their hereditary characters. This step, not considered by us, consists in formation of genetic codes, i.e., of the ability of the primary-originated entities for translating their own nucleotide sequences into the functional properties and structures of complicated organisms.

The primary entities originated as a result of the following thermodynamically-caused principal processes:

- (a) Diffusion of NO_3^- -ions into the methane-hydrate localizations;
- (b) Syntheses of lots and lots of different nucleosides from CH_4 molecules and NO_3^- -ions in the pairs of adjacent large/small gas-hydrate cavities through formation of different N-bases within large cavities and their "sprouting" into adjacent small cavities with formation of ribose-like "tails" and simultaneous origination of the tetrahedral chiral C-atom in each nucleoside, i.e., origination of the chirality phenomenon;
- (c) Diffusion of PO_4^{3-} -ions into the methane-hydrate localizations along small cavities and formation of lots and lots of primary RNA mono-strands and H-bonded DNA double strands possessing random sequences of N-bases;
- (d) Liquefaction of the gas-hydrate matrix under the effect of heat and water evolution as a result of the chemical reactions of DNA and RNA syntheses and formation of the semi-liquid super-cytoplasm;
- (e) In the super-cytoplasm, continuation of the processes of formation and elongation of RNAs and DNA double helixes, development of the DNA ability for the vertical transmission of the nucleotide sequences, formation of organo-phosphorus compounds, their precipitation around DNA double helixes with formation of semipermeable interstices, and origination of proto-cells;
- (f) Development of the intracellular processes, replication of chiral DNA double helixes, cellular mitosis and symbiosis, syntheses of chiral amino-acids and primary proteins, separation of unicellular entities into plants and animals, etc.

The origination of species includes, as one of the first steps, formation of DNA double helices and development of the mechanism of the vertical transmission of their principal species characters, namely, their lengths and N-base sequences.

Just the gas-hydrate structure together with the thermodynamic regulations represent the factors that transform a noise into the order, i.e., transform the random arrangement of N-bases in the primary DNA double strands into the ordered arrangement of N-bases in all DNA double helices resulted from the replication of these double strands and create prerequisites for the genetic code. Among a multiplicity of the entities thus generated, those of them, which are able of accommodating themselves to the environment, propagate and form new species.

It is quite possible that this way can be reproduced experimentally as is described by us earlier (Ostrovskii and Kadyshevich 2007a, 2007b, 2012b; Kadyshevich and Ostrovskii 2009).

A number of the observable and revealed events and phenomena count in favor of the LOH-Theory. The most important of them are specified below.

Living matter origination underground within methane-hydrate localizations is now unambiguously proved:

- (1) by multiple discoveries of different species of living entities in isolated underground methane-hydrate localizations,
- (2) by the fact that living matter was produced from methane rather than methane was produced from living matter.

In underground methane-hydrate localizations, bacteria could originate by no other realistic chemical way but from methane and from nitrate- and phosphate-ions diffusing from the adjacent minerals; in any event, no other thermodynamically permitted mechanism for this process is proposed.

The colonies of living entities use methane of methane-hydrate together with niters and phosphates that diffuse from the nearby underground or underseabed layers for their propagation, and time transforms their remains into kerogen.

When discussing in (Ostrovskii and Kadyshevich 2000) the approaches to clarification of the mechanism and chemism of living matter origination, we didn't know about the occurrence of living matter deeply underground in the methane medium. Nevertheless, in the just referred paper, it is written: "It may happen that information on hydrate and, generally, on clathrate semifluid structures will become a guiding star in understanding the phenomena and regularities responsible for the origination and reproduction of living matter." When suggesting this prediction, we relied on our discoveries and on the critical stoichiometry of 17 H₂O molecules per one pair of hydrogen-bonded DNA–DNA amido-groups in double helices. After such a stoichiometry, the subsequent watering of the system leads to dissociation of the dimers. In (Ostrovskii and Kadyshevich 2000), we originally stated the determining role of the gas-hydrate structure and of methane as its guest component in the processes associated with origination and subsequent transformations of simplest entities. The further development of this idea and the chemical and thermodynamic grounds of

living-matter origination were published in (Ostrovskii and Kadyshevich 2006) and were developed in the next works.

The phenomenon of the occurrence of bacteria in the CH₄-hydrate localizations underground and underseabed at great depths counts in favor of the LOH-Theory. At present, this phenomenon is confirmed by a number of studies performed by different researchers. Initially, we will consider it as applied to the conventional deposits of hydrocarbons and, after that, will consider the peculiarities inherent in unconventional shale deposits.

In (Parkes et al. 1994), different species of bacteria, including those unknown on the Earth's surface, were identified underseabed at depths down to at least 500 m under the Pacific Ocean bed. Ten years later, D'Hondt et al. (2004) confirmed the occurrence of diverse microbial communities in deeply buried underseabed sediments over the eastern Pacific Ocean; mention also the works by Inagaki et al. (2006) and Morono et al. (2011), where different microbial cells were discovered underseabed in the Pacific Ocean area together with the methane-hydrate and nitrogen deposits.

A rather comprehensive study of the underseabed Pacific Ocean biosphere was performed by Schippers et al. (2005) within the methane-hydrate localization near the Central American coastal regions enriched with potassium and sodium niter deposits. The underseabed biosphere was identified as the huge living prokaryotic colony of 10⁵–10⁶ entities per cubic centimeter density. The colony was extended over the underseabed ground layer down to 400 m under the water column of 427–5086 m. The sediment temperature varied between 274 and 299 K. According to (Ostrovskii and Kadyshevich 2007a, 2007b), the temperature regime fixed by Schippers et al. (2005) within the localization filled with the CH₄-hydrate and bacteria population shows the exothermicity of the chemical processes that proceeded there. The occurrence of the living colonies and the exothermicity of the chemical processes that accompany the metabolism of these prokaryotes confirm the LOH-Theory (Ostrovskii and Kadyshevich 2006, 2007a, 2007b, 2012a, 2014a; Kadyshevich and Ostrovskii 2009, 2015).

Large bacterial colonies were also found in western regions of Siberia under the Earth's surface at depths down to 6820 m; living matter was also associated with methane-hydrate deposits (Oborin and Khmurchik 2008).

Thus, the results obtained by Parkes et al. (1994), D'Hondt et al. (2004), Inagaki et al. (2006), Morono et al. (2011), Schippers et al. (2005), and Oborin and Khmurchik (2008) show that different simplest entities and their precursors are abundant underground and underseabed within CH₄-hydrate localizations.

These living entities could populate the deep underground layers by no way other than to originate there. Thus, their occurrence is in the context of the LOH-Theory.

Meanwhile, the question about the source of bacterial communities obtained a new aspect in the last decades in connection with the development of the technology of the shale-hydrocarbons production because some researchers assumed that methane and other hydrocarbons occurring in shales had originated on the basis of entities that also occur there. Below, it is shown that this assumption has no grounds. This question requires a detailed consideration.

Shale hydrocarbon deposits represent foliated, laminary, finely-grained, sedimentary rocks of highly-porous structure filled with methane-hydrate, kerogen, and bacteria under the pressure of gaseous methane with admixture of other hydrocarbons and gases of other nature. All chemical elements necessary for the living-matter synthesis are present in shale deposits and in the minerals adjacent to them, and the ambient conditions may correspond to those necessary, according to (Ostrovskii and Kadyshevich 2007a, 2007b, 2014a), for natural bio-syntheses.

As noted above, the opinion exists that the sequence of the processes in shales for hundreds of millions of years is as follows: entities → kerogen → methane. This statement leaves aside the question of the entities origin and, therefore, is doubtful conceptually. The fact of the matter is that there are scientific grounds to think that the underground processes proceed in the following sequence: methane → methane-hydrate → (methane-hydrate + NO_3^- + PO_4^{3-}) → (entities + ($\text{N}_2 + \text{O}_2 + \text{NH}_3 + \text{CO}_2$)) → (kerogen + entities + mineralized PO_4). Just such a sequence of the processes responds to the thermodynamics and chemical stoichiometry.

The following scientific data obtained in the course of the several recent decades count in favor of the last sequence of events.

First, the detailed decade studies performed in the context of the API Project 43 didn't confirm the possibility of the underground methane formation from kerogen and from bacteria (e.g., Heald 1952–1953; Tornabene 1981).

Second, the cosmic experiments revealed huge amounts of methane and other paraffin and olefin hydrocarbons on the remote cold celestial objects Titan and Europa (Jennings et al. 2009; Nixon et al. 2012; Vance et al. 2016) and this fact testifies that methane and other low-molecular hydrocarbons had originated in the Solar System in the period of the planets formation and transformation, i.e., before the living-matter origination on the Earth.

Third, according to Kucherov and Kolesnikov (2008) and Ivanov et al. (2008), the experimental studies and thermodynamic calculations performed by the authors of these publications and by a number of other researchers proved that hydrocarbons can be produced from Earth's minerals underground in the mantle/crust boundary vicinities and then diffuse to the upper underground layers of the Earth. In addition, recently, Klein et al. (2019) arrived at the conclusion that olivine ($(\text{Mg,Fe})_2\text{SiO}_4$) and its water inclusions can lead to the methane formation in so great amounts which are capable of providing the Earth's living-matter origination. Notice that Klein et al. (2019) factually sustained our conclusion first published 20 years ago about living-matter origination on the basis of underground methane-hydrate.

The studies performed by Heald (1952–1953), Tornabene (1981), Jennings et al. (2009), Nixon et al. (2012), Vance et al. (2016), Kucherov and Kolesnikov (2008), Ivanov et al. (2008), and Klein et al. (2019) count in favor of the notion that at least a portion of the Earth's methane had formed by abiogenic mechanisms long before the Earth's living-matter origination. The same conclusion was made in review paper by Ostrovskii (2010). Just the occurrence of abiogenic methane had provided the primary living-matter origination on the Earth as long ago as earlier than 3850 Mya.

Consider now the phenomenon of the occurrence of bacteria in the CH_4 -hydrate localizations as applied to the unconventional shale deposits.

Brazilian researchers De Goes et al. (2018) stated that *actinobacteria*, *firmicutes*, and *proteobacteria* dominate in the bacterial content of the unconventional oil/gas fields in St. Matthew of the South and even consider the possibility of using this bacterial mass as a component of the complex agricultural nutrient.

In the work by Gaspar et al. (2014), deleterious microorganisms, including Clostridia and other spore-forming bacteria capable of secreting powerful poisons and toxins, such as *C.botulinum*, *C.tetani*, etc., were detected in the technological water of the shale gas/oil production process. The authors of this work assumed without any proofs that these bacteria were introduced from the Earth surface. An analogous conclusion was made by Borton et al. (2018), where no bacteria were noticed within the wells before application of the hydraulic fracturing technology on the outer surface of the shale laminas. However, the methane-hydrate, bacteria, and kerogen are housed within the shale porous structure rather than on the outer surface of the shale laminas and it may happen that bacteria are capable of emitting together with methane into the ambient space only after the gas-hydrate structure disruption by the hydraulic fracturing.

In addition, the sensitivity of the instrument used for the observation of the underground shales in (Borton et al. 2018) isn't specified. The fact is that the sizes of a number of viruses, viroids, some bacteria, and archaea are beyond the sensitivity of the widely distributed optical measuring instruments. According to the study by Shcherbakova (2018), some anaerobic bacteria and archaea have sizes about 100 nm; according to Zhu et al. (2020), for example, coronaviruses are 60–140 nm thick (thinner than the human hair by a factor of 30). The objects of so minor sizes could be revealed in the laboratories equipped with high-resolution electron microscopes, rather than under the field conditions.

By the above-considered reasons, the conclusion by Borton et al. (2018) that no entities occur in shale hydrocarbon deposits before application of the hydraulic fracturing technology is not convincing.

Meanwhile, the results by Mohan et al. (2013) prove, apparently, definitely the occurrence of bacteria, at least, in some shale deposits of hydrocarbons by the example of the technological water study in the basin of the Marcellus (Pennsylvania, USA) hydrocarbon deposit. The authors of this work studied, particularly, the microbial community changes in the Marcellus shale gas operation from drilling through hydraulic fracturing and production phases. Source water used in the hydraulic fracturing technology, fracturing fluids, and early production phases contained microbial communities that were relatively unchanged and composed mostly of aerobic species within the classes *Alphaproteobacteria* and *Gammaproteobacteria*. However, over the course of production, the microbial community shifted toward one dominated by anaerobic halophiles; after production for 187 days, both diversity and abundance had greatly decreased and the community was almost entirely composed of a *Firmicutes* phylotype. This experiment confirms the population of the underground reservoir by such bacteria before hydraulic fracturing: first, Firmicutes phylotype were absent in the source technological mixture used for the hydraulic fracturing, and, second, these bacteria are anaerobic as is expectable for underground entities. The results of Mohan et al. (2013) are in the context of the principal conclusion of Gaspar et al. (2014) that the more targeted microbial control and treatment

strategies are needed. Such a possibility is taken into account by the engineers who develop the hydraulic fracturing technology, and, therefore, an admixture of a so-called biocide (Kahrilas et al. 2015) intended for killing entities is introduced into the water/sand mixture used, according to this technology, for destroying the methane-water bond in the underground methane-hydrate and for the natural shale-gas emission.

The work by Mohan et al. (2013) represents, apparently, the *experimentum crucis*, which shows that, before using the hydraulic fracturing technology, the initial system contains anaerobic bacteria. This means that bacteria exist, at least, in some underground methane-hydrate localizations, and, because such systems are not connected with the Earth's surface but are connected with adjacent minerals only, they could originate there only as a result of chemical interactions between these minerals, and, as follows from the above formulated Discoveries, only methane and nitrate- and phosphate-ions could be the sources for their synthesis.

This conclusion represents one of the confirmations of the LOH-Theory.

The precursors of living matter and simple living entities originated repeatedly in different time periods when the ambient conditions were appropriate in numerous CH₄-hydrate deposits located in the regions enriched with nitrates and phosphates or close to deposits of these minerals.

Today, different species of the unicellular and multicellular successors of these original simple entities populate numerous deep underground methane-hydrate localizations. The species composition and generic composition of these entities are unpredictable because the conditions of their origination and evolution are unknown, rather specific, and different in different regions and in different localizations; these entities can be DNA- or RNA-based, can be of any chirality, and can be unchiral. In addition, the adaptability of these entities to variations in ambient conditions can be very specific.

The occurrence of multiple species of viruses, along with bacteria, within different depth methane-hydrate localizations was confirmed in a number of studies.

In our opinion, viruses are the “undeveloped” bacteria, which are generated alongside with bacteria under the conditions of deficiency of some source mineral or as a result of variations in the ambient conditions. Therefore, different species (strains) of viruses companion bacteria frequently. According to Suttle (2005), “...viruses exist wherever life is found...the effect of viruses on global systems and processes continues to unfold, overthrowing the idea that viruses and virus-mediated processes are sidebars to global processes.”

In (Emerson et al. 2018), living entities were recently discovered in the Swedish methane-containing soil along permafrost thaw-gradient. Along this soil level, 1907 viral populations were identified. Soils contain always some nitrate and phosphate inclusions, and the CH₄-enriched permafrost thaw-gradient conditions are similar to the conditions that arise at the boundaries of thawing glaciers. The occurrence of a multitude of viruses along the permafrost thaw-gradient boundary means the simultaneous occurrence of a bacterial microflora there. This discovery represents a weighty confirmation for the notion of origination of simple living matter, including bacteria and viruses, nearby the boundary of melting glaciers in the Earth's breakup periods.

Daly et al. (2019), when studying the interiors of hydraulically fractured wells, found the biosphere consisting of bacteria, archaea, and different viruses. It was also stated that diverse and active viral populations play a critical role in microbial community development within deep underground ecosystems rather than are introduced from the outside.

Multiple microorganisms, viruses, archaea, and bacteria, were also discovered underseabed in the eastern sediment-covered flank of the Juan de Fuca Ridge by Nigro et al. (2017). In this work, the hydraulic fracturing technology was not applied before the sampling, i.e., they couldn't be of the terrestrial origin. In the samples taken at the depths of 117–292 m, the virus concentrations varied from 0.2×10^5 to $2 \times 10^5 \text{ ml}^{-1}$ and were manyfold higher than the concentrations of prokaryote-like cells. The strains of the discovered viruses differ from those known among the terrestrial ones. The authors of this work concluded that these unknown viruses are active participants in the ecology of the underground microorganisms.

The results obtained by Pan et al. (2014) show that viruses are present in underground deposits together with carbon-containing substances and nitrates and that they are connected with the carbon biochemistry.

The above-referred scientific works give grounds to conclude that bacteria and viruses were discovered in, at least, some of the depth shale deposits used currently for hydrocarbon production. Therewith, we have no information on the detection of coronaviruses either underground or underseabed. It is the authors' opinion that the depth colonies of living microorganisms, including bacteria and viruses, can populate the deep layers by no way other than to originate there.

Some other observations of the natural phenomena count in favor of the LOH-Theory.

As written above, according to the LOH-Theory, the LMSEs had formed repeatedly in the underground CH_4 -hydrate localizations in the post-glaciation periods of the Earth's history, when such localizations were not far from the Earth's surface and diffusion of NO_3^- - and PO_4^{3-} -ions in the moist soil was defrosted. Indeed, the paleontological data (Zak 2014) show that the explosive living-matter expansion proceeded late in the cold periods, about (Mya) 3900 (after the faint Sun period), 2100, and 542. Figure 9 illustrates the coincidence of the post-glaciation periods with the living species prosperity.

The same figure illustrates one more phenomenon that counts in favor of the LOH-Theory. According to the data of Kump (2008), the atmospheric oxygen content increased step-wise just in the periods mentioned in the previous paragraph. Meanwhile, the processes of living-matter origination are associated with oxygen emission. Oxygen emitted to the atmosphere in the course of syntheses of N-bases and riboses, as is seen from the reaction Eq. (2), and in the course of syntheses of AAs, as is shown in (Kadyshevich and Ostrovskii 2015). The temporal correlation between the periods of the explosive living matter expansion and the periods of the step-wise increase in the atmospheric oxygen content also confirms the LOH-Theory.

The primary entities precursors such as N-bases, nucleosides, and nucleotides, nucleic acids as simplest biological substances, and nucleic-acid-based viroids, viruses, unicellular bacteria, and simple multicellular organisms of various and

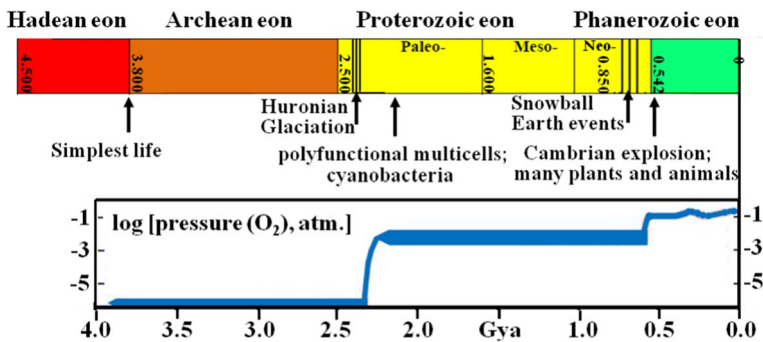


Fig. 9 The time relation between the atmospheric O_2 content stepwise increases and the Earth's species diversity development

unpredictable modifications had first originated after 3900 Mya and have been repeatedly appearing under favorable conditions, because nothing but source substances and ambient conditions determines the proceeding of chemical reactions.

Apparently, Nature had proved the correctness of the Life Origination Hydrate Theory.

Entities of different types can occur in our days in those underground or underseabed localizations which satisfy definite conditions. Numerous studies of the underground methane-hydrate localizations confirm this phenomenon. It cannot be excluded that these entities can emit into the atmosphere when the pressure of overlying ground layers is taken off.

At present there are no doubts that simple living matter of different species originates underground on the basis of methane within the methane-hydrate honeycomb structures, as follows from the LOH-Theory.

According to the LOH-Theory, DNAs and RNAs can originate in the case of deficiency of NO_3^- -ions in the CH_4 -hydrate structures. The aforesaid means that diffusion of even small quantities of NO_3^- - and PO_4^{3-} -ions into the methane-hydrate structure from the environment can initiate formation of nucleic acids in it. As for PO_4^{3-} -ions, it is known that phosphatic rocks commonly accompany shales (Prothero and Schwab 2003). The occurrence of the DNA- and RNA-containing entities in the shales testifies that NO_3^- - and PO_4^{3-} -ions are, really, in contact with CH_4 ; possibly, water promotes the process of their diffusion.

All pre-cellular and cellular entities contain C, N, P, O, and H as their component elements and, according to the LOH-Theory, are capable of originating in the CH_4 -hydrate structures under conditions of diffusing there of NO_3^- - and PO_4^{3-} -ions from the environment. In the course of these reactions, such side-products as O_2 , N_2 , NH_3 , CO_2 , and S-containing gases are produced as follows from reactions (1)–(4) and other reactions presented, e.g., in (Ostrovskii and Kadyshevich 2006, 2014a). Therefore, the occurrence of these gases in the underground CH_4 -hydrate localizations containing entities could confirm the formation of entities in these localizations.

Of course, some of these substances could be mineralized for the millions of years of their existence within the shale localizations and H_2O and CH_4 could be introduced into the CH_4 -hydrate composition; however the occurrence of the chemical elements O, N, C, and P in the gas phase within the space of the shale localizations or in the compositions of the neighboring mineral rocks could testify in favor of the conclusion that the reactions under consideration proceed really at present or proceeded there in the past before depletion of one of the necessary components.

Indeed, the available data show that the emission of O_2 , N_2 , NH_3 , CO_2 , and S^{2-} -containing gases from the shale-gas wells is really observable in the course of the gas production (Speight 2017). Such gases are obtainable just from the well space. They couldn't be emitted from kerogen as a result of application of the hydraulic fracturing technology, because kerogen begins to emit gas as a result of its heating above at least 520 K. This means that the occurrence of these gases in the produced gas counts in favor of the occurrence of reactions (1)–(4) in the past and, may be, at present in the shale-gas localizations. The real occurrence of these gases in the shale space is shown below by some real examples.

According to Skea (2015), the shale-gas contains, as a rule, 95% of methane, other paraffins from ethane to pentane, CO_2 , H_2S , and N_2 . In (<https://noyabrsk-dobycha.gazprom.ru/about/chayanda/>), the oil/gas/condensate field gas has the following composition: CH_4 —84%, C_2H_6 —4%, C_3H_8 —1%, N_2 —1%, CO_2 —0.05%. The gas samples taken from different CH_4 -hydrate deposits contain much more N_2 than O_2 : 4% and 0.005%, respectively, according to Davidson et al. (1986) and 11.4% and 0.2%, respectively, according to MacDonald et al. (1995); meanwhile, these N_2/O_2 ratios are much higher than the N_2/O_2 ratio in the Earth's atmosphere. This means that the samples could not be contaminated by atmospheric air during their collection and storage. Apparently, N_2 was produced through the CH_4 or some other hydrocarbon reduction by niter in the deposits of hydrocarbon-hydrates as a result of reactions (1) and (2), because the potential sources of N_2 in the Earth's crust are unknown.

Thus, O_2 , N_2 , NH_3 , CO_2 , and S^{2-} -containing gases were present in all these wells and the N_2 amount was manifold greater than the O_2 amount in accordance with Eq. (1) and because O_2 is a rather reactive gas and it could interact with the mineral surroundings.

The aforesaid leads to the conclusion that the occurrence of the inorganic gases, namely, O_2 , N_2 , NH_3 , CO_2 , and gases, containing S^{2-} in the gas emitted from the wells substantiates the proceeding of the chemical reactions that could lead to formation of entities within the shale porous structure.

All chemical elements of which these gases are composed are also found in kerogen as a result of its heating.

The other source substance used by Nature for the DNAs, RNAs, and cells syntheses, namely, PO_4^{3-} ions, was mineralized with time. It is discoverable, for example, in the resulted shale systems (e.g., (Prothero and Schwab 2003; Kholodov and Nedumov 2011)). The phosphate-ions had entered into the shale structure for the hundreds of millions of years after the beginning of the kerogen formation process. According to Prothero and Schwab (2003), the phosphatic sedimentary rocks are commonly accompanied by or interbedded with shales, sandstone, or other minerals.

It is also necessary to take into account the following. Shales exist for a long time, many tens or even several hundreds of millions of years, and gas-hydrate structures are capable of forming under limited ranges of ambient conditions. In particular, no realistic CH_4 pressures can lead to CH_4 -hydrate formation if the temperature is higher than 330–340 K. Therefore, the mineral content of the shales could liquefy and freeze repeatedly over a period of their history. Therewith, the well-soluble NO_3^- -ions could be washed out and removed by water and the PO_4^- -ions could mineralize in the compositions of the nearest minerals.

The aforesaid shows that all theoretical side products that could be produced as a result of the methane transformation into entities precursors and protein-free bacteria and simplest multicellular organisms and subsequent formation of kerogen are really observable in the system within shale porous structure, around the shales, or in the composition of minerals occurring around the shale localizations.

The last point upon which we dwell in this paper is the experimental verification of the LOH-Theory. For the enthusiasts who would wish to be the first to synthesize DNA-like molecules, it is sufficient to have a temperature- and pressure-controlled autoclave with the possibility of sampling without disruption of the reaction conditions and absorption or discharge of the escaping oxygen, appropriate analytical techniques and methods, detailed acquaintance with our related publications cited above, and patience. Taking into account the results by Konovalov (1892, 1893a, 1893b), Hass et al. (1936), and Zhou et al. (2019), it should be expected that experiments will continue for years; therewith, noticeable changes in the medium composition can be detected at intervals of several months.

We don't consider here and don't plan consideration of the mechanisms of the subsequent living matter development, i.e., transformation of different multitudes of identical DNA double strands and simplest organisms into organisms containing different functional proteins, whose formation and functioning is governed by the N-base arrangement along the DNA strands. The Theory under consideration is in the context of Crick's (1968) foresight that the primary self-reproducing biological mechanisms included only nucleic acid and didn't include protein; as for proteins, they were added into the system later.

The further way of transformation of simplest entities into multifunctional organisms requires the appearance of special mechanisms, the totalities of which are termed genetic codes. The LOH-Theory doesn't solve the mystery of appearance of genetic codes, but it proposes mechanism that transforms natural minerals to simplest self-reproducing entities and, thus, brings the biology close to the understanding of the mystery of the appearance of genetic codes. It is proved practically that it is possible to change directionally the properties of plants and animals by changing the nucleotide sequence in DNAs, to explain some unhealthy properties of entities by the peculiarities in nucleotide sequence inherent in DNAs and to correct them by changing the DNA chemical compositions and that the specific generic and even familial characters are caused by definite nucleotide sequences in DNAs.

Yčas (1969) wrote 50 years ago in the conclusive chapter of the book "The biological code" that life is a very complicated physicochemical phenomenon and that the biology of the future will attempt to recover its physical and chemical essence. In this paper, we endeavor to contribute to this foresight.

5 Specification of the Results Obtained in the Work

It is a received idea that the living matter origination problem represents one of the most complicated problems of natural history. In this paper, we consider the following subproblems, entering into it:

- discovery of a triad of minerals, which are necessary and sufficient as the mineral precursors of the simplest living matter;
- evidence of the possibility to obtain nucleic acids, amino-acids, and proteins from the discovered triad of minerals as a result of thermodynamically conditional syntheses with a decrease in the free energy;
- revelation of the natural matrix capable of stimulating the nontrivial and rather complex structures inherent in the principal components of biological chemical substances;
- clarification of the ambient conditions suitable for chemical transformation of the chosen triad of minerals into a multitude of primary individual different DNAs containing random N-base sequences and clarification of physicochemical mechanisms of such processes;
- clarification of the biophysicochemical mechanism of transformation of the multitudes of randomness that are the multitudes of individual different DNAs into the multitudes of directedness that are the multitudes of the DNA double-strands, each multitude containing identical DNA double-strands capable of vertical transmitting their N-base sequences;
- revelation of the possible mechanism of the functional differentiation between simplest plants and animal entities;
- revelation of the causes and mechanisms of the chirality and racemization delay phenomena origination;
- clarification of the way of transformation of inanimate mineral substances into the pre-cellular and unicellular living matter possessing prerequisites for formation of genetic codes.

In our opinion, one of the most important principal scientific results obtained in this work lies in the conclusion that the nucleic acids, amino-acids, and proteins could be produced by Nature on the basis of the above-specified triad of minerals as a result of thermodynamically conditional chemical reactions, which proceed with a decrease in the Gibbs free energy of the reacting mineral system. Before our works, the opinion about the necessity of external energy for formation of simplest living entities and biologically active substances from minerals had dominated in science.

In the framework of investigation of the principal sub-problems listed above, the following set of information was revealed.

- (a) It is stated on the basis of 3D simulation that the DNA and RNA components and their multicomponent fragments are geometrically compatible with the methane gas-hydrate structure II, i.e., the modeled lengths of chemical bonds between

DNA (RNA) fragments and of inter-strand H-bonds in the DNA double-helix fragments arranged within gas-hydrate structural cavities coincide well with the lengths of the corresponding bonds measured by the X-ray method in DNA (RNA) crystals (see the Table). This information was obtained on the basis of two-dimensional simulation and was then confirmed quantitatively on the basis of three-dimensional computer simulation.

- (b) The natural conditions of the methane activation by nitrate ions are revealed, and it is stated that all chemical reactions that lead to synthesis of the nucleic acids, amino-acids, proteins, and other living-matter components from the minerals of the specified triad of natural substances are thermodynamically permissible, i.e., proceed with a decrease in the Gibbs free energy.
- (c) The mechanism of differentiation of simplest entities into the plants and animals and the cause of the manifold predominance of the animal species over the plant ones is proposed.
- (d) The phenomena of chirality and of racemization delay as applied to different natural substances are explained, and the conditions of their revelation are specified.
- (e) The cause of the absence of the Cy(Py)–Ad(Pu), Th(Py)–G(Pu), G(Pu)–Ad(Pu), and Cy(Py)–Th(Py) H-bonds between strands in the DNA double helixes and the selective occurrence of only the Cy(Py)–G(Pu) and Th(Py)–Ad(Pu) H-bonds is revealed; therewith, the cause of unrealizability of the G(Pu)–Ad(Pu), and Cy(Py)–Th(Py) H-bonding is revealed on the basis of three-dimensional simulation and the cause of unrealizability of the Cy(Py)–Ad(Pu) and Th(Py)–G(Pu) H-bonding is revealed on the basis of two-dimensional simulation.

It is stated on the basis of 3D simulation that the DNA and RNA components and their multicomponent fragments are geometrically compatible with the methane gas-hydrate structure II, i.e., the modeled lengths of chemical bonds between DNA (RNA) fragments and of inter-strand H-bonds in the DNA double-helix fragments arranged within gas-hydrate structural cavities coincide well with the lengths of the corresponding bonds measured by the X-ray method in DNA (RNA) crystals (see the Table).

This set of information allows, in our opinion, for specification of the sources, natural conditions, mechanisms, and succession of the processes that had led to the origin of a multitude of multitudes of simplest living entities.

6 General Conclusion

1. The Life Origination Hydrate Theory (LOH-Theory), initiated in 2000, first specifies the natural sources, ambient conditions, chemical processes, biophysicochemical regulations, and mechanisms underlying the origination and propagation of the DNA double helixes and simplest self-replicating living organisms possessing a set of heritable characters, such as the DNA nucleotide sequence

and length, and also possessing the prerequisites for the next step of evolution that is the appearance of genetic codes.

2. The LOH-Theory bears upon the following three our Discoveries:
 - (a) highly-concentrated semi-liquid undisturbed systems water/functional polymer have, at rather low temperatures, matrix gas-hydrate structure;
 - (b) DNA molecules are dimensionally compatible with matrix gas-hydrate structure II;
 - (c) CH_4 -hydrate and NO_3^- - and PO_4^{3-} -ions represent the unique triad of natural minerals that is necessary and sufficient for syntheses of all principal living-matter constituents with no external energy.
3. Just the natural underground and underseabed localizations of CH_4 -hydrate (or, may be, of hydrates of other low-molecular hydrocarbons), which has a matrix honeycomb structure, served as the maternities for origination of the simplest entities from the above-specified mineral triad under the natural conditions favorable for the intra-soil diffusion of ions into such localizations and for long-continued existence of gas-hydrate structures.
4. The Earth's natural conditions most favorable for the living matter origination arose thrice in succession to three glaciation periods, the CH_4 -hydrate localizations occurred in different Earth's regions, various primary entities originated in each favorable period within appropriate CH_4 -hydrate localizations, and, thus, the preconditions for the future species diversity were provided.
5. The LOH-Theory allowed the pioneering explanation of the mechanism of origination of the prerequisites for existence of multitudes of genetic codes, i.e., of the mechanism of origination of multitudes of primary DNA double strands with different random N-base sequences and of the mechanism of the appearance of the property of transformation of the random N-base sequences inherent in each primary DNA double strand into the ordered and vertically transmittable N-base sequences characteristic for all subsequent DNA double strands obtained as a result of replications of each of primary progenitors; the possibility of the vertical transmission of the DNA nucleotide sequence, i.e., of the transformation of the random N-base sequences into the ordered N-base sequences is caused by the peculiarities of the gas-hydrate matrix and by thermodynamic preferences.
6. It is shown on the basis of the LOH-Theory and of available data that just methane rather than bacteria is the primary population of the underground conventional and unconventional methane-hydrate localizations.
7. The reactions of LMSEs formation proceeded with O_2 and N_2 emission to the atmosphere, and the periods of the intensive living-matter origination coincided with the periods of the stepwise increase in the atmospheric O_2 content; therewith, the ancient Earth's atmosphere transformed to the present O_2/N_2 one.
8. The mechanism of origination of the phenomenon of chirality of organic substances, in particular, of the biologically active ones, and the cause and mechanism of the racemization delay are first clarified.

9. It is assumed that the entities differentiation into plants and animals proceeded at the step of unicellular living organisms, the cause and mechanism of this differentiation are proposed, and the manifold predominance of the animal species over the plant ones is first explained.
10. The occurrence of underground conventional and unconventional methane-hydrate localizations populated with bacteria of different species, which is proved by analyses of available information, counts in favor of the LOH-Theory.
11. The occurrence of the admixtures of N_2 , O_2 , NH_3 , and CO_2 in the gases emitting from the underground CH_4 -hydrate localizations also indirectly counts in favor of the LOH-Theory, because all these gases are the side products of living matter origination.
12. The LOH-Theory can be experimentally verified; the principal construction of the apparatus and the methodical grounds are proposed.

The consequence of the adequate understanding of the mechanisms of life origination and metabolism development is not limited to explaining the species diversity and history of the emergence of interspecific and intraspecific differences. In our opinion, the adequate understanding of these processes can be of practical importance for the daily life of human communities and each individual. For example, knowledge of the sources and conditions for origination and development of microorganisms can contribute to the improvement of methods for combating various infections, including viral diseases. In addition, the processes underlying the life origination and metabolism development are, apparently, reproduced to a large degree in every cell of a living organism during DNA replication and cell mitosis. If this is true, the mechanisms of these processes in modern highly organized organisms should be similar to the mechanisms of the processes that were formed at the stage of the emergence and complication of the simplest living entities. Therewith, in our opinion, modern mechanisms should be controlled basically by the same fundamental laws of physical biochemistry that controlled the life-sustenance processes in organisms of the distant past. Just this assumption underlies the MRH-Theory (Kadyshevich and Ostrovskii 2007; Ostrovskii and Kadyshevich 2011, 2012b) and Life-Prolongation Theory (Ostrovskii and Kadyshevich 2014c) proposed by us and, possibly, could underlie the first step on the way to production of food from minerals, i.e., to execution of the work that is performed by plants.

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Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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