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HYDRATE HYPOTHESIS OF LIVING MATTER ORIGINATION (LOH-HYPOTHESIS)
Thermodynamic grounds of formation of living matter simplest elements from hydrocarbons and niter

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In the context of the LOH-hypothesis, the following questions are discussed: (1) Could N-bases and riboses originate from CH_4-hydrocarbons and niter at the expense of internal energy? (2) How had methane-hydrate originated? (3) How had CH_4 and NO_3^- met together? (4) Why are DNA and RNA monomer links similar and limited in size? (5) Why were N-bases and riboses limited in their chemical growth? (6) Why are the sequences of N-bases in DNA and RNA molecules not random? (7) Why do DNA and RNA compositions usually contain only five chemical elements? (8) Why do only five N-bases usually enter the DNA and RNA compositions, and why are other ones random? (9) Could D-ribose, desoxy-D-ribose, thymine, and uracil be simultaneously produced in the reaction of niter with methane? (10) Why did Nature select D-riboses for DNA and RNA construction?

Keywords: *life origination hydrate hypothesis, life-origin thermodynamics, origin of life*

Introduction

General principles of the life origination hydrate hypothesis

Life origination hydrate hypothesis (LOH-hypothesis) [1–7] had been initiated by the results [8–10] of our calorimetric studies of water vapor interaction with monomer and polymer substances modeling biologically active molecules. The LOH-hypothesis differs principally from the life-origination hypotheses (such as [11–16]) proposed earlier.

We associate living matter origination with the appearance of DNA- and RNA-like molecules and try to reveal the simplest and most realistic way by which Nature went. We believe that protein is the secondary product of DNA and RNA interaction with the environment. According to our opinion, the processes that led to living-matter origination and to its subsequent development are thermodynamically conditioned, natural, and inevitable and that all they are governed by universal physical and chemical laws.

Living matter exists at and under the Earth's surface and under seawater to such depths as, at least, 10.5 km. After thermodynamic works of the last decade [3, 4, 7, 17–20], it became obvious that no external energy is necessary for living matter origination from simple natural substances. Apparently, calm environmental conditions with no electric discharges, strong temperature variations, and so on are necessary for formation of so long and regular molecules as DNA and RNA. The underground and underseabed layers satisfy these conditions to the utmost.

According to the LOH-hypothesis, the living matter simplest elements (LMSE), namely N-bases, riboses, and nucleosides, and also nucleotides, DNA- and RNA-like molecules, amino acids, and protocells originated and, possibly, originate in our days from CH_4 (or other CH_4-hydrocarbons), niters, and phosphates under the Earth's surface or seabed within honeycomb structures of hydrocarbon hydrates. It is well known that methane (and also aliphatic, alicyclic, and aliaromatic compounds) is capable of interacting with nitrate ions under pressure, yielding different organic substances (M. Konovalov's reaction, 1888). The underground deposits of CH_4 and other hydrocarbons could result from the reaction between H_2 and CO_2. Carbon dioxide could be produced from carbonates as a result of their thermal decomposition induced by the gravitational compression of the young-Earth crust. Hydrogen could be desorbed from the solid aggregates of which the young Earth was composed. These aggregates had adsorbed hydrogen from nebula before they were captured by the Earth's gravitational force in the period of the Earth origination as a planet body. Thus, the living-matter sources are H_2, carbonates, and phosphates, which resulted from transformation of the nebula. The nebula that was the progenitrix for the Solar System arose after

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the supernova explosion. These processes are detailed in [3, 7].

The LOH-hypothesis allows for answering the following questions. (1) Could N-bases and riboses originate from CH_4-hydrocarbons and niter at the expense of internal energy of the source substances? (2) How had methane-hydrate originated? (3) How had CH_4 and NO_3^- met together? (4) Why are DNA and RNA monomer links similar and limited in size? (5) Why were N-bases and riboses limited in their chemical growth? (6) Why are the sequences of N-bases in DNA and RNA molecules not random? (7) Why do DNA and RNA compositions usually contain only five chemical elements? (8) Why do only five N-bases usually enter the DNA and RNA compositions, and why are other ones random? (9) Could *D*-ribose, desoxy-*D*-ribose, thymine, and uracil be simultaneously produced in the reaction of niter with methane? (10) Why did Nature select *D*-riboses for DNA and RNA construction?

We will consider the answers to these questions one-by-one and will give the thermodynamic substantiation in the form in which it is possible at present. The thermodynamic estimates are obtained for the standard conditions on the basis of the data [18–21] on the enthalpy of formation $\Delta_f H_j^0$ and absolute entropy S_j^0 of substances (Table 1).

Thermodynamic grounds of LMSE formation

Could N-bases and riboses originate from methane hydrocarbons and niter at the expense of internal energy of the source substances?

Before considering the answer to this question, we should remind the following. In living matter, the inheritance of characters is realized through nucleic acids (DNA and RNA). Each molecule of nucleic acid represents the linear polymer system of nucleosides. Each nucleoside unit consists of an N-base group bound with a ribose group. The nucleoside units are linked to each other through phosphate groups in such a way that each phosphate group is located between two neighboring ribose groups. As N-bases, Th and Cy (pyrimidine bases) and G and Ad (purine bases) usually enter DNA molecules and U (pyrimidine base, instead of Th), Cy, G and Ad usually enter RNA molecules. As ribose groups, desoxy-*D*-ribose (DDR) enters DNA molecules and DR enters RNA molecules. The genetic code is determined by the sequence of location of N-bases in DNA molecules. The molar ratios Ad/Th and G/Cy in DNA molecules and Ad/U and G/Cy in RNA molecules are equal to unity. Each sort of DNA or RNA molecules is characterized by an individual molar ratio (Ad+Th)/(G+Cy) or (Ad+U)/(G+Cy), respectively. For bacteria, this ratio can be above or below unity; for higher organisms, the range of variations in this ratio is comparatively narrow, e.g., for most of animals, it is usually between 1.3 and

Table 1 Standard enthalpies of formation ($\Delta_f H_j^0$) and absolute entropies (S_j^0)

j	Substance	Formula	$\Delta_f H_j^0$ (*T*)/kJ mol^{-1}		S_j^0 (T)/J K^{-1} mol^{-1}	
1	Thymine (Th) (cr)	$C_5H_6N_2O_2$	–462.8	[19]	160.1	[18]
2	Cytosine (Cy) (cr)	$C_4H_5N_3O$	–221.3	[19]	140.8	[18]
3	Guanine (G) (cr)	$C_5H_5N_5O$	–183.9	[19]	160.2	[18]
4	Adenine (Ad) (cr)	$C_5H_5N_5$	96	[19]	152.0	[18]
5	Uracil (U) (cr)	$C_4H_4N_2O_2$	–429.4	[19]	128.0	[18]
6	Xanthine (X) (cr)	$C_5H_4N_4O_2$	–379.6	[19]	160.5	[19]
7	Hypoxanthine (Hs) (cr)	$C_5H_4N_4O$	–110.8	[19]	145.1	[19]
8	*D*-ribose (DR) (cr)	$C_5H_{10}O_5$	–1050.9	[20]	175.7	[20]
9	Water (lq)	H_2O	–285.83	[21]	69.95	[21]
10	Potassium nitrate (cr)	KNO_3	–494.0	[21]	132.9	[21]
11	Potassium hydroxide (cr)	KOH	–424.58	[21]	78.87	[21]
12	Methane (gas)	CH_4	–74.6	[21]	186.26	[21]
13	Ethane (gas)	C_2H_6	–84	[21]	229.06	[21]
14	Propane (gas)	C_3H_8	–103.89	[21]	270.0	[21]
15	Ethylene (gas)	C_2H_4	52.4	[21]	219.21	[21]
16	Propylene (gas)	C_3H_6	20.42	[21]	267.0	[21]
17	Nitrogen (gas)	N_2	0	[21]	191.58	[21]
18	Oxygen (gas)	O_2	0	[21]	205.04	[21]
19	Hydrogen (gas)	H_2	0	[21]	130.57	[21]

1.5 (the Ad, G, Th and Cy contents in the human sperm are 31, 19, 31, and 19%, respectively); and, for higher plants, it is between 1.1 and 1.7 [22].

The authors of all earlier hypotheses of life origination proceeded from the assumption that some external energy is necessary for LMSE formation. We will show thermodynamically that the full LMSE set that is necessary for the RNA formation can be obtained from methane and niter at the expense of the internal energy of the source substances. The calculations will be performed for RNA, because no thermodynamic functions for DDR, which belongs to DNA, are available. However, qualitative estimations of the feasibility of DDR formation will be given below.

Let us write the reaction of formation of the full set of N-bases and DR necessary for origination of an RNA molecule in the form

$$a_1KNO_3+a_2C_nH_m=a_3U+a_4Ad+a_5Cy+a_6G+4DR+a_1KOH+a_7H_2O+a_8N_2 \quad (1)$$

where C_nH_m is the formula of a source aliphatic hydrocarbon and a_1–a_8 are the stoichiometric coefficients (therewith, the stoichiometric coefficients for KNO_3 and KOH are the same). Equation (1) shows how many molecules of each of the source substances are consumed and how many molecules of each of the products are produced counting on 4DR molecules in the average over the chain. This equation corresponds to the situation when oxygen of niter reacts completely; i.e., O_2 is not produced. Different species are characterized by different molar ratios (Ad+U)/(G+Cy). Therefore, we can introduce the notation

$$r=(a_3+a_4)/(a_5+a_6) \quad (2)$$

and express the stoichiometric coefficients a_3–a_6 of Eq. (1) through r. We can also write

$$a_3=a_4;\ a_5=a_6 \quad (3)$$

since, in RNA molecules, the molar ratio (Ad/U)=1 and (G/Cy)=1). In each RNA molecule, the number of N-bases is equal to the number of *D*-ribose groups. Therefore,

$$2a_3+2a_5=4 \quad (4)$$

From Eqs (2)–(4), we obtain

$$a_3=a_4=2r/(r+1);\ a_5=a_6=2/(r+1) \quad (5)$$

After substitution of Eq. (5) into Eq. (1), we have

$$a_1KNO_3+a_2C_nH_m=[2r(C_4H_4N_2O_2+C_5H_5N_5)+2(C_4H_5N_3O+C_5H_5N_5O)]/(r+1)+4C_5H_{10}O_5+a_1KOH+a_7H_2O+a_8N_2 \quad (6)$$

Then, we fit the stoichiometric coefficients a_1, a_2, a_7 and a_8 for Eq. (6). These coefficients can be expressed as follows:

$$a_1=1.6+7.6m/n-(3.6r+4)/(r+1) \quad (7)$$

$$a_2=38/n \quad (8)$$

$$a_7=15.2m/n-20.8-(7.2r+8)/(r+1) \quad (9)$$

$$a_8=0.8+3.8m/n-(10+8.8r)/(r+1) \quad (10)$$

Equation (6) with coefficients (7)–(10) was used to calculate the changes in the standard Gibbs free energy (Δ_iG^0, where i is the reaction number) for the processes of formation of the full set of substances necessary for synthesis of RNA molecules from niter and different aliphatic hydrocarbons. The calculations performed for the sets characterized by different r values allow the following conclusions. The changes in the Gibbs free energy for the reactions of niter with CH_4, C_2H_6, C_3H_8, C_2H_4 and C_3H_6 are negative and rather great in magnitude and vary only slightly with the r value. For example, the Δ_iG^0 values for the reaction between niter and methane at r=0.0625, 1.00 and 16.0 are equal to –8227, –8281 and –8336, respectively, and the Δ_iG^0 values for the reaction between niter and ethane at r=0.0625, 1.00 and 16.0 are equal to –6050, –6104 and –6159, respectively.

These results mean that the LMSE could originate from methane hydrocarbons and niter at the expense of the internal energy of the source substances and that thermodynamics allows wide variations in relative yields of N-bases. Significant variations in the equilibrium relation between produced N-bases correspond to so small variations in the Gibbs free energy changes as several tens of kilojoules. The Gibbs free energy variations of such an order could result from variations in the reaction conditions and in the nature of reactants (e.g., from the replacement of KNO_3 by $NaNO_3$). This conclusion is important, because it shows that different sets of N-bases could originate in different historical periods in any one region or in any one historical period in different regions of the globe.

Our calculations are performed for the standard conditions. However, the Δ_iG^0 values for the reactions under consideration are so high in magnitude that there are no doubts that these reactions are thermodynamically feasible within the phases of hydrocarbon hydrates under real conditions.

How had methane-hydrate originated?

The H_2 molar content in the chemically active components of the protoplanetary nebula (after deduction of He) exceeded 99%. The particles of the protoplanetary dust had been covered with chemisorbed hydrogen capable of different polarization of the surfaces of various chemical natures as a result of the electron structure inherent in H-atoms. The electrostatic dif-

ferences caused by hydrogen chemisorption at dust particles had stimulated adhesion of the particles to each other and to big protoplanetary conglomerates. Hydrogen chemisorption had led to occlusion of significant amounts of hydrogen inside the young-planet body. As the planetary body had been growing, compacting, and heating, hydrogen had been desorbing to the voids between agglomerated masses and to the mineral porous structures. As the young planet increased in size, it had become saturated with internal reservoirs filled with H_2 of high pressure. The progressive heating of the Earth's interior had stimulated decomposition of carbonates and CO_2 emission into the reservoirs filled with H_2. Thus, the intra-terrestrial reservoirs filled with the heated (H_2+CO_2) mixtures had been formed. Inside such reservoirs, the conditions favorable for the chain reaction

$$4H_2(g)+CO_2(g)=CH_4(g)+2H_2O(l) \qquad (11)$$

could arise. Apparently, the step of initiation of the chains proceeded at the walls of the reservoirs filled with the (H_2+CO_2) mixture. The walls were reduced, at least partially, with hydrogen, and thus this reaction could be catalyzed by reduced metals. It is seen from Eq. (11) that the gas volume decreases during this reaction. Therefore, this process stimulated H_2 and CO_2 diffusion into the reservoirs from the outside. The change in the standard Gibbs free energy for this reaction is rather high in magnitude and is equal to –130.6 kJ mol^{-1}; i.e., the reaction should proceed up to almost complete consumption of one of the source gases under rather wide variations in the reaction parameters.

With time, the exothermal process of Earth's crust compacting was decaying and the Earth's crust was cooling. This phenomenon favored formation of methane-hydrate (and hydrates of other hydrocarbons) within underground reservoirs filled with methane and water. Gas-hydrates are honeycomb, solid or semi-liquid, mineral substances with cubic (structure I, a=1.20 nm), face-centered cubic (structure II, a=1.73 nm), or hexagonal (structure H, a=1.23 nm and c=1.02 nm) lattices composed of large and small cavities, where the waters (hosts) are the vertices of the cavities and other atoms, molecules, or atomic groups (guests) are included within the cavities; as guests, particles of one type or two different types can be included into the large cavities and, in addition, particles of a third type can be included into the small cavities [23, 24]. In gas-hydrates, the guest–water interactions are provided by the van der Waals forces. For our consideration, it is important that hydrates of hydrocarbons could originate in the Earth's crust before origination of the simplest species of living matter. The capability for hydrate formation is a fundamental property of water molecules.

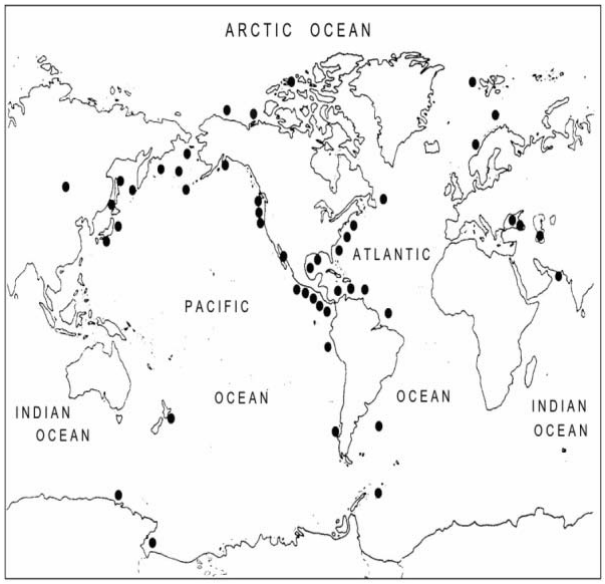

Fig. 1 Submarine hydrocarbon-hydrates [23]; circles mark the regions, where submarine hydrocarbon-hydrates or their characteristic features are revealed

How had CH_4 and NO_3^- met together?

At present, there are many underseabed methane-hydrate deposits (see the map, Fig. 1). In 2004, the methane mass in the proven methane-hydrate deposits was estimated as 6.4×10^{12} tons [25], and this estimate grows continuously. Underground methane-hydrate deposits are also known. Near some of them, niter deposits are located, for example, along the west coast of the Central and South America. Apparently, the niter deposits were still more abundant in the Arhean period because niter is water-soluble. In the regions characterized by neighboring locations of methane hydrate and niters, NO_3^--ions diffused into the methane hydrate structures and reacted with methane.

Note the following. In literature, there is no common opinion on the history of formation of niters. Some authors believe that niters resulted from rookeries or from 'necropolises' of Archean animals. Other authors suppose that this opinion is erroneous. Indeed, it is difficult to explain why poorly soluble phosphates that belonged to the remains of the animals disappeared and deposits of soluble nitrates were stored (in Chile, about 5 million tons of natural $NaNO_3$ were extracted). We suppose that the localizations of such individual minerals as niters arose in the Earth's crust as a result of nebular processes and falling of meteorite-like objects on the Earth in the period of planet formation.

Gas-hydrate hydrocarbons could interact with the NO_3^--ions diffused not only from the land niter deposits but also from oceanic water.

Why are the DNA and RNA monomer links similar and limited in size?

According to the LOH-hypothesis, the nucleosides formed within the cavities of methane-hydrate structures (or, maybe, within the structural cavities of hydrates of other hydrocarbons) and their sizes were limited by the sizes of the structural cavities.

The following figure (Fig. 2) illustrates the structures of the hydrate cavities.

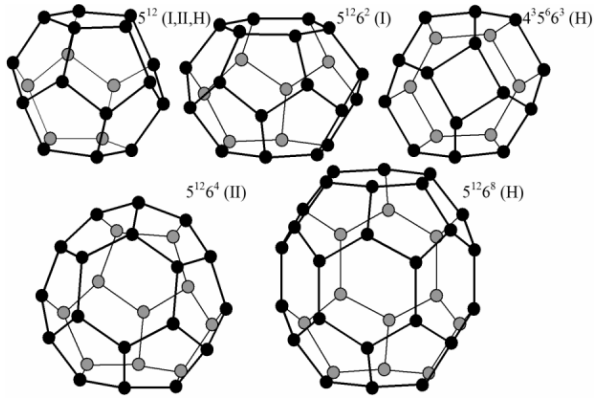

Fig. 2 Hydrate cavities of the structures I, II and H

For the crystal structures I, II and H, the unit cell formulas are $(S)_2{\cdot}(L)_6{\cdot}46H_2O$, $(S)_{16}(L+)_8{\cdot}136H_2O$ and $(S)_5(L{+}{+}){\cdot}34H_2O$, respectively (S is the small guest, L is the large guest, L+ is the larger guest, and L++ is the largest guest). Hydrate structures remain stable when the guest contents are below their stoichiometric values by 20–25%. Each unit crystal cell of the structure I, II or H contains 2 small 5^{12} (20 waters) and 6 large $5^{12}6^2$ (24 waters) cavities, 16 small 5^{12} and 8 large $5^{12}6^4$ (28 waters) cavities, or 3 small 5^{12}, 2 small $4^35^66^3$ (20 waters) and 1 large $5^{12}6^8$ (36 waters) cavities, respectively. According to [24], the 5^{12}, $5^{12}6^2$, $5^{12}6^4$, $4^35^66^3$, and $5^{12}6^8$ cavities are capable of housing the molecules having diameters of 0.36–0.44 (such as Ar, O_2, N_2, and CH_4), 0.36–0.54 (such as CO_2 and C_2H_6), 0.56–0.62 (such as C_3H_8 and $(CH_3)_3CH$), 0.36 (such as CH_4) and 0.70–0.86 (such as $(CH_3)_3CC_2H_5$) nm, respectively. It was shown that water solutions of cyclic organic liquids consisting of rather large molecules, such as furan $(CH)_4O$ and tetrahydrofuran $(CH_2)_4O$, form solid hydrate structure II at temperatures below 298 K [26]. Sometimes, atoms of large-sized guest molecules partake in the formation of the 'walls' of the cavities [27], for example, in the so-called semi-clathrate hydrates, such as hydrates of *n*-propylamine and other alkyl-amines. Under some conditions, the hydrate structures can recrystallize from one structure to another; recrystallization as such requires not much energy.

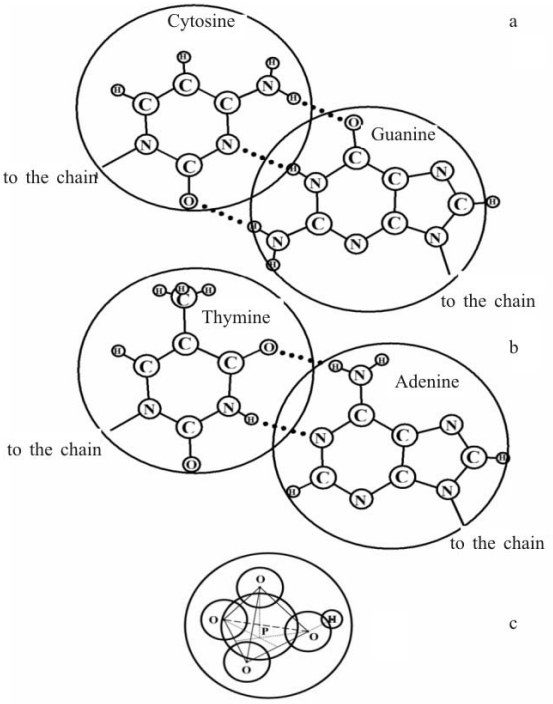

Fig. 3 Illustration of the coincidence between the sizes of the hydrate structure II large cavities and N-bases of the neighboring hydrogen-bound DNA molecules in double helixes and of the coincidence between the sizes of the hydrate structure II small cavity and phosphate group:
a – Cy–G pairing with neighboring large cavities,
b – Th–Ad pairing with neighboring large cavities and
c – phosphate group within a small cavity

These data gave us grounds to assume that so large-sized molecules as N-bases could be produced within the cavities of hydrate structures. The correlation between the sizes of individual components of the DNA and RNA molecules and the sizes of the structural cavities of hydrates (Fig. 3 drawn to a scale) counts in favor of this assumption. The large cavities are as if 'moulds' for N-bases, and the small cavities are as if 'moulds' for phosphate groups and riboses. (Note that the large cavities of the hydrate structure H are somewhat 'more roomy' than those of the hydrate structure II, and it cannot be excluded that the structure H is the matrix for the LMSE formation.) Just the sizes of the structural cavities limit growing of the links. The links are similar because their formation proceeds from the same substances, in the cavities of the same size, slowly step by step with decreasing in the Gibbs free energy over the entire methane-hydrate localization up to full filling of the cavities. Thus, the entire localization reaches its final state by the same time. Although N-bases are similar, they are not identical, and the cause of this phenomenon is as follows. Let one of the cavities be completely filled with a purine base in such a way that the atomic van der Waals radii of this N-base overstep the plane of any window

of this cavity (Fig. 3). In this case, the neighboring cavity should contain an N-base of a lesser size, because the distance between any two atoms of neighboring molecules should exceed the sum of their van der Waals radii.

Why were N-bases and riboses limited in their chemical growth?

The answer to this question is, apparently, clear after the answers to the previous questions. The subsequent chemical transformations were hampered by the occurrence of the hydrate matrix and by filling of the large and small cavities with N-bases and riboses, respectively, and also by exhaustion of methane.

Why are the sequences of N-bases in DNA and RNA molecules not random?

The authors of [28] note 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. In particular, this criticism relates to Oparin's hypothesis. In our case, the arrangement of N-bases is not random. Some order is stimulated by the occurrence of the hydrate matrix. An additional ordering arises from the definiteness in the sizes of the hydrate cavities, atoms, and van der Waals radii of atoms. An analysis of the sizes of N-bases shows that two purines can not be housed in neighboring cavities. In addition, the hydrate-structure geometry allows for housing pyrimidines of only definite compositions in the cavities adjacent to the cavity occupied by a definite purine. Thus, according to our hypothesis, the arrangement of N-bases in DNA and RNA molecules is not random and contains elements of ordering.

Why do DNA and RNA compositions usually contain only five chemical elements?

Methane is a rather inert substance, and, under conditions of methane-hydrate stability, very few underground minerals are capable of interacting chemically with it. Therefore, the methane-hydrate structure as if 'swallows' selectively the nitrate ions and converts them to N-bases and riboses. Diffusion of NO_3^--ions into the hydrate structure is stimulated by the decrease in the Gibbs free energy in the process of chemical interaction of NO_3^- with methane. A similar situation arises when phosphate ions contact with the hydrate structure filled with nucleosides. The foreign atoms rarely entering the DNA and RNA compositions in addition to C, N, P, O and H come from the walls of the reservoirs filled with methane-hydrate, admixtures to the source CH_4 and H_2O, etc.

Why do only five N-bases usually enter the DNA and RNA compositions, and why are other ones random?

We believe that just the thermodynamics is instrumental in the selection of N-bases to be further incorporated in nucleic acids. This opinion is illustrated by the reaction between guanine and water yielding xanthine. If the reactions leading to formation of N-bases and riboses proceed in a closed system, equilibrium should be established after a time. It is clear that equilibrium in the reaction system suggests equilibrium between all its components, in agreement with the detailed equilibrium principle; this property gives a possibility to elucidate whether xanthine can exist in the system containing guanine and water.

For the reaction

$$C_5H_5N_5O+H_2O=C_5H_4N_4O_2+NH_3 \qquad (12)$$

proceeding under standard conditions, $\Delta_{12}(G^0)=7.32$ kJ mol^{-1}.

This estimate relating to the standard conditions means that equilibrium (12) is shifted to the left and xanthine formation is thermodynamically disadvantageous. Apparently, the analogous cause hampers entering of other N-bases but Ad, G, Th, Cy and U into DNA and RNA molecules. The absolute change in the free energy is small; therefore, nucleic acids may contain xanthine under certain conditions differing from standard ones. Indeed, xanthine sometimes enters the compositions of natural nucleic acids. This consideration also shows that the gas mixtures formed in the process of LMSE origination could contain NH_3.

Could D-ribose, desoxy-D-ribose, Th and U be simultaneously produced in the reaction of niter with methane?

As was said in 'Could N-bases and riboses originate from methane hydrocarbons and niter at the expense of internal energy of the source substances?', the thermodynamic functions for DDR are not available. However, some qualitative estimates for the thermodynamic feasibility of DDR formation in the chemical system under consideration can be made. We will give the thermodynamic estimate showing that DDR and Th can be produced along with DR and U, Ad, G and Cy as a result of interaction between niter and methane. Let us consider the reaction of formation of Th and DDR from U and DR.

$$C_4H_4N_2O_2(cr)+CH_4(g)+C_5H_{10}O_5(cr)= C_5H_6N_2O_2(cr)+C_5H_{10}O_4(cr)+H_2O(l) \qquad (13)$$

At first, we estimate the entropy change in this reaction. As the first approximation, we take that the entropy of DDR is equal to the entropy of DR. According to Table 1, approximately, $\Delta_{13}S_j^0 = -84.21$ J mol^{-1} K^{-1} and the contribution of the entropy term to the $\Delta_{13}G^0$ value, $T\Delta_{13}S_j^0 = -25.11$ kJ mol^{-1}. Now, we use the following approach. We suppose that $\Delta_{13}G^0=0$, calculate the $\Delta_f H_j^0$ value for DDR ($C_5H_{10}C_4$(cr)), and obtain –781.1 kJ mol^{-1}. This result, in combination with the data of Table 1, means that, for the reaction

$$C_5H_{10}O_5(cr)+H_2(g)=C_5H_{10}O_4(cr)+H_2O(l) \quad (14)$$

$\Delta_{14}(\Delta_f H_j^0) = -16.09$ kJ mol^{-1}. It is known that the reactions of such a type, in which hydrogen reduces organic substances with water formation, are characterized by negative enthalpy changes much higher in their magnitudes than the obtained value. This means that the magnitude of $\Delta_f H_j^0$ for DDR is apparently higher than 781.1 kJ mol^{-1}. Thus, it could be expected that the products of oxidation of simple hydrocarbons by niters within the hydrate structure can contain DDR together with Th, Ad, G, Cy, U and DR. Relative contents of these components depend on the conditions. It is possible that the conditions, at which reaction (13) proceeds predominantly in any one of two directions, differ not very significantly. This means that reaction (13) in different time periods or in rather close methane-hydrate localizations could provide formation of DNA or RNA molecules. Thus, after melting of the hydrate structures as a result of heating or as a result of the occurrence of excessive water, DNA and RNA molecules could be mixed.

Why did Nature select D-*riboses rather than* L-*riboses or their mixtures for DNA and RNA construction?*

D-riboses and *L*-riboses as well as desoxy-*D*-riboses and desoxy-*L*-riboses are identical in the sizes and almost identical in their thermodynamic characteristics and reaction abilities, but the molecules of each of these pairs are not identical in the spatial arrangement of their functional groups. For unknown reason, Nature selected just *D*-ribose and desoxy-*D*-ribose for construction of RNA and DNA molecules, respectively. This feature of RNA and DNA molecules is termed monochirality. The mechanism of arising of the phenomenon of monochirality of biologically active molecules is one of the most intriguing scientific problems. Many physicists and chemists tackled it. Different hypothetical causes of this phenomenon were discussed, including such nontrivial ones as the fundamental asymmetry of the Universe and the weak interaction causing nuclear beta decay [29, 30].

We assume that the DNA and RNA monochirality is a natural inevitable consequence of the methane-hydrate matrix geometry, chemical properties of the reactants, thermodynamic characteristics of the chemical processes proceeding in the matrix, and termination of the reaction processes by the step of full filling of the structural matrix.

All these factors taken together should lead, in our opinion, to the unique possible result, namely, to the formation of DNA- and RNA-like molecules inside the hydrate structure. We believe that formation of DNA- and RNA-like molecules inside the hydrate structure is possible on the exclusive basis of *D*-forms of ribose and desoxyribose. This assumption represents the rigid constituent of the LOH-hypothesis. It should be verified by the subsequent three-dimensional computer simulation, which should be performed for different possible hydrate structures.

Conclusions

Figure 4 represents principal general scheme of living-matter origination for the situations when the first step is the CO_2 diffusion to the underground reservoir filled with H_2 or the H_2O diffusion to the underground reservoir filled with CH_4.

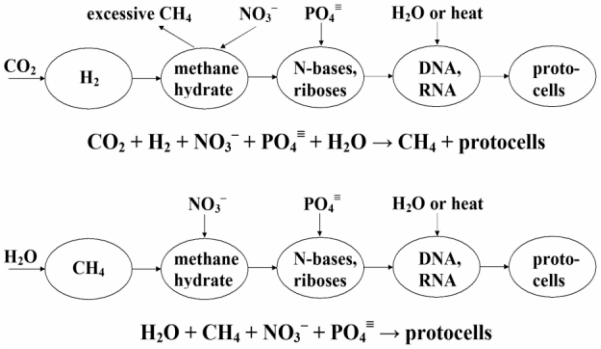

Fig. 4 General hypothetical scheme of living-matter origination

According to the LOH-hypothesis, living matter originated repeatedly; in one localization, different DNA- and RNA-like molecules and different protocells could originate in the same time period. It cannot be excluded that living matter can originate in our time because the process of living-matter origination is not associated with any rare situations and environmental conditions.

Our hypothesis was, apparently, confirmed by observations [31]. Innumerable prokaryotic colonies were found in the Pacific Ocean at depths of 400 m and more under the seabed in the regions containing underseabed methane-hydrate deposits. No other C-source but CH_4 occurs around these colonies. Large bacterial

colonies were found also under the Earth's surface at depths down to 6820 m [32]. In both observations, living matter was associated with a methane medium. Thus, living matter apparently originates and reproduces on the basis of methane-hydrate.

One more fact counts in favor of our hypothesis. According to [33–35], the gas sampled for analyses from underseabed methane-hydrate localizations contained significant amounts of N_2 and very small amounts of O_2: 4% of N_2 and 0.005% of O_2 in [33] and 11.4% of N_2 and 0.2% of O_2 in [34]. Thus, the N_2/O_2 ratio in the samples is much higher than that in the atmosphere; evidently, the samples could not have been contaminated by atmospheric nitrogen during their collection and storage. Potential sources of elemental nitrogen in the Earth's crust are not numerous. Therefore, it is quite possible that nitrogen was produced by reduction of methane with niter ('Could N-bases and riboses originate from methane hydrocarbons and niter at the expense of internal energy of the source substances?').

An important feature of our hypothesis is a possibility for its computer ('Why did Nature select *D*-riboses rather than *L*-riboses or their mixtures for DNA and RNA construction?') and experimental testing. It is sufficient to house methane-hydrate, niter, and apatite into an abiotic autoclave thermostated at about 280 K and supplied with a pressure-relief valve and instruments allowing the performance of repeated chemical analyses of the gaseous and condensed reaction products and to have patience; of course, a number of technical problems relating to provision and prolonged maintenance of abiotic conditions, analytical techniques and procedures, and so on should be solved. However, the game is worth the candle!

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