

Thermodynamics of formation of nitrogen bases and D-ribose from mineral substances in light of the problem of origination of simplest elements of living matter

V.E. Ostrovskii^{a,*}, E.A. Kadyshevich^b

^a *Karpov Institute of Physical Chemistry, Vorontsovo Pole Street 10, Moscow 105064, Russia*

^b *Oboukhov Institute of Atmospheric Physics, Russian Academy of Sciences, Pyzhevsky 3, 119017 Moscow, Russia*

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Abstract

The paper represents a further development of our hydrate hypothesis of simplest living matter origination (SLMO) from inorganic and simplest organic mineral substances. It is supposed that the sources of SLMO are simplest aliphatic hydrocarbons, niters, and phosphates. Thermodynamic calculations demonstrating a principal possibility for simultaneous syntheses of different nitrogen bases, D-ribose, and desoxy-D-ribose from these source substances are presented. The most probable principal mechanism of SLMO and the principal conditions necessary for realization of the proposed chemism of SLMO in the framework of the proposed mechanism are considered. A principal means for testing the hypothesis is proposed. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

We proceed from the assumptions that the Earth's living matter had originated on our planet from inorganic and simplest organic substances as an inevitable product of the atomistic world and that the same rather simple natural phenomenon is the core of the processes of origination and reproduction of living matter. We believe that living matter was originating multiply and, maybe, originates now and that the diversity of the available forms of living matter is caused mainly by some variations in parameters of the native medium. In all probability, stable undisturbed conditions favor simplest living matter origination (SLMO) and this process proceeds so slowly that its direction is thermodynamically favorable. "Nature makes no jumps" (Nature non facit saltus (Lat.)): we had this Latin aphorism at heart when thinking over the problems of this paper.

Before proceeding to the gist of this paper, we reference very briefly to the principal notions on the DNA and gas-hydrate structures. These notions are necessary for our considerations.

Any DNA molecule represents desoxy-D-ribose sugar groups, phosphate groups, and nitrogen bases (N-bases) connected in a regular sequence; natural DNA can exist in the forms of single or dimer double-helix molecules [1] (Fig. 1). In the DNA composition, the following N-bases are most abundant: adenine (Ad), cytosine (Cy), guanine (G), and thymine (Th); in the ribonucleic acid (RNA) composition, uracil (U) is included instead of Th. The groups of other chemical nature in the DNA composition are few and far between.

The formulas of the substances considered in this paper are given in Table 1.

Gas-hydrates [2,3] represent structured honeycomb solid or semi-liquid substances with cubic lattices composed of large and small cavities, where the waters (hosts) are the vertices of the cavities and other molecules or atomic groups (guests) are included within the cavities. The capability for hydrate formation is a fundamental property of water molecules. As guests, particles of one nature or two different natures can be included into large cavities and, in addition, particles of a third nature can be included into small cavities. Gas-hydrates containing guest particles of two or more different chemical natures are termed mixed gas-hydrates. Gas-hydrates are widely distributed in nature. For example, natural methane deposits exist frequently

* Corresponding author.

E-mail addresses: vostrov@cc.nifhi.ac.ru, ostrovv@rol.ru (V.E. Ostrovskii).

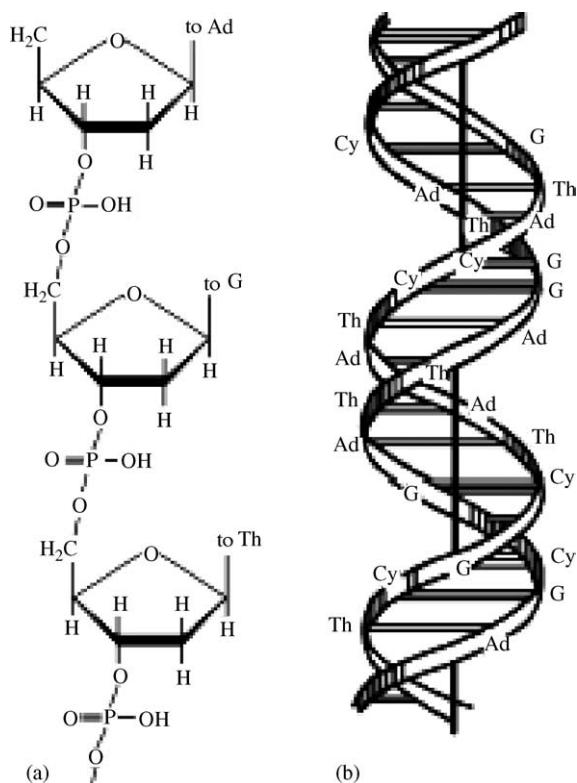


Fig. 1. Fragments of: (a) DNA helix and (b) DNA double helix.

in the form of gas-hydrates. In gas-hydrates, the guest–water interactions are provided by van der Waals forces. Two gas-hydrate structures (structures I and II) are the most abundant ones. The sizes of the gas-hydrate cavities are strictly fixed; for example, the free sizes of the large and small cavities of the structure II are equal to 0.69 and 0.48 nm, respectively (Fig. 2). In the ideal structure II of a trivial gas-hydrate with filled large

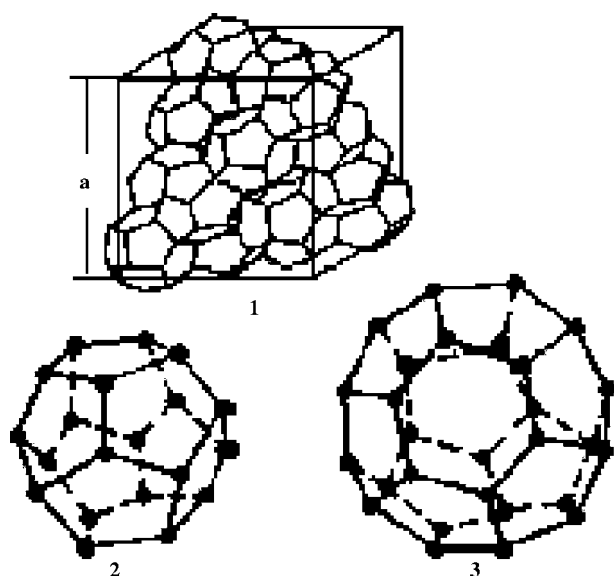


Fig. 2. Crystal lattice of gas-hydrates of the structure II: (1) unit crystal-cell consisting of 136 waters forming 16 small and 8 large cavities; $a = 1.74$ nm; (2) small cavity, pentadecahedron with $d = 0.48$ nm; (3) large cavity, hexadecahedron with $d = 0.69$ nm.

cavities and unfilled small cavities or with filled large and small cavities, 17 or 5.67 waters, respectively, fall at 1 guest particle. In the ideal structure I of a trivial gas-hydrate with filled large cavities and unfilled small cavities or with filled large and small cavities, 7.67 or 5.75 waters, respectively, fall at 1 guest particle. The structures II and I can exist when the guest quantity is deficient, i.e., up to stoichiometric coefficients (n) of 20–21 and 8–9, respectively.

We consider the following fundamental problems:

- (1) on the most probable principal SLMO chemism;
- (2) on the most probable principal SLMO mechanism;
- (3) on the principal conditions necessary for realization of the proposed chemism in the framework of the proposed mechanism.

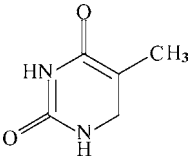
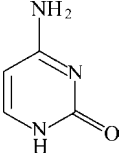
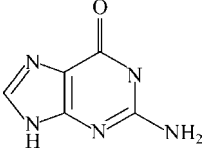
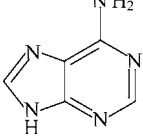
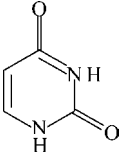
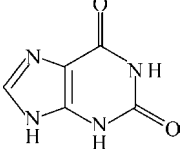
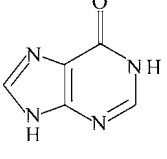
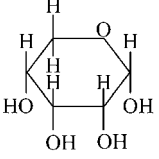
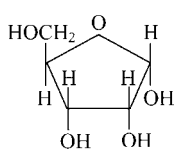
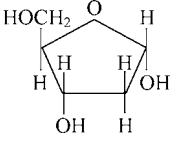
A rather founded consideration of problem (1) is possible after works [4,5], which give the standard enthalpies of formation $\Delta_f H^0$ and entropies (S^0) for different solid N-bases. The corresponding values obtained recently for D-ribose [6] are also used by us (data of [6] on $\Delta_f H^0$ correlate well with the earlier results of [7,8]). Problems (2) and (3) are discussed in the context of our previous works [9–11]. The results and discussions given below were announced in Refs. [12,13].

2. Probable principal chemism of the simplest living matter origination

In order that manifestations of living matter would be as diverse as they are at present, SLMO should proceed in different local regions, on the basis of widely distributed minerals, and multiply in different historical epochs. On the other hand, in order that the chemical compositions of DNA (and RNA) molecules inherent in different kinds of living matter would be so similar as they are in fact, the mineral parent substances producing living matter and the conditions of transformation of these parent substances into living matter should be rather similar if not the same. In addition, the number of principal mineral parent substances necessary for formation of simplest elements of living matter should be minimum and their concentrations should be sufficiently high in order that these mineral parent substances could contact with each other for a rather long time in any one local region. Lastly, the long-term processes of SLMO proceed, most likely, under the Earth's surface, where the conditions are rather stable, but not at the surface–atmosphere interface affected by significant daily, seasonal, and occasional weather variations.

We believe that living matter originates on the basis of only three principal mineral parent substances, such as methane (or another simple hydrocarbon), niter (most probably, sodium niter, i.e., the so-called Chile saltpeter or potassium niter), and apatite $\text{Ca}_5\text{X}(\text{PO}_4)_3$ ($\text{X} = \text{F}, \text{Cl}, \text{or OH}$). (In this connection, we note that an opinion exists that some phosphorites are formed as a result of transformations of bird's excrements in bird-colony regions or animal remains in the regions of mass plagues of different animals or as a result of vital functions of the so-called “phosphoro-bacteria”. However, it is universally accepted

Table 1
Formulas and formula weights of the substances under consideration

Substance	Formula	Formula weight (g/mol)
Thymine (C ₅ H ₆ N ₂ O ₂)		126.11
Cytosine (C ₄ H ₅ N ₃ O)		111.10
Guanine (C ₅ H ₅ N ₅ O)		151.13
Adenine (C ₅ H ₅ N ₅)		135.13
Uracil (C ₄ H ₄ N ₂ O ₂)		112.09
Xantine (C ₅ H ₄ N ₄ O ₂)		152.11
Hypoxantine (C ₅ H ₄ N ₄ O)		136.11
D-Ribose (C ₅ H ₁₀ O ₅)	  pyranose form furanose form	150.11
Desoxy-D-ribose (C ₅ H ₁₀ O ₄)		134.11

that apatites are of mineral origin.) Large-scale deposits of each of these minerals occur in nature. The key problem determining the permissibility of the assumption of SLMO from these minerals is as follows: whether the thermodynamics allows formation of N-bases and 2-desoxy-D-ribose (and D-ribose) from simplest hydrocarbons and sodium (and potassium) niter. The thermodynamic feasibility of the addition reactions between N-bases, 2-desoxy-D-ribose (or D-ribose), and phosphate groups is beyond question (see Refs. [14–17]).

In the context of this problem, we consider below the changes in the standard enthalpies, entropies, and Gibbs free energies for the reactions of formation of D-ribose and N-bases (Th, Cy, G, Ad, and U entering always into the composition of DNA or RNA and also xantine (X) and hypoxantine (HX)) from several simplest hydrocarbons and potassium niter (for NaNO₃, the conclusions are qualitatively the same). The thermodynamic parameters for desoxy-D-ribose are not available. The available standard thermodynamic parameters for the substances used for calculations are listed in Table 2.

It is known that the molar ratios Ad/Th and G/Cy in DNA molecules and the molar ratios Ad/U and G/Cy in RNA molecules are equal to unity. Meanwhile, in different species, the relative numbers of Ad and G are not the same (for example, in the human sperm, the Ad, G, Th, and Cy percentages are about 31, 19, 31, and 19). We consider below a hypothetical averaged situation when the molar ratio Ad/G is equal to unity and solve the question, whether such a situation can arise on the basis of reactions between simplest hydrocarbons and niters in a medium containing no other chemically active elements.

In other words, we consider a question on the thermodynamic feasibility of potassium niter and methane, ethane, propane, ethylene, or propylene interactions leading to formation of equimolecular quantities of Cy, G, Ad, and U and to simultaneous formation of D-ribose in a molar ratio of 1/1 to the sum of N-bases under the standard conditions. We believe that such a

process proceeds up to the state of formation of nitrogen, which is rather inert and is not inclined to further reactions. We analyze the feasibility of the stoichiometric balance for such reactions and calculate the thermodynamic parameters for the corresponding reactions.

The stoichiometric equations and the calculated changes in the enthalpy, entropy, and Gibbs free energy for such reactions (reactions (1)–(5)) are presented in Table 3. The $\Delta_i G^0$ values are calculated by the formula $\Delta_i G^0 = \Delta_i(\Delta_f H_j^0) - T\Delta_i S_j^0$ (i is the reaction number). It is seen that, in the nitrogen medium, reactions (1)–(3) proceed with N₂ evolution and reactions (4) and (5) proceed with N₂ consumption. For each of reactions (1)–(5), the $\Delta_i G^0$ values are negative; i.e., in principle, they could be realized under standard conditions in a suitable medium; the rate of the reactions is of no importance for our consideration, because the Nature is not in a hurry.

The $\Delta_i G^0$ magnitudes are maximum for the process with CH₄ and decrease gradually downcolumn in Table 3; for all reactions under consideration, they are so high that there is no doubt that significant variations in the relative equilibrium concentrations of Ad and G are thermodynamically possible.

In reality, each of processes (1)–(5) could be realized under the condition that the KNO₃ molecules diffuse into hydrate structures of methane rather slowly. The heat effects of these processes are very significant, and too rapid heat evolution within any minor volume could lead to the local overheating and to a disturbance in the equilibrium proceeding of the reactions. The critical values of the rates for the reactions under consideration represent a special problem being beyond the scope of this paper. Note only that the molar heat of each of processes (1)–(5) evolves as a result of successive interactions of several tens of parent molecules within eight separated cavities (see Ref. [10]) of the gas-hydrate structure.

Although thermodynamic data on desoxy-D-ribose are not available, some qualitative estimations of the thermodynamic

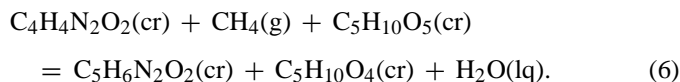
Table 2
Available standard enthalpies of formation and absolute entropies

j	Substance	Formula	$\Delta_f H_j^0(T)$ (kJ/mol)	$S_j^0(T)$ (J/molK)
1	Thymine(cr)	C ₅ H ₆ N ₂ O ₂	−462.8 [5]	160.1 [4]
2	Cytosine(cr)	C ₄ H ₅ N ₃ O	−221.3 [5]	140.8 [4]
3	Guanine(cr)	C ₅ H ₅ N ₅ O	−183.9 [5]	160.2 [4]
4	Adenine(cr)	C ₅ H ₅ N ₅	96 [5]	152.0 [4]
5	Uracil(cr)	C ₄ H ₄ N ₂ O ₂	−429.4 [5]	128.0 [4]
6	Xanthine(cr)	C ₅ H ₄ N ₄ O ₂	−379.6 [5]	160.5 [5]
7	Hypoxanthine(cr)	C ₅ H ₄ N ₄ O	−110.8 [5]	145.1 [5]
8	D-Ribose(cr)	C ₅ H ₁₀ O ₅	−1050.9 [6]	175.7 [6]
9	Water(lq)	H ₂ O	−285.83 [18]	69.95 [18]
10	Potassium nitrate(cr)	KNO ₃	−494.0 [18]	132.9 [18]
11	Potassium hydroxide(cr)	KOH	−424.58 [18]	78.87 [18]
12	Methane(g)	CH ₄	−74.6 [18]	186.26 [18]
13	Ethane(g)	C ₂ H ₆	−84 [18]	229.06 [18]
14	Propane(g)	C ₃ H ₈	−103.89 [18]	270.0 [18]
15	Ethylene(g)	C ₂ H ₄	52.4 [18]	219.21 [18]
16	Propylene(g)	C ₃ H ₆	20.42 [18]	267.0 [18]
17	Nitrogen(g)	N ₂	0 [18]	191.58 [18]
18	Oxygen(g)	O ₂	0 [18]	205.04 [18]
19	Hydrogen(g)	H ₂	0 [18]	130.57 [18]

Table 3
Changes in the enthalpy $\Delta_f(\Delta_f H_f^0)$, entropy $\Delta_f S_f^0$, and Gibbs free energy $\Delta_f G^0$ for reactions (1)–(5) of Cy, G, Ad, U, and D-ribose formation from hydrocarbons and potassium niter

Reaction	$\Delta_f(\Delta_f H_f^0)$ (kJ/mol)	$\Delta_f S_f^0$ (J/mol K)	$\Delta_f G^0$ (kJ/mol)
28.2KNO ₃ (cr) + 38CH ₄ (g) = C ₄ H ₄ N ₂ O ₂ (cr) + C ₄ H ₅ N ₃ O ₂ (cr) + C ₃ H ₅ N ₃ O ₂ (cr) + C ₃ H ₅ N ₃ O ₂ (cr) + 28.2KOH(cr) + 32.4H ₂ O(lq) + 6.6N ₂ (g)	(1) -9410	-3787	-8281
20.6KNO ₃ (cr) + 19C ₂ H ₆ (g) = C ₄ H ₄ N ₂ O ₂ (cr) + C ₄ H ₅ N ₃ O ₂ (cr) + C ₃ H ₅ N ₃ O ₂ (cr) + 4C ₃ H ₅ N ₃ O ₂ (cr) + 20.6KOH(cr) + 17.2H ₂ O(lq) + 2.8N ₂ (g)	(2) -6832	-2442	-6104
18.0(6)KNO ₃ (cr) + 12.1(6)C ₃ H ₈ (g) = C ₄ H ₄ N ₂ O ₂ (cr) + C ₄ H ₅ N ₃ O ₂ (cr) + C ₃ H ₅ N ₃ O ₂ (cr) + 4C ₃ H ₅ N ₃ O ₂ (cr) + 18.0(6)KOH(cr) + 12.1(3)H ₂ O(lq) + 15.1(3)N ₂ (g)	(3) -5840	-1970	-5253
13KNO ₃ (cr) + 19C ₂ H ₄ (g) + N ₂ (g) = C ₄ H ₄ N ₂ O ₂ (cr) + C ₄ H ₅ N ₃ O ₂ (cr) + C ₃ H ₅ N ₃ O ₂ (cr) + 4C ₃ H ₅ N ₃ O ₂ (cr) + 13KOH(cr) + 2H ₂ O(lq)	(4) -5607	-3635	-4523
12KNO ₃ (cr) + 12.1(6)C ₃ H ₆ (g) + 1.5N ₂ (g) = C ₄ H ₄ N ₂ O ₂ (cr) + C ₄ H ₅ N ₃ O ₂ (cr) + C ₃ H ₅ N ₃ O ₂ (cr) + 4C ₃ H ₅ N ₃ O ₂ (cr) + 12KOH(cr) + .5H ₂ O(lq)	(5) -5082	-2708	-4273

feasibility of its formation in the chemical system under consideration can be made. Consider the reaction of Th and desoxy-D-ribose formation from U and D-ribose:



First, we estimate the entropy change in this reaction. As the first approximation, we take that the entropies of desoxy-D-ribose and D-ribose are the same. According to Table 2, approximately, $\Delta_6 S_j^0 = -84.21 \text{ J/mol K}$ and the contribution of the entropy term to the $\Delta_6 G^0$ value, $T\Delta_6 S_j^0 = 25.11 \text{ kJ/mol}$. Now, we apply the following approach. We assume that $\Delta_6 G^0 = 0$ and, under this assumption, calculate the $\Delta_f H_j^0$ value for desoxy-D-ribose, $\text{C}_5\text{H}_{10}\text{O}_4(\text{cr})$. This value is equal to -781.16 kJ/mol . This result, in combination with the data of Table 2, means that, for the reaction of D-ribose reduction by H₂ to desoxy-D-ribose and water, $\text{C}_5\text{H}_{10}\text{O}_5(\text{cr}) + \text{H}_2(\text{g}) = \text{C}_5\text{H}_{10}\text{O}_4(\text{cr}) + \text{H}_2\text{O}(\text{lq})$, the enthalpy change $\Delta_f(\Delta_f H_f^0) = -16.09 \text{ kJ/mol}$. Actually, similar reactions of reduction of organic substances are characterized by negative enthalpy changes, which are significantly higher in magnitude than the last value. This means that, for desoxy-D-ribose, the $\Delta_f H_j^0$ magnitude is higher than 781.16 kJ/mol . Thus, we can conclude that the equilibrium composition obtainable on the basis of simple hydrocarbons and niters in the N₂ medium should include Th, Ad, G, Cy, U, D-ribose, and desoxy-D-ribose. The relative contents of these components can vary depending on the conditions.

We calculated also the thermodynamic parameters for the reactions of formation of N-bases (including Th, Ad, G, Cy, U, X, and HX) from potassium niter and different hydrocarbons in the O₂ medium. These calculations correspond to the situation when processes (1)–(5) stop at the step of incomplete consumption of oxygen.

The results of calculations performed for reactions of potassium niter and methane ((7)–(13)), ethane ((14)–(20)), propane ((21)–(27)), ethylene ((28)–(34)), or propylene ((35)–(41)) with formation of Th, Ad, G, Cy, U, X, and HX are given in Table 4.

Let us summarize the results obtained for reactions (7)–(13) leading to formation of Th, Cy, G, Ad, U, X, and HX, respectively. All N-bases under consideration can coexist in the oxygen medium under standard conditions. Each of these reactions proceeds with a decrease in the Gibbs free energy. In the process of formation of Th and U, oxygen is consumed, while, in the process of formation of other N-bases, oxygen emerges from the reacting system. If the equilibrium responds to the sum of equilibriums (7)–(13), oxygen emerges.

The results obtained for the reactions of potassium niter with ethane ((14)–(20)) are qualitatively similar to those obtained for the reactions of potassium niter with methane.

The results obtained for the reactions of potassium niter with propane ((21)–(27)) are qualitatively similar to those obtained for reactions (14)–(20) and (21)–(27), except for one peculiarity: the adenine synthesis cannot proceed separately according to reaction (24), because the change in the Gibbs free energy for this reaction is positive. However, the increase in the Gibbs free

Table 4
Changes in the enthalpy $\Delta_r(\Delta_f H_j^0)$, entropy $\Delta_r S_j^0$, and Gibbs free energy $\Delta_r G^0$ for reactions (7)–(41)

Reaction		$\Delta_r(\Delta_f H_j^0)$ (kJ/mol)	$\Delta_r S_j^0$ (J/mol K)	$\Delta_r G^0$ (kJ/mol)
2KNO ₃ (cr) + 5CH ₄ (g) + 2O ₂ (g) = C ₅ N ₂ O ₂ H ₆ (cr) + 6H ₂ O(lq) + 2KOH(cr)	(7)	-1666	-869.6	-1407
3KNO ₃ (cr) + 4CH ₄ (g) = C ₄ N ₃ OH ₅ (cr) + 4H ₂ O(lq) + 3KOH(cr) + 0.5O ₂ (g)	(8)	-858.0	-384.0	-743.5
5KNO ₃ (cr) + 5CH ₄ (g) = C ₅ N ₅ OH ₅ (cr) + 5H ₂ O(lq) + 5KOH(cr) + 2O ₂ (g)	(9)	-893.0	-281.4	-809.0
5KNO ₃ (cr) + 5CH ₄ (g) = C ₅ N ₅ H ₅ (cr) + 5H ₂ O(lq) + 5KOH(cr) + 2.5O ₂ (g)	(10)	-613.1	-187.1	-557.3
2KNO ₃ (cr) + 4CH ₄ (g) + 1.5O ₂ (g) = C ₄ N ₂ O ₂ H ₄ (cr) + 5H ₂ O(lq) + 2KOH(cr)	(11)	-1421	-682.9	-1218
4KNO ₃ (cr) + 5CH ₄ (g) = C ₅ N ₄ O ₂ H ₄ (cr) + 6H ₂ O(lq) + 4KOH(cr)	(12)	-1444	-567.2	-1275
4KNO ₃ (cr) + 5CH ₄ (g) = C ₅ N ₄ OH ₄ (cr) + 6H ₂ O(lq) + 4KOH(cr) + 0.5O ₂ (g)	(13)	-1175	-480.1	-1032
2KNO ₃ (cr) + 2.5C ₂ H ₆ (g) + 0.75O ₂ (g) = C ₅ N ₂ O ₂ H ₆ (cr) + 3.5H ₂ O(lq) + 2KOH(cr)	(14)	-1114	-429.5	-986.3
3KNO ₃ (cr) + 2C ₂ H ₆ (g) = C ₄ N ₃ OH ₅ (cr) + 2H ₂ O(lq) + 3KOH(cr) + 1.5O ₂ (g)	(15)	-416.7	-31.95	-407.2
5KNO ₃ (cr) + 2.5C ₂ H ₆ (g) = C ₅ N ₅ OH ₅ (cr) + 2.5H ₂ O(lq) + 5KOH(cr) + 3.25O ₂ (g)	(16)	-341.4	158.7	-388.7
5KNO ₃ (cr) + 2.5C ₂ H ₆ (g) = C ₅ N ₅ H ₅ (cr) + 2.5H ₂ O(lq) + 5KOH(cr) + 3.75O ₂ (g)	(17)	-61.48	253.0	-136.9
2KNO ₃ (cr) + 2C ₂ H ₆ (g) + 0.5O ₂ (g) = C ₄ N ₂ O ₂ H ₄ (cr) + 3H ₂ O(lq) + 2KOH(cr)	(18)	-980.1	-330.8	-881.4
4KNO ₃ (cr) + 2.5C ₂ H ₆ (g) = C ₅ N ₄ OH ₄ (cr) + 3.5H ₂ O(lq) + 4KOH(cr) + 1.25O ₂ (g)	(19)	-892.3	-127.1	-854.4
4KNO ₃ (cr) + 2.5C ₂ H ₆ (g) = C ₅ N ₄ O ₂ H ₄ (cr) + 3.5H ₂ O(lq) + 4KOH(cr) + 1.75O ₂ (g)	(20)	-623.5	-40.02	-611.6
2KNO ₃ (cr) + 1.(6)C ₃ H ₈ (g) + 0.(3)O ₂ (g) = C ₅ N ₂ O ₂ H ₆ (cr) + 2.(6)H ₂ O(lq) + 2KOH(cr)	(21)	-913.1	-279.8	-829.7
3KNO ₃ (cr) + 1.(3)C ₃ H ₈ (g) = C ₄ N ₃ OH ₅ (cr) + 1.(3)H ₂ O(lq) + 3KOH(cr) + 1.8(3)O ₂ (g)	(22)	-255.6	87.93	-281.8
5KNO ₃ (cr) + 1.(6)C ₃ H ₈ (g) = C ₅ N ₅ OH ₅ (cr) + 1.(6)H ₂ O(lq) + 5KOH(cr) + 3.(6)O ₂ (g)	(23)	-140.0	308.4	-232.0
5KNO ₃ (cr) + 1.(6)C ₃ H ₈ (g) = C ₅ N ₅ H ₅ (cr) + 1.(6)H ₂ O(lq) + 5KOH(cr) + 4.1(6)O ₂ (g)	(24)	139.9	402.7	19.79
2KNO ₃ (cr) + 1.(3)C ₃ H ₈ (g) + 0.1(6)O ₂ (g) = C ₄ N ₂ O ₂ H ₄ (cr) + 2.(3)H ₂ O(lq) + 2KOH(cr)	(25)	-819.0	-374.9	-707.2
4KNO ₃ (cr) + 1.(6)C ₃ H ₈ (g) = C ₅ N ₄ O ₂ H ₄ (cr) + 2.(6)H ₂ O(lq) + 4KOH(cr) + 1.(6)O ₂ (g)	(26)	-691.0	-45.84	-677.3
4KNO ₃ (cr) + 1.(6)C ₃ H ₈ (g) = C ₅ N ₄ OH ₄ (cr) + 2.(6)H ₂ O(lq) + 4KOH(cr) + 2.1(6)O ₂ (g)	(27)	-422.2	109.8	-454.9
2KNO ₃ (cr) + 2.5C ₂ H ₄ (g) = C ₅ N ₂ O ₂ H ₆ (cr) + H ₂ O(lq) + 2KOH(cr) + 0.5O ₂ (g)	(28)	-740.8	-323.5	-644.3
3KNO ₃ (cr) + 2C ₂ H ₄ (g) = C ₄ N ₃ OH ₅ (cr) + 3KOH(cr) + 2.5O ₂ (g)	(29)	-117.8	52.89	-133.6
5KNO ₃ (cr) + 2.5C ₂ H ₄ (g) = C ₅ N ₅ OH ₅ (cr) + 5KOH(cr) + 4.5O ₂ (g)	(30)	32.20	264.7	-46.72
5KNO ₃ (cr) + 2.5C ₂ H ₄ (g) = C ₅ N ₅ H ₅ (cr) + 5KOH(cr) + 5O ₂ (g)	(31)	312.1	359.0	205.1
2KNO ₃ (cr) + 2C ₂ H ₄ (g) = C ₄ N ₂ O ₂ H ₄ (cr) + H ₂ O(lq) + 2KOH(cr) + 0.5O ₂ (g)	(32)	-681.2	-246.0	-607.8
4KNO ₃ (cr) + 2.5C ₂ H ₄ (g) = C ₅ N ₄ O ₂ H ₄ (cr) + H ₂ O(lq) + 4KOH(cr) + 2.5O ₂ (g)	(33)	-518.8	-21.10	-512.5
4KNO ₃ (cr) + 2.5C ₂ H ₄ (g) = C ₅ N ₄ OH ₄ (cr) + H ₂ O(lq) + 4KOH(cr) + 3O ₂ (g)	(34)	-250.0	66.02	-269.6
2KNO ₃ (cr) + 1.(6)C ₃ H ₆ (g) = C ₅ N ₂ O ₂ H ₆ (cr) + H ₂ O(lq) + 2KOH(cr) + 0.5O ₂ (g)	(35)	-643.8	-220.5	-578.1
3KNO ₃ (cr) + 1.(3)C ₃ H ₆ (g) = C ₄ N ₃ OH ₅ (cr) + 3KOH(cr) + 2.5O ₂ (g)	(36)	-40.27	135.3	-80.61
5KNO ₃ (cr) + 1.(6)C ₃ H ₆ (g) = C ₅ N ₅ OH ₅ (cr) + 5KOH(cr) + 4.5O ₂ (g)	(37)	129.2	367.7	19.53
5KNO ₃ (cr) + 1.(6)C ₃ H ₆ (g) = C ₅ N ₅ H ₅ (cr) + 5KOH(cr) + 5O ₂ (g)	(38)	409.1	462.0	271.3
2KNO ₃ (cr) + 1.(3)C ₃ H ₆ (g) = C ₄ N ₂ O ₂ H ₄ (cr) + H ₂ O(lq) + 2KOH(cr) + 0.5O ₂ (g)	(39)	-603.6	-163.6	-554.8
4KNO ₃ (cr) + 1.(6)C ₃ H ₆ (g) = C ₅ N ₄ O ₂ H ₄ (cr) + H ₂ O(lq) + 4KOH(cr) + 2.5O ₂ (g)	(40)	-421.8	81.92	-446.2
4KNO ₃ (cr) + 1.(6)C ₃ H ₆ (g) = C ₅ N ₄ OH ₄ (cr) + H ₂ O(lq) + 4KOH(cr) + 3O ₂ (g)	(41)	-153.0	169.0	-203.4

energy is rather small in magnitude and the total change in the Gibbs free energy is negative if reactions (21)–(27) are coupled.

As for the reactions of KNO₃ with C₂H₄ ((28)–(34)), all they proceed with liberation of oxygen. In other respects, the situation is analogous qualitatively to that peculiar for the set of reactions (21)–(27).

For the reactions of KNO₃ with propylene ((35)–(41)), the changes in the Gibbs free energy are positive for formation of adenine (36) and guanine (37).

Table 5
Changes in the enthalpy $\Delta_r(\Delta_f H_j^0)$, entropy $\Delta_r S_j^0$, and Gibbs free energy $\Delta_r G^0$ for reactions (42)–(46)

Reaction		$\Delta_r(\Delta_f H_j^0)$ (kJ/mol)	$\Delta_r S_j^0$ (J/mol K)	$\Delta_r G^0$ (kJ/mol)
4KNO ₃ (cr) + 5CH ₄ (g) = C ₅ H ₁₀ O ₅ (cr) + 3H ₂ O(lq) + 4KOH(cr) + 2N ₂ (g)	(42)	-1258	-378.7	-1145
3KNO ₃ (cr) + 2.5C ₂ H ₆ (g) = C ₅ H ₁₀ O ₅ (cr) + H ₂ O(lq) + 3KOH(cr) + 1.5N ₂ (g)	(43)	-918.4	-377.4	-805.9
2.(6)KNO ₃ (cr) + 1.(6)C ₃ H ₈ (g) = C ₅ H ₁₀ O ₅ (cr) + 0.(3)H ₂ O(lq) + 2.(6)KOH + 1.(3)N ₂ (g)	(44)	-787.7	-141.6	-745.5
2KNO ₃ (cr) + 2.5C ₂ H ₄ (g) + H ₂ O(lq) = C ₅ H ₁₀ O ₅ (cr) + 2KOH(cr) + N ₂ (g)	(45)	-757.2	-358.8	-650.2
2KNO ₃ (cr) + 1.(6)C ₃ H ₆ (g) + H ₂ O(lq) = C ₅ H ₁₀ O ₅ (cr) + 2KOH(cr) + N ₂ (g)	(46)	-660.2	-256.6	-583.7

Table 5 presents the enthalpy, entropy, and Gibbs free energy changes calculated for reactions (42)–(46) of D-ribose formation from potassium niter and methane, ethane, propane, ethylene, and propylene, respectively. These reactions proceed with liberation of N₂.

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

Table 6

Changes in the enthalpy $\Delta_i(\Delta_f H_j^0)$, entropy $\Delta_i S_j^0$, and Gibbs free energy $\Delta_i G^0$ for reactions (47) and (48)

Reaction	$\Delta_i(\Delta_f H_j^0)$ (kJ/mol)	$\Delta_i S_j^0$ (J/mol K)	$\Delta_i G^0$ (kJ/mol)
$C_5H_4N_4O + H_2O = C_5H_6N_2O_2 + N_2$ (47)	-66.17	136.6	-106.9
$C_5H_4N_4O_2 + C_5H_5N_5 + H_2O = C_5H_5N_5O + C_5H_6N_2O_2 + N_2$ (48)	-77.27	129.4	-115.9

To confirm this statement, we consider reactions (47) and (48) listed in Table 6. It is seen that the changes in the standard Gibbs free energy for the reactions of HX interaction with water up to Th and N_2 formation and of X interaction with Ad and water up to G, Th, and N_2 formation are negative.

The consideration performed in this paragraph allows us to believe that the DNA- (and RNA-) like molecules could originate in the past and, may be, continue to originate now from methane (and, may be, from other simple hydrocarbons), niters, and phosphates (apatites are most probable).

3. Probable principal mechanism of simplest living matter origination and conditions necessary for realization of the proposed chemism in the framework of the proposed mechanism

In Refs. [9,10], we came to the conclusion that a short-range ordering similar to that occurring in the gas-hydrate structure II exists in DNA–water systems and that DNA transformations, including its replication in the course of mitosis, are closely associated with the processes of formation and destruction of

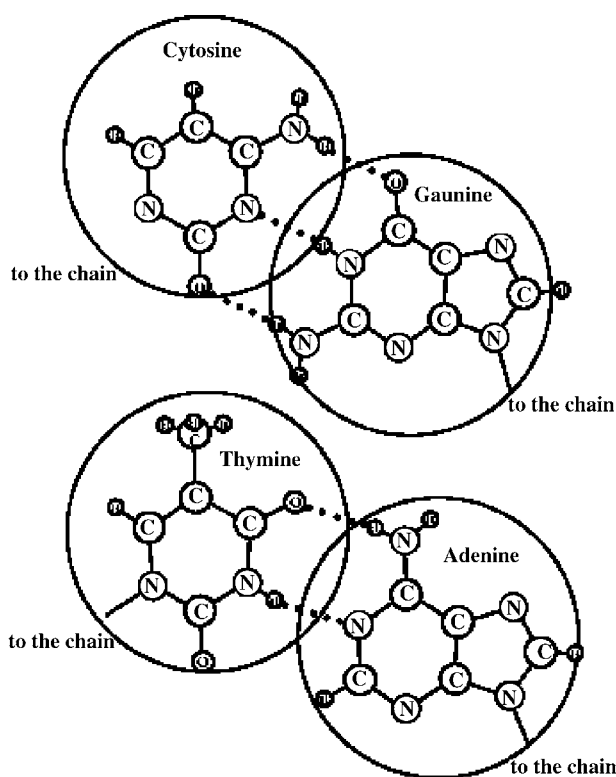


Fig. 3. Agreement between the sizes of N-bases entering into a DNA double helix and of large cavities (large circles, $d = 0.69$ nm) of the hydrate structure II (the figure is given in proper scale).

this gas-hydrate structure. One of the factors that led us to this conclusion is a close agreement between the sizes of different building blocks of DNA and RNA molecules and the sizes of the cavities of the hydrate structure II. Fig. 3 illustrates a close agreement between the sizes of the N-bases entering into DNA molecules and of large cavities of the gas-hydrate structure II.

Similarly, Fig. 4 illustrates a close agreement between the sizes of phosphate groups entering into DNA molecules and of small cavities of the gas-hydrate structure II.

We believe that the processes leading to DNA formation can proceed in the Earth's crust, including near-bottom sea layers, where structured deposits of hydrate of hydrocarbons contact with or are located not far from deposits of niters, $NaNO_3$, or KNO_3 . At the first stage, the NO_3^- ions diffusing from the deposit periphery interact with neighboring methane molecules (or, may be, with molecules of other hydrocarbons) within the large cavities of the hydrate structures in the purlieu of methane-hydrate deposits. These reactions result in formation of precursors of N-bases and in evolution of oxygen. It is well known that the methane–water hydrate systems have usually the hydrate structure I. Meanwhile, the sizes of molecules of N-bases and sugars correspond to the hydrate structure II. Therefore, in the course of the process under consideration, the hydrate structure I should be transformed to the hydrate structure II. As the reaction front moves into a hydrate mass, the completeness of consumption of oxygen increases, nitrogen evolves instead of oxygen, and molecules of sugars are produced along with precursors of N-bases. Gradually, precursors are being transformed (within the large cavities where they are housed) into molecules of N-

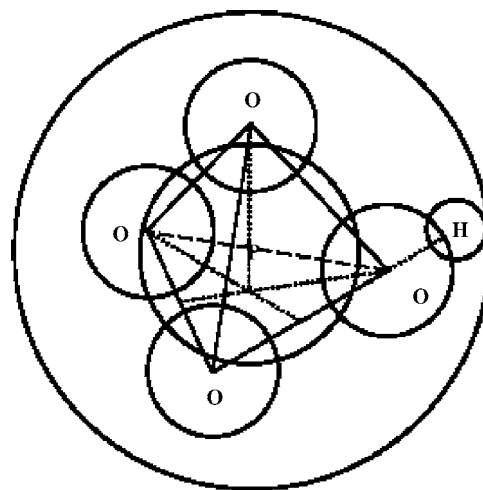


Fig. 4. Agreement between the sizes of phosphate groups entering into a DNA double helix and of small cavities (large circle, $d = 0.48$ nm) of the hydrate structure II (the figure is given in proper scale).

bases; therewith, the corresponding cavities are being filled up completely. In the course of the process, the nascent molecules of N-bases and of sugars consume molecules of hydrocarbons and replace them within the large cavities of the hydrate; nitrogen and hydrates of metal oxides gradually diffuse from the system. The Cy and Th molecules originate in immediate proximity to the G and Ad molecules, respectively, because the Cy–G and Th–Ad hydrogen interactions lower the energy of the system. We believe that the above thermodynamic calculations prove that formation of N-bases and ribose within the phase of hydrates of methane or some other hydrocarbons is quite feasible. The thermodynamic feasibility of interaction of several N-bases with ribose and phosphoric acid under standard conditions follows from [14]. There is no doubt that similar processes are possible with other N-bases. Such a “crude product” can wait arbitrarily long until phosphate ions necessary for DNA (and RNA) formation diffuse to it. Diffusion of phosphates from any remote source can lead to formation of DNA- and RNA-like molecules. Small cavities of such a “crude product” are free or are engaged with methane, which can be replaced by phosphate groups because their chemical affinity to the “crude product” is high.

In view of the use of our thermodynamic calculations for substantiation of the feasibility of formation of DNA-like molecules within methane-hydrate (and some other hydrocarbon-hydrate) phases under natural conditions, we consider necessary to make the following remarks. All calculations are performed for the standard conditions; meanwhile, the conditions of DNA formation, according to our view, differ from the standard ones. However, on the one hand, exact thermodynamic calculations are impossible on the basis of available data and it is unlikely that they will be possible in the near future and, on the other hand, the above calculations are sufficient for the qualitative conclusions made in this paper. The point is that hydrates are the substances of variable composition, their thermodynamic functions can be determined exactly for some ideal compositions only, and the partial molar thermodynamic functions (especially, entropy) of the host and guests can vary significantly for different non-stoichiometric compositions; in addition, if data for some hydrates of hydrocarbons are available, any information for other hydrates is absent. In addition, the Gibbs free energy change for hydrate formation from mineral guest and host substances is rather small because of the van der Waals nature of guest–water and water–water interactions in hydrates. These peculiarities allow us to consider the results of our calculations as a good reason for the above conclusions.

The problem considered in the last paragraph is closely connected with the third fundamental problem formulated in Section 1 as a subject for consideration in this paper, i.e., with the problem of principal conditions necessary for realization of the proposed chemism of SLMO. Namely, the range of natural conditions suitable for DNA origination should be outlined and the question should be analyzed as to whether these conditions could differ from the standard ones so much that the results calculated for the standard conditions would be inapplicable under the conditions of DNA origination. At about 273 K, the equilibrium pressure of CH₄ over its hydrate is about 25 atm and decreases in the presence of N₂ (a so-called auxiliary gas)

and the equilibrium vapor pressures of many organic substances over their hydrates are well below 1 atm. It is also necessary to take into account that the lower the temperature, the lower the rates of chemical and diffusion processes. Therefore, we believe that the processes of DNA origination proceed within natural hydrate structures and that the temperatures and pressures most favorable for these processes are around 273 K and 10–20 atm, respectively. Such distinctions of the conditions from the standard ones cannot influence principally our conclusions. This consideration, on the one hand, answers the question on the conditions necessary for realization of the proposed chemism of DNA origination in the framework of the proposed mechanism and, on the other hand, shows that our conclusions, which are made on the basis of calculation performed for the standard conditions, are applicable for the most probable conditions of DNA origination by the proposed mechanisms. A rather close location of niter and phosphate deposits to hydrocarbon hydrate deposits promotes formation of DNA- (and RNA-) like molecules.

The proposed mechanism allows multiple originations of simplest elements of living matter in different regions of the globe; some differences in chemical compositions of DNA molecules could be associated with peculiarities in chemical compositions of corresponding environments. Our approach allows understanding how it might happen that the parent substances of simplest elements of living matter remain in contact during a rather long period sufficient for their transformations.

Thus, we considered three principal problems listed in Section 1. In addition to the conclusion given at the end of Section 2, we suppose that simplest living matter origination begins from DNA and RNA formation within the phase of methane-hydrate (and, may be, within the thickness of hydrates of other simplest hydrocarbons) and that, if our assumption is right, the DNA-like molecules and, may be, deposits of such molecules can be found in the vicinities of methane deposits at a depth of several hundreds of meters under the Earth's surface.

4. Concluding remarks

This paper develops our hydrate hypothesis of simplest living matter origination. This hypothesis was proposed in Refs. [9–11] on the basis of calorimetric, kinetic, and stoichiometric studies of water vapor and liquid water interactions with polymer and monomer organic substances bearing H₂N[−], O^{2−} [19,20], and other functional groups [21–24] and on the basis of an analysis of available data on thermodynamic and stoichiometric aspects of water interactions with DNA and DNA-like molecules, on some principal phenomenological questions associated with observations of the mitosis processes, on the structures, properties, and conditions of formation and destruction of gas-hydrates [9,10], and on the structural characteristics of H₂N[−] and O^{2−} groups in different chemical substances [9].

This gas-hydrate hypothesis allowed us to explain some phenomena, e.g., the available facts that, in DNA–H₂O systems, the waters located around G desorb faster than the waters located around other N-bases and the waters located around N-bases desorb faster than the waters located around phosphate groups. It

also allowed us to propose a possible principal physico-chemical cause of double-helix unwinding in the course of mitosis. We suggest that the start of DNA double-helix unwinding results from neutralization of the DNA–DNA interactions by the waters diffusing into cells from outside. Waters diffuse continuously into each cell. Right after replication and formation of two new cell membranes, the water content inside each cell newly formed is deficient. In parallel with the process of duplication, waters diffuse into these cells, steadily form a cavity (similar to the large cavities of the gas-hydrate structure) around each N-base (see Fig. 3), and thus steadily neutralize the AG–AG (AGs are the amino groups of nitrogen bases) interactions in the newly formed DNA double helix. The process of water diffusion through the cell membranes is rather slow, and thus the equilibrium distribution of waters along the DNA double helix exists at every instant. Realization of the critical state of complete neutralization of the AG–AG interactions in a DNA double helix gives a signal for its unwinding and subsequent replication. In the perfect gas-hydrate structure II, the critical water content corresponds to a (water)/(guest) stoichiometry of $n = 17$. In living systems, this stoichiometry can be around this level, because only short-range ordering rather than perfect structuring can be expected inside living cells and because other polar molecules housed within cells can influence the critical (water)/(AG) stoichiometry (details see in Ref. [10]).

The new data and discussions presented in this paper show that it is not impossible that the occurrence of KNO_3 (NaNO_3) and $\text{Ca}_5\text{X}(\text{PO}_4)_3$ (natural minerals with $\text{X} = \text{F}, \text{Cl}, \text{or OH}$) in the vicinities of deposits of CH_4 -hydrates (or, may be, hydrates of other simple hydrocarbons) at a depth of several tens or several hundreds of meters under the Earth's surface led in the past and, possibly, leads at present to formation of deposits of DNA- and RNA-like molecules. At present, several regions, where deposits of niters and methane-hydrates are located at not large distances from each other, are known. For example, along the Pacific coast of America, several deposits of submarine methane-hydrates are found along the coasts of California [25,26], Oregon [27], Peru [28], etc. Meanwhile, deposits of potassium and sodium niters occur in the coastal ridges of northern Chili, Bolivia, California, etc. [29]. Note that niters are water-soluble substances and they occur at present in arid desert regions only; the occurrence of these salts in the Earth's crust after the 5-billion-year period of the Earth's history means that, in former times, they were much more abundant.

One more fact counts in favor of our concept or, at least, is not in contrast with it. According to several publications (e.g., Refs. [30,31]), the gas sampled from gas-hydrate deposits contained significant amounts of nitrogen and very small amounts of oxygen: 4% of N_2 and 0.005% of O_2 in Ref. [30] and 11.4% of N_2 and 0.2% of O_2 in Ref. [31]. It is seen that the ratios between the N_2 and O_2 concentrations were much higher than the corresponding ratios inherent in the atmosphere; therefore, it is obvious that N_2 could not be acquired by the samples from the atmosphere during sampling. The possible sources of N_2 origination within the Earth's crust are not numerous, and it is quite probable that N_2 was reduced from a nitrate by methane according to reactions similar to (1)–(3).

Needless to say that we by no means call into question the importance of the well-known intracellular phenomena, processes, and particles, such as electrostatics, nucleosomes, helicases, and so on. However, in our eyes, none of them can be considered as the core phenomenon providing the living matter origination and the mechanisms of their appearance should be considered individually.

Meanwhile, we doubt whether anybody can guarantee the mutation origin of the modified viruses revealing themselves from time to time in nature. It is hardly probable that there are good reasons to exclude the possibility that an underground natural bio-laboratory exists anywhere in the south-eastern coastal Eurasia or in the Earth's crust under the Great China Rivers.

One of the important distinctive features of our hypothesis is that it could be subjected to experimental testing. It is sufficient to house methane-hydrate, niter, and apatite into an abiotic autoclave thermostated at about 273 K and to supply this apparatus with an equipment allowing performance of multifold chemical analyses; of course, some technical problems (relating to the analytical procedures, abioticity of the medium, etc.) should be solved before such an experiment and, may be, the wait of results will be rather long. However, “the game is worth the candle”. Note that this experiment differs principally from the well-known Miller–Urey experiment proposed in 1953. The last is based on the assumption that living matter originated on the Earth's surface as a result of a unique random event or of a number of random events initiated by atmospheric electric discharges. For the semi-centennial, no principal progress in detailing the mechanism of living matter origination was achieved on this basis. In contrast to this assumption, we believe that living matter originated in the Earth's crust as a result of regular, thermodynamically dictated transformations of simple mineral substances. Detection of the processes going in the direction of DNA origination in the experiment proposed by us could prove that living matter is a natural phenomenon appropriate necessarily to the atomistic world during a definite period of its development and that, in the geological period when big water masses exist, the life had originated on the Earth multiply and, may be, originates in our time.

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