

STUDYING THE HYDROLOGICAL CONDITIONS FOR ORIGIN OF FIRST ORGANIC FORMS OF LIFE IN HOT MINERAL WATER WITH HDO

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Introduction

The previous biological experiments with D₂O and structural-conformational studies with deuterated macromolecules, performed by us, enable to modeling conditions under which the first living forms of life might be evolved [1–3]. The content of deuterium in hot mineral water may be increased due to the physical-chemical processes of the deuterium accumulation. It can be presumed that primary water might contain more deuterium at early stages of evolution of first living structures, and deuterium was distributed non-uniformly in the hydrosphere and atmosphere [4]. The primary reductive atmosphere of the Earth consisted basically of gas mixture CO, H₂, N₂, NH₃, CH₄, lacked O₂–O₃ layer protecting the Earth surface from rigid short-wave solar radiation carrying huge energy capable to cause radiolysis and photolysis of water. The processes accompanying accumulation of deuterium in the hydrosphere are solar radiation, volcanic geothermal processes and electric discharges in the atmosphere. These natural processes could lead to the enrichment of the hydrosphere by deuterium in the form of HDO which evaporates more slowly than H₂O, and condenses faster. If this is true, this is a significant fact regarding thermal stability of deuterated macromolecules in the preservation of life under thermal conditions, because chemical bonds with participation of deuterium are stronger than those ones formed of hydrogen.

The natural prevalence of deuterium makes up approximately 0,015–0,020 atom%, and depends strongly on the uniformity of substance and the total amount of matter formed in the course of early Galaxy evolution [5]. The average ratio of D/¹H in nature makes up approximately 1:5700. In natural waters, the deuterium is distributed irregularly: from 0,02–0,03 mol.% for river water and sea water, to 0,015 mol.% for water of Antarctic ice – the most purified from deuterium natural water containing in 1,5 times less deuterium than that of seawater. According to the international SMOW standard isotopic shifts for D and ¹⁸O in sea water: D/¹H = (155,76±0,05)·10⁻⁶ (155,76 ppm) and ¹⁸O/¹⁶O = (2005,20±0,45)·10⁻⁶ (2005 ppm). For the SLAP standard isotopic shifts for D and ¹⁸O in seawater make up D/¹H = 89·10⁻⁶ (89 ppm) and for a pair of ¹⁸O/¹⁶O = 1894·10⁻⁶ (1894 ppm). In surface waters, the ratio D/¹H = ~ (1,32–1,51)·10⁻⁴, while in the coastal seawater – ~ (1,55–1,56)·10⁻⁴. The natural waters of CIS countries are characterized by negative deviations from SMOW standard to (1,0–1,5)·10⁻⁵, in some places up to (6,0–6,7)·10⁻⁵, but however there are also observed positive deviations at 2,0·10⁻⁵.

The constant sources of deuterium are explosions of nova stars and thermonuclear processes frequently

occurring inside the stars. Probably, it could explain a known fact, why the amount of deuterium is slightly increased during the global changes of climate in warming conditions. The gravitational field of the Earth is insufficiently strong for the retaining of lighter hydrogen, and our planet is gradually losing hydrogen as a result of its dissociation into interplanetary space. Hydrogen evaporates faster than heavy deuterium, which can be collected by the hydrosphere. Therefore, as a result of this natural process of fractionation of H/D isotopes throughout the process of Earth evolution there should be an accumulation of deuterium in the hydrosphere and surface waters, while in the atmosphere and in water vapour deuterium content tends to be low. Thus, on the planet there occurs a natural process of separation of H and D isotopes, playing an essential role in the maintenance of life on the planet.

The second point regards the influence of temperature on the biochemical processes in living matter. Our recent studies have shown that the most favorable for the origin of life and living matter seem to be hot alkaline mineral waters interacting with CaCO₃ [6, 7]. According to the law for conservation of energy the process of self-organization of primary organic forms in water solutions may be supported by thermal energy of magma, volcanic activity and solar radiation. According to J. Szostak, the accumulation of organic compounds in small isolated lakes is more possible compared to the ocean [8]. It is most likely that life originated near a hydrothermal vent: an underwater spout of hot water. The geothermal activity gives more opportunities for the origination of life. In 2009 A. Mulikjanian and M. Galperin demonstrate that the cell cytoplasm contains potassium, zinc, manganese and phosphate ions, which are not particularly widespread in the sea aquatorium [9]. J. Trevors and G. Pollack proposed in 2005 that the first cells on the Earth assembled in a hydrogel environment [10]. Gel environments are capable of retaining water, oily hydrocarbons, solutes, and gas bubbles, and are capable of carrying out many functions, even in the absence of a membrane. Hydrocarbons are an organic compounds consisting entirely of hydrogen and carbon. The data presented in this paper show that the origination of living matter most probably occurred in hot mineral water. This may occurred in ponds and hydrothermal vents in seawater or hot mineral water. An indisputable proof of this is the presence of stromatolites fossils. They lived in warm and hot water in zones of volcanic activity, which could be heated by magma and seem to be more stable than other first sea organisms [11].

Therefore, the purpose of the research was studying the hydrological conditions of primary hydrosphere (temperature, pH, isotopic composition) for possible processes for

origin of first organic forms in hot mineral water with HDO. Various samples of water from Bulgaria, as well water with varying deuterium content were studied within the frames of the research.

Experimental Part

Material and Methods

Chemicals

For preparation of water with varying content of deuterium (HDO) was used D₂O (99,9 atom.%) from the Russian Research Centre "Isotope" (St. Petersburg, Russian Federation). D₂O was preliminary distilled over KMnO₄ with the subsequent control of isotope enrichment by ¹H-NMR-spectroscopy on a Bruker WM-250 device ("Bruker", Germany) (working frequency: 70 MHz, internal standard: Me₄Si).

Biological Objects

The objects of the study were used the cactus juice of *Echinopsis pachanoi* and the Mediterranean jellyfish *Cotylorhiza tuberculata* (Chalkida, Greece, Aegean Sea).

Water Samples

The samples of water were taken from various water springs of Bulgaria:

- 1 – Mineral water (Rupite, Bulgaria);
- 2 – Seawater (Varna resort, Bulgaria);
- 3 – Mountain water (Teteven, Bulgaria);
- 5 – Deionized water (the control).
- 6 – Water with varying deuterium content (HDO).

IR-Spectroscopy

IR-spectra of water samples were registered on Bruker Vertex ("Bruker", Germany) Fourier-IR spectrometer (spectral range: average IR – 370–7800 cm⁻¹; visible – 2500–8000 cm⁻¹; permission – 0.5 cm⁻¹; accuracy of wave number – 0.1 cm⁻¹ on 2000 cm⁻¹) and on Thermo Nicolet Avatar 360 Fourier-transform IR (M. Chakarova).

DNES-Spectral Analysis

The research was made with the method of differential non-equilibrium spectrum (DNES). The device measures the angle of evaporation of water drops from 72° to 0°. As the main estimation criterion was used the average energy ($\Delta E_{H...O}$) of hydrogen O...H-bonds between H₂O molecules in water's samples. The spectra of water were measured in the range of energy of hydrogen bonds 0,08–0,1387 eV with using a specially designed computer program.

High-Frequency Coronal Electric Discharge Experiments

A device for high-frequency coronal electric discharge was used in this study, constructed by I. Ignatov and Ch. Stoyanov. The frequency of the applied saw-tooth electric voltage was 15 kHz, and the electric voltage – 15 kV. The electric discharge was obtained using a transparent firm polymer electrode on which a liquid sample of water (2–3 mm) was placed. The spectral range of the photons released upon electric discharge was from $\lambda = 400$ to $\lambda = 490$ nm and from $\lambda = 560$ to $\lambda = 700$ nm.

Results and Discussion

Studying Various Water Samples on the Feasibility for Origin of Life

We have carried out the research of various samples of mineral water obtained from mineral springs and seawater from Bulgaria (Fig. 1, curves 1–5). For this aim we employed IR-spectrometry and the DNES method relative to the control – deionized water.

For calculation of the function $f(E)$ represented the energy spectrum of water, the experimental dependence between the wetting angle (θ) and the energy of hydrogen bonds (E) is established:

$$f(E) = \frac{14,33 f(\theta)}{[1 - (1 + bE)^2]^2}, \quad (1)$$

where $b = 14,33 \text{ eV}^{-1}$

The relation between the wetting angle (θ) and the energy (E) of the hydrogen bonds between H₂O molecules is calculated by the formula:

$$\theta = \arcsin(-1 - 14,33E) \quad (2)$$

Cactus juice was also investigated by the DNES method (Fig. 1, curve 1). The cactus was selected as a model system because this plant contains approximately 90 % of water. The closest to the spectrum of cactus juice was the spectrum of mineral water contacting with Ca²⁺ and HCO₃⁻ ions (Fig. 1, curve 2). DNES-spectra of cactus juice and mineral water have magnitudes of local maximums (E , eV) at -0,1112; -0,1187; -0,1262; -0,1287 and -0,1387 eV. The similar local maximums in the DNES-spectrum between the cactus juice and seawater were detected at -0,1362 eV. The DNES-spectrum of the control sample of deionized water (Fig. 1, curve 5) was substantially different from DNES-spectra of seawater and mineral water.

Another important parameter was measured by the DNES method – the average energy ($\Delta E_{H...O}$) of hydrogen H...O-bonds among the individual molecules H₂O, which makes up -0,1067±0,0011 eV. When the water temperature is changed, the average energy of hydrogen H...O-bonds alternates. This testified about the restructuring of average energies of hydrogen H...O-bonds among individual H₂O molecules with a statistically reliable increase of local maximums in DNES-spectra.

As it was shown from these experimental data, the closest to the IR-spectrum of the cactus juice was mineral water from Rupite Village (Bulgaria), which the DNES and the IR spectrum are shown in Fig. 2 and Fig. 3 (Thermo Nicolet Avatar 360 Fourier-transform IR). IR-spectra of the cactus juice and mineral water containing HCO₃⁻ (1320–1488 mg/l), Ca²⁺ (29–36 mg/l), pH (6,85–7,19), have local maximums at $\lambda = 8,95$; 9,67; 9,81; 10,47 and 11,12 μm (Fourier-IR spectrometer Bruker Vertex). The common local maximums in the IR-spectrum between the cactus juice and seawater are detected at $\lambda = 9,10 \mu\text{m}$. The local maximums obtained with the IR method at $\lambda = 9,81 \mu\text{m}$ ($k = 1019 \text{ cm}^{-1}$) and $\lambda = 8,95 \mu\text{m}$ ($k = 1117 \text{ cm}^{-1}$) (Thermo Nicolet Avatar 360 Fourier-transform IR) are located on the spectral curve of the local maximum at $\lambda = 9,7 \mu\text{m}$ ($k = 1031 \text{ cm}^{-1}$) (Fig. 3). With the DNES method, the results of which are shown in Table, were

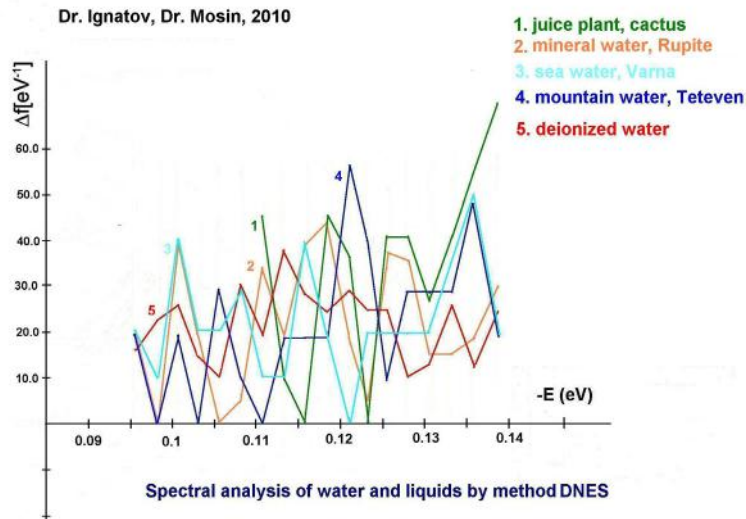


Fig. 1. DNES-spectra of water samples of various origin: 1 – the cactus juice; 2 – mineral water from Rupite village (Bulgaria); 3 – seawater (Varna, Bulgaria); 4 – mountain water (Teteven, Bulgaria); 5 – deionized water (the control)

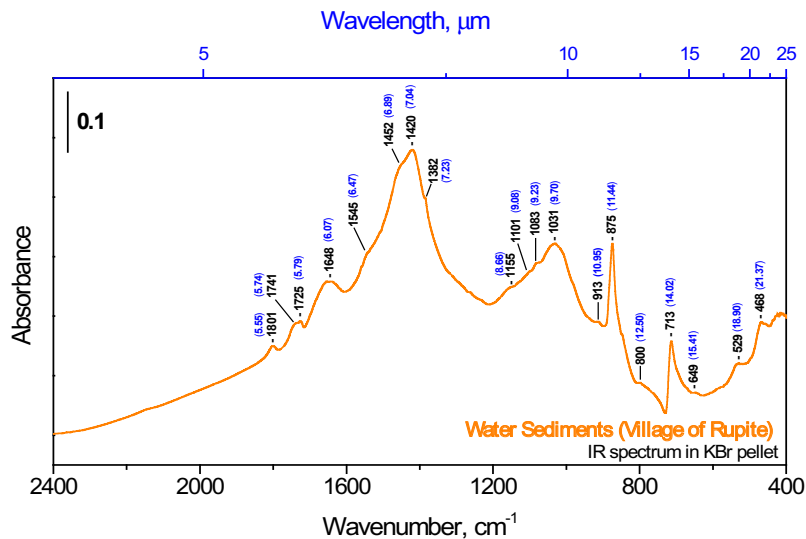


Fig. 2. IR-spectrum of water sediments obtained from Rupite Village (Bulgaria)

obtained the following results – 8,95; 9,10; 9,64; 9,83; 10,45 and 11,15 μm (wave length λ , μm), or – 897; 957; 1017; 1037; 1099 and 1117 cm^{-1} (wave numbers, k , cm^{-1}).

The results with the Mediterranean jellyfish *Cotylorhiza tuberculata* indicated that the jellyfish has local maximums in IR-spectra at $\lambda = 8,98$ and $\lambda = 10,18$ μm (Fig. 3).

Before the measurements the jellyfish was kept in seawater for several days. On comparison the seawater has a local maximum at $\lambda = 8,93$ μm in IR-spectra. These results were obtained with Thermo Nicolet Avatar 360 Fourier-transform IR. With the DNES method the local maximums in spectra for jellyfish are detected at $\lambda = 8,95$ and $10,21$ μm , and for seawater – at $\lambda = 9,10$ μm . A differential spectrum was recorded between jellyfish and seawater by using the Thermo Nicolet Avatar 360 Fourier-transform IR method. In the IR-spectrum of jellyfish are observed the more pronouncedly expressed local maximums, detected by Thermo Nicolet Avatar 360 Fourier-transform IR and the DNES method. The measure-

ments demonstrate that two common local maximums are observed in IR-spectra of jellyfish and seawater. These maximums are not observed in the IR-spectrum of the cactus juice and mineral water from Rupite (Bulgaria). Jellyfish contains approximately 97 (w/w) % of water and is more unstable living organism compared to those ones formed the stromatolites. The explanation for this is the smaller concentration of salts in jellyfish and, therefore, the smaller number of local maximums in the IR-spectrum in relation to seawater.

Such a character of IR- and DNES-spectra and distribution of local maximums may prove that hot mineral alkaline water is preferable for origin and maintenance of life compared to other types of water analyzed by these methods. Thus, in hot mineral waters the local maximums in the IR-spectrum are more manifested compared to the local maximums obtained in IR-spectrum of the same water at a lower temperature. The difference in the local maximums from $t = +20$ $^{\circ}\text{C}$ to $t = +95$ $^{\circ}\text{C}$ at each $+5$ $^{\circ}\text{C}$ according to the Student

Table

The characteristics of spectra of water of various origin obtained by the DNES-method*

-E, eV			λ, μm	k, cm ⁻¹
Cactus juice	Mineral water from Rupite Village (Bulgaria)	Seawater		
0,1112	0,1112	–	11,15	897
0,1187	0,1187	–	10,45	957
0,1262	0,1262	–	9,83	1017
0,1287	0,1287	–	9,64	1037
0,1362	–	0,1362	9,10	1099
0,1387	0,1387	–	8,95	1117

Notes: *The function of the distribution of energies Δf was measured in reciprocal electron volts (eV⁻¹). It is shown at which values of the spectrum -E (eV) were observed the biggest local maximums of this function; λ – wave length; k – wave number.

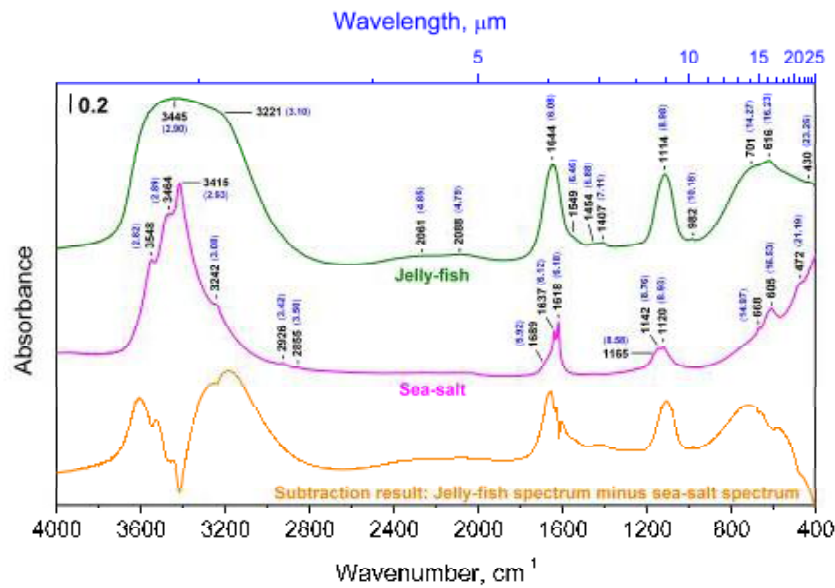
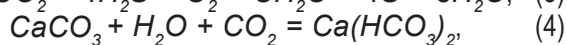


Fig. 3. IR-spectrum of seawater obtained from Varna (Bulgaria) and jellyfish *Cotylorhiza tuberculata*, Chalkida (Greece), Aegean Sea

t-criterion makes up $p < 0,05$. These data indicate that the origination of life and living matter depends on the structure and physical-chemical properties of water, as well as its temperature and the pH value. The most closed to the IR- and the DNES-spectrum of water, which contains bicarbonates and calcium ions typical for the formation of stromatolites, is the IR-spectrum of cactus juice. For this reason cactus juice was applied as a model system. The most closed to the local maximums in IR-spectrum of the cactus juice are local maximums in IR-spectra of alkaline mineral water interacting with CaCO_3 and then seawater. In connection with these data the following reactions participating with CaCO_3 in aqueous solutions are important:



The equation (3) shows how some chemosynthetic bacteria use energy from the oxidation of H_2S and CO_2 to S and formaldehyde (CH_2O). The equation (4) is related to

one of the most common processes in nature: in the presence of H_2O and CO_2 , CaCO_3 transforms into $\text{Ca}(\text{HCO}_3)_2$. In the presence of hydroxyl OH^- ions, CO_2 transforms into HCO_3^- (equation (5)). Equation (6) is valid for the process of formation of the stromatolites – the dolomite layered accretionary structures formed in shallow seawater by colonies of cyanobacteria. In 2010 D. Ward described fossilized stromatolites in the Glacier National Park (USA) [13]. Stromatolites aged 3,5 billion years had lived in warm and hot water in zones of volcanic activity, which could be heated by magma. This suggests that the first living forms evidently evolved in hot geysers [14]. It is known that water in geysers is rich in carbonates, while the temperature is ranged from +100 °C to +150 °C. In 2011 a team of Japanese scientists under the leadership of T. Sugawara showed that life originated in warm or, more likely, in hot water [15]. From an aqueous solution of organic molecules, DNA and synthetic enzymes were created proto cells. Under experimental conditions the initial solution was heated to a temperature close to the water's boiling point +95 °C. Then the temperature was lowered to +65 °C with the formation of proto cells with primitive membrane. These experiments are excellent confirmation

of the possibility that first organic forms of life originated in hot water.

The above-mentioned data can predict a possible transition from synthesis of small organic molecules under the temperatures +70 –100 °C to more complex organic molecules as proteins. There are reactions of condensation–dehydration of amino acids into separate blocks of peptides that occur under alkaline conditions, with pH = 9–11. The important factor in reaction of condensation of two amino acid molecules into dipeptide is allocation of H₂O molecule when a peptide chain is formed. Because the reaction of polycondensation of amino acids is accompanied by dehydration, the H₂O removal from the reaction mixture speeds up the reaction rates. This testifies that formation of early organic forms may have occurred nearby active volcanoes, because at early periods of geological history volcanic activity occurred more actively than during subsequent geological times. However, the dehydration accompanies not only amino acid polymerization, but also association of other small blocks into larger organic molecules, and also polymerization of nucleotides into nucleic acids. Such association is connected with the reaction of condensation, at which from one block a proton is removed, and from another – a hydroxyl group with the formation of H₂O molecule.

In 1969 the possibility of existence of condensation–dehydration reactions under conditions of primary hydrosphere was proven by M. Calvin [16]. From most chemical substances hydrocyanic acid (HCN) and its derivatives – cyanoamid (CH₂N₂) and dicyanoamid (HN(CN)₂) possess the dehydration ability and the ability to catalyze the process of linkage of H₂O from primary hydrosphere [17]. The presence of HCN in primary hydrosphere was proven earlier by S. Miller's early experiments [18]. The chemical reactions with HCN and its derivatives are complex with a chemical point of view; in the presence of HCN, CH₂N₂ and HN(CN)₂ the condensation of separate blocks of amino acids accompanied by dehydration, can proceed at normal temperatures in strongly diluted H₂O–solutions. These reactions show the results of synthesis from separate smaller molecules to larger organic molecules of polymers, e.g. proteins, polycarboxydrates, lipids, and ribonucleic acids. Furthermore, the polycondensation reactions catalyzed by HCN and its derivatives depend on acidity of water solutions in which they proceed [19]. In acid aqueous solutions with pH = 4–6 these reactions do not occur, whereas alkaline conditions with pH = 9–10 promote their course. There has not been unequivocal opinion, whether primary water was alkaline, but it is probable that such pH value possessed mineral waters adjoining with basalts, i.e. these reactions could occur at the contact of water with basalt rocks, that testifies our hypothesis.

It should be noted, that the geothermal sources might be used for synthesis of various organic molecules. Thus, amino acids were detected in solutions of formaldehyde CH₂O with hydroxylamine NH₂OH, formaldehyde with hydrazine (N₂H₄) in water solutions with HCN, after the heating of a reactionary mixture to +95 °C [20]. In model experiments the reaction products were polymerized into peptide chains that are the

important stage towards inorganic synthesis of protein. In a reactionary mixture with a HCN–NH₃ solution in water were formed purines and pyrimidines. In other experiments amino acid mixtures were subjected to influence of temperatures from +60 °C up to +170 °C with the formation of short protein–like molecules resembling early evolutionary forms of proteins subsequently designated as thermal proteinoids. They consisted of 18 amino acids usually occurring in protein hydrolyzates. The synthesized proteinoids are similar to natural proteins on a number of other important properties, e.g. on the linkage by nucleobases and ability to cause the reactions similar to those catalyzed by enzymes in living organisms as decarboxylation, amination, deamination, and oxidoreduction. Proteinoids are capable to catalytically decompose glucose [21] and to have an effect similar to the action of α–melanocyte–stimulating hormone [22].

Under certain conditions (temperature, pH) in hot mixture of thermal proteinoids in water solutions are formed elementary structures like proteinoid microspheres with diameter 5–10 μm [23]. The best results on the polycondensation were achieved with the mixes of amino acids containing aspartic and glutamic acids, which are essential amino acids occurring in all modern living organisms. By morphological features the proteinoid microspheres with a diameter ~5–10 μm resemble cell membrane, which in certain conditions (pH = 4–5) may be double. The catalyst for their formation could serve sulfur and its derivatives which were found in ancient rocks in the form of grains of sulfides, as well as pyrite sands. Synthesis of proteinoid microspheres from a mixture of thermal proteinoids is important because it provides material for the next stage of the evolution of life. This is the stage from disparate organic molecules to organized proteinoid molecules having organized structure and separated from the surrounding environment by the primitive membrane.

In further experiments was used the gas electric discharge analogous to S. Miller's experiments [24]. The first experiments on the modeling of non–equilibrium conditions with gas electric discharge simulating primary atmosphere and electrosynthesis of organic substances from anorganic ones under the energy of the electric field in a primary oxygen–free atmosphere were held in 1953 by S. Miller (USA) [24]. For this aim the mixture of water and gases consisted of hydrogen (H₂), methane (CH₄), ammonia (NH₃) and carbon monoxide (CO) was placed into a closed glass container being exposed by pulsating electrical spark discharges at the temperature of boiling water; oxygen was not allowed into the unit. After the processing the reaction mixture by the electric discharge it was found that from the initial inorganic substance was synthesized organic compounds – aldehydes and amino acids. The experiments found that approximately ~10–15 % of carbon was transferred into an organic form. However, about ~2 % of carbon was detected in the amino acids, the most common of which was glycine. The initial analysis showed the presence in the reaction mixture obtained after the processing by the spark electric discharge 5 amino acids. A more complete analysis carried

out in 2008 [25], showed the formation by electrosynthesis in the reaction mixture 22 amino acids having from 5 to 20 carbon atoms in the molecule. Interestingly is that along with the amino acids in the reaction mixture after the treatment with electric spark discharges were detected trace amounts of nucleic acid precursors – nucleosides.

It should be noted that in the implementation of the gas discharge effect as well as in experiments of S. Miller are modeled extreme non-equilibrium conditions with gas electric discharge, resulting that in a thin layer of air gap with thickness $\sim 100 \mu\text{m}$ are formed reactive radicals reacting with each other to form new compounds (electrosynthesis). Such extreme conditions are thought to have occurred in the primary oxygen-free atmosphere of the Earth, which supposedly consisted of a mixture of water and gases – H_2 , CH_4 , NH_3 and CO , subjected to spark electrical discharges (lightning) under the conditions of high solar (UV) and geothermal activity.

The analogous experiment was conducted by the authors under laboratory conditions. According to our previous experiments, the first living structures may have evolved in warm and hot mineral water with a high content of bicarbonate (HCO_3^-) anions, cations of alkali metals (Na^+ , Ca^{2+} , Mg^{2+} , Zn^{2+}) and deuterium in the form of HDO [26]. There occurred gas electric discharge (lightning) in the primordial atmosphere close to the water surface. In the course of experiment was used the similar gas electric discharge on water drops placed on the electrode of the device for the gas electric discharge formation. The similar composition and water temperature were modeled on the electrode of the gas discharge device made of hostafan, with electric voltage – 15 kV, electric impulse duration – 10 μs ; electric current frequency – 15 kHz, wherein the air gap layer on the boundary with water sample was formed the electrical discharge, similar to plasma phenomena (lightning) and the electrostatic discharge on the surface of organic and inorganic samples of various kinds. Water drops were heated up to the boiling point in an electric field of high frequency and the electric discharge was applied, analogous as that in the primordial atmosphere. As a result, an organized structure with a size of 1,2–1,4 mm was formed in interelectrode space (Fig. 4). It was formed as a result of accretion of smaller elementary structures sized up 5–10 μm into the biggest structure having the size 1,2–1,4 mm and concentrated in the space where the electric field is applied.

It should be noted that no structure was organized in a control sample of water being placed on the electrode. Before its placement on the electrode, the water was heated to boiling point and then cooled down. The structure organization increased with the increase of the duration of the gas electric discharge. Moreover, in experiments was observed the formation of small structures and their further “adjoining” to the larger structure. The large structure was preserved the original size for some time in the absence of the electric discharge.

This experiment shows that self-organization in water under certain external thermal conditions may take place. In natural conditions water is heated up to $+100 \text{ }^\circ\text{C}$ by the



Fig. 4. – The organized structure in water sample subjected to the temperature $+100 \text{ }^\circ\text{C}$ in the electric field of high voltage and frequency (I. Ignatov, 2014). The material of the electrode – hostafan; the electric voltage – 15 kV, the electric impulse duration – 10 μs ; the electric current frequency – 15 kHz.

magma. The structure formed from heated water was evidently a result of self-organization. Living organisms are complex self-organizing systems. Thermodynamically they belong to the open systems because they constantly exchange substances and energy with the environment. The changes in the open systems are relatively stable in time. The stable correlation between components in an open system is called a dissipative structure. According to I. Prigozhin, the formation of dissipative structures and the elaboration to living cells is related to changes in entropy [27].

Taking into account these views it may be concluded that the initial stage of evolution, apparently, was connected with formation at high temperature of the mixtures of amino acids and nitrogenous substances – analogues of nucleic acids. Such synthesis is possible in aqueous solutions under thermal conditions in the presence of H_3PO_4 . The next stage is the polycondensation of amino acids into thermal proteinoids at temperatures $65\text{--}95 \text{ }^\circ\text{C}$. After that in a mix of thermal proteinoids in hot water solutions were formed the membrane like structures.

Our data are confirmed by experiments of T. Sugawara (Japan), who in 2011 created the membrane like proto cells from an aqueous solution of organic molecules, DNA and synthetic enzymes under the temperature close to the water boiling point $+95 \text{ }^\circ\text{C}$ [28]. This data confirm the possibility that first organic forms of life might have been originated in hot mineral water.

CONCLUSIONS

The experimental data testify that the origination of first organic forms of life depends on physical-chemical properties of water and external factors – temperature, pH, electric discharges and isotopic composition. Hot mineral alkaline water interacting with CaCO_3 is most closed to these conditions. Next in line with regard to its quality is seawater. For

chemical reaction of dehydration–condensation to occur in hot mineral water, water is required to be alkaline with the pH ranged 9–11. In warm and hot mineral waters the local maximums in IR–spectra from 8 to 14 μm were more expressed in comparison with the local maximums measured in the same water samples with lower temperature. The content of deuterium in hot mineral water may be increased due to the physical chemical processes of the deuterium accumulation stipulated by the solar radiation, volcanic geothermal processes and electric discharges in the atmosphere. These natural processes could lead to the enrichment of the hydrosphere by deuterium in the form of HDO which evaporates more slowly than H_2O , but condenses faster. If the primary hydrosphere really contained HDO, that this may explain the thermal stability of the first organic life forms in the hot mineral water, as the thermal stability of deuterated macromolecules like DNA and proteins in D_2O solutions is somewhat higher than their protonated forms due to isotopic effects of deuterium.

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References

1. Ignatov I., Mosin O.V. Color coronal (Kirlian) spectral analysis in modeling of nonequilibrium conditions with the gas electric discharges simulating primary atmosphere. S. Miller's experiments // *Naukovedenie*. – 2013. – № 3(16). – P. 1–15 [in Russian] [Online] Available: URL: <http://naukovedenie.ru/PDF/05tvn313.pdf> (May 10, 2013).
2. Ignatov I., Mosin O.V. Origin of life and living matter in hot mineral water // *Advances in Physics Theories and Applications*. – 2015. – Vol. 39. – P. 1–22.
3. Ignatov I., Mosin O.V. // Modeling of possible conditions for origin of first organic forms in hot mineral water // *European Journal of Molecular Biotechnology*. – 2014. – Vol. 6. – № 4. – P. 169–179.
4. Ignatov I., Mosin O.V. Possible processes for origin of life and living matter with modeling of physiological processes of bacterium *Bacillus subtilis* as model system in heavy water // *Journal of Natural Sciences Research*. – 2013. – Vol. 3. – № 9. – P. 65–76.
5. Linsky J.L. D/H and nearby interstellar cloud structures / Ed. J.I. Linsky. In: *Space Science Reviews*. – NY: Springer Science, Business Media. – 2007. – Vol. 130. – 367 p.
6. Ignatov I., Mosin O.V. Isotopic composition of water and its temperature in modeling of primordial hydrosphere experiments / VIII Int. Conference Perspectives of the Development of Science and Technique, Biochemistry and Biophysics. Moscow. – 2012. – Vol. 15. – P. 41–49.
7. Ignatov I., Mosin O.V. Modeling of possible processes for origin of life and living matter in hot mineral and seawater with deuterium // *Journal of Environment and Earth Science*. – 2013. – Vol. 3. – № 14. – P. 103–118.
8. Szostak J.W. An optimal degree of physical and chemical heterogeneity for the origin of life? // *Philos. Trans. Royal Soc. Lond. Biol. Sci.* – 2011. – Vol. – 366. – № 1580. – P. 2894–901.
9. Mulikjanian A.Y., Galperin M.Y. On the origin of life in the Zinc world. Validation of the hypothesis on the photosynthesizing zinc sulfide edifices as cradles of life on Earth // *Biology Direct*. – 2009. – Vol. 4. – P. 26.
10. Trevors J.I., Pollack G.H. Hypothesis: origin of life in hydrogel environment // *Progress in biophysics and molecular biology*. – 2005. – Vol. 89. – № 1. – P. 1–8.
11. Ignatov I. Origin of life and living matter in hot mineral water / 7th Ann. Conference on the Physics, Chemistry and Biology of Water. 12–16 October 2012. NY: Vermont Photonics, USA. – 2012. – P. 67.
12. Ignatov I., Mosin O.V. Color coronal Kirlian spectral analysis in modelling nonequilibrium conditions with the gas electric discharges, simulating primary atmosphere // *Biomedical Radio Electronics*. – 2014. – № 2. – P. 38–47 [in Russian].
13. Schirber M. First fossil–makers in hot water // *Astrobiology magazine*. – 2010 – [Online] Available: URL: <http://www.astrobio.net/exclusive/3418/first-fossil-makers-in-hot-water> (January 3, 2010).
14. Ponsa M.L., Quitte G., Fujii T., Rosing M.T., Reynarda B., Moynier F., Doucheta Ch., Albaredea F. Early archean serpentine mud volcanoes at Isua, Greenland, as a niche for early life // *Proc. Natl. Acad. Sci. U.S.* – 2011. – Vol. 108. – P. 17639–17643.
15. Kurihara K., Tamura M., Shohda K., Toyota T., Suzuki K., Sugawara T. Self–Reproduction of supramolecular giant vesicles combined with the amplification of encapsulated DNA // *Nature Chemistry*. – 2011. – Vol. 4. – № 10. – P. 775–781.
16. Calvin M. *Chemical evolution* / Ed. M. Calvin. – Oxford: Clarendon. – 1969. – 278 p.
17. Mathews C.N., Moser R. Peptide synthesis from hydrogen–cyanide and water // *Nature*. – 1968. – Vol. 215. – P. 1230–1234.
18. Miller S.L. A production of amino acids under possible primitive Earth conditions // *Science*. – 1953. – Vol. 117. – № 3046. – P. 528–529.
19. Abelson P. Chemical events on the “primitive” earth // *Proc. Natl. Acad. Sci. U.S.* – 1966. – Vol. 55. – P. 1365–1372.
20. Harada I., Fox S.W. Thermal synthesis of natural amino acids from a postulated primitive terrestrial atmosphere // *Nature*. – 1964. – Vol. 201. – P. 335–336.
21. Fox S.W., Krampitz G. Catalytic decomposition of glucose in aqueous solution by thermal proteinoids // *Nature*. – 1964. – Vol. 203. – P. 1362–1364.
22. Fox S.W., Wang C.T. Melanocytostimulating hormone: Activity in thermal polymers of alpha–amino acids // *Science*. – 1968. – Vol. 160. – P. 547–548.
23. Nakashima T. Metabolism of proteinoid microspheres / Ed. T. Nakashima. In: *Origins of life and evolution of biospheres*. – 1987. – Vol. 20. – № (3–4) – P. 269–277.
24. Miller S.L. A production of amino acids under possible primitive Earth conditions // *Science*. – 1953. – Vol. 117. – № 3046. – P. 528–529.
25. Johnson A.P., Cleaves H.J., Dworkin J.P., Glavin D.P., Lazcano A., Bada J.L. The Miller volcanic spark discharge experiment // *Science*. – 2008. – Vol. 322. – № 5900. – P. 404–412.
26. Ignatov I., Mosin O. Microorganisms in the presence of D_2O and IR spectra in hot mineral water with more deuterium atoms for origin of life and living matter // *Journal of Health, Medicine and Nursing*. – 2014. – Vol. 5. – P. 80–93.
27. Nikolis P., Prigozhin I. Self–organization in non–equilibrium systems / Ed. P. Nikolis, I. Prigozhin. – Moscow: Mir. – 1979. – 512 p. [in Russian].
28. Sugawara T. Self–reproduction of supramolecular giant vesicles combined with the amplification of encapsulated DNA // *Nature Chemistry*. – 2011. – Vol. 1127. – P. 775–780.

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STUDYING THE HYDROLOGICAL CONDITIONS FOR ORIGIN OF FIRST ORGANIC FORMS OF LIFE IN HOT MINERAL WATER WITH HDO

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The isotopic composition, the temperature and the pH value of water were analyzed in experiments with prognosis of primary hydrosphere and hydrological conditions for origin of first organic forms in hot mineral water with HDO. For this aim we performed experiments with hot mineral water from Bulgaria and water with varying content of deuterium using IR- and DNES-spectroscopy. As model systems were used cactus juice of *Echinopsis pachanoi* and Mediterranean jellyfish *Cotylorhiza tuberculata*. The reactions of condensation-dehydration occurring in alkaline aqueous solutions at $t = 65-95\text{ }^{\circ}\text{C}$ and $\text{pH} = 9-10$, resulting in synthesis from inorganic molecules the larger organic molecules as polymers and short polipeptides, were discussed, as well as the possible mechanisms of the deuterium accumulation in form of HDO in hot water. It was shown that hot alkaline mineral water with temperature from $+65\text{ }^{\circ}\text{C}$ to $+95\text{ }^{\circ}\text{C}$ and the pH value from 9 to 11 is more suitable for the origination of life and living matter than other analyzed water samples. In hot mineral waters the local maximums in IR-spectra are more manifested compared to the local maximums obtained in IR-spectra of the same water at a lower temperature. The difference in the local maximums from $+20\text{ }^{\circ}\text{C}$ to $+95\text{ }^{\circ}\text{C}$ at each $+5\text{ }^{\circ}\text{C}$ according to the Student t -criterion makes up $p < 0,05$.

Keywords: deuterium, hydrosphere, evolution, origin of life, IR spectroscopy, DNES.

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ИЗУЧЕНИЕ ГИДРОЛОГИЧЕСКИХ УСЛОВИЙ ПРОИСХОЖДЕНИЯ ОРГАНИЧЕСКИХ ФОРМ ЖИЗНИ В ГОРЯЧЕЙ МИНЕРАЛЬНОЙ ВОДЕ С HDO

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Изучен состав воды, температура и значение pH в экспериментах по моделированию первичной гидросферы и возможных условий возникновения органических форм жизни в горячей минеральной воде с HDO. Для этой цели проведены исследования горячей минеральной воды из Болгарских источников методами ИК- и ДНЭС-спектроскопии. В качестве модельных систем использовали сок кактуса *Echinopsis pachanoi* и средиземноморскую

медузу *Cotylorhiza tuberculata*. Рассмотрены реакции конденсации-дегидратации в щелочных водных растворах со значением $\text{pH} = 9-10$, результатом которых является синтез из мелких молекул более крупных органических молекул полимеров как коротких полипептидов, а также механизмы аккумуляции дейтерия в форме HDO в горячей минеральной воде. Показано, что горячие минеральные воды с температурой от $+65\text{ }^{\circ}\text{C}$ до $+95\text{ }^{\circ}\text{C}$ и значением pH от 9 до 11 более пригодны для возникновения жизни, чем другие исследованные образцы воды. В горячей минеральной воде локальные максимумы в ИК-спектре проявлялись больше всего, по сравнению с локальными максимумами в ИК-спектре той же воды при более низкой температуре. Разница в локальных максимумах от $+20\text{ }^{\circ}\text{C}$ до $+95\text{ }^{\circ}\text{C}$ при увеличении температуры на каждый $+5\text{ }^{\circ}\text{C}$ составила в соответствии с t -критерием Стьюдента $p < 0,05$.

Ключевые слова: дейтерий, гидросфера, эволюция, возникновение жизни, ИК-спектроскопия, ДНЭС.

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ВИВЧЕННЯ ГІДРОЛОГІЧНИХ УМОВ ПОХОДЖЕННЯ ОРГАНІЧНИХ ФОРМ ЖИТТЯ В ГОРЯЧІЙ МІНЕРАЛЬНІЙ ВОДІ З HDO

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Вивчено склад води, температура і значення pH в експериментах з моделювання первинної гідросфери та можливих умов виникнення органічних форм життя в горячій мінеральній воді з HDO. Для цієї мети проведені дослідження горячою мінеральною водою з Болгарських джерел методами ІЧ- і ДНЕС-спектроскопії. В якості модельних систем використовували сік кактуса *Echinopsis pachanoi* і середземноморську медузу *Cotylorhiza tuberculata*. Розглянуто реакції конденсації-дегідратації в лужних водних розчинах зі значенням $\text{pH} = 9-10$, результатом яких є синтез з дрібних молекул більш великих органічних молекул полімерів як короткі поліпептиди, а також механізми аккумуляції дейтерію у формі HDO в горячій мінеральній воді. Показано, що горячі мінеральні води з температурою від $+65\text{ }^{\circ}\text{C}$ до $+95\text{ }^{\circ}\text{C}$ і значенням pH від 9 до 11 більш придатні для виникнення життя, ніж інші досліджені зразки води. У горячій мінеральній воді локальні максимуми в ІК-спектрі проявлялися найбільше, порівняно з локальними максимумами в ІЧ-спектрі тієї ж води при більш низькій температурі. Різниця в локальних максимумах від $+20\text{ }^{\circ}\text{C}$ до $+95\text{ }^{\circ}\text{C}$ при збільшенні температури на кожний $+5\text{ }^{\circ}\text{C}$ склала відповідно за t -критерієм Стьюдента $p < 0,05$.

Ключові слова: дейтерій, гідросфера, еволюція, виникнення життя, ІЧ-спектроскопія, ДНЕС.

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