

Modeling of Possible Conditions For Origin of First Organic Forms in Hot Mineral Water

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Abstract

The composition of water, its temperature and pH value was analyzed in experiments with modelling of primary hydrosphere and possible conditions for origin of first organic forms in hot mineral water. For this aim the authors performed experiments with hot mineral and seawater from Bulgaria by IR-spectrometry (DNES-method). As model systems were used cactus juice of *Echinopsis pachanoi* and Mediterranean jellyfish *Cotylorhiza tuberculata*. It was considered the reactions of condensation and dehydration in alkaline aqueous solutions with pH = 9–10, resulting in synthesis from separate molecules larger organic molecules as polymers and short polipeptides. It was shown that hot alkaline mineral water with temperature from +65 °C to +95 °C and pH value from 9 to 11 is more suitable for the origination of life and living matter than other analyzed water samples. The pH value of seawater on contrary is limited to the range of 7,5 to 8,4 units. Two common local maximums were observed in the IR-spectra of jellyfish and seawater, which were more pronouncedly expressed in IR-spectra of jellyfish.

Keywords: deuterium, hydrosphere, evolution, origin of life, IR-spectrometry.

1. Introduction

Previous biological experiments with D₂O and structural-conformational studies with deuterated molecules, performed by us, enable to modeling conditions under which the first living forms of life might be evolved (Ignatov & Mosin, 2013a; Ignatov & Mosin, 2013b; Ignatov & Mosin, 2013c). 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 (Ignatov & Mosin, 2012). 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 H_2O , 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.

Natural prevalence of deuterium makes up approximately 0.015–0.020 at.%, and depends strongly on the uniformity of substance and the total amount of matter formed in the course of early Galaxy evolution (Linsky, 2007). 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 processes in living matter. 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 $CaCO_3$ (Ignatov, 2010; Ignatov & Mosin, 2013d). 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 open lakes is more possible compared to the ocean (Szostak, 2011). Life began near a hydrothermal vent: an underwater spout of hot water. Geothermal activity gives more opportunities for the origination of life. In 2009 A. Mulkidjanian and M. Galperin demonstrate that the cell cytoplasm contains potassium, zinc, manganese and phosphate ions, which are not particularly widespread in the sea aquarium (Mulkidjanian & Galperin, 2009). J. Trevors and G. Pollack proposed in 2005 that the first cells on the Earth assembled in a hydrogel environment (Trevors & Pollack, 2005). 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 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 (Ignatov, 2012).

The purpose of the research was studying the conditions of primary hydrosphere (temperature, pH, isotopic composition) for possible processes for origin of life and living matter in hot mineral water. Various samples of water from Bulgaria were studied within the frames of the research.

2. Material and Methods

2.1. Objects of Studying

The research by the IR-spectrometry (DNES-method) was carried out with samples of water 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).

As two model systems were used cactus juice of *Echinopsis pachanoi* and Mediterranean jellyfish *Cotylorhiza tuberculata* (Chalkida (Greece), Aegean Sea), which were both investigated by the IR-spectrometry.

2.2. 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}); Thermo Nicolet Avatar 360 Fourier-transform IR (M. Chakarova); Differential Non-equilibrium Spectrum (DNES).

2.3. 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 (Ignatov & Mosin, 2013e). 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.

3. Results and Discussion

We have carried out the research of various samples of mineral water from mineral springs and seawater from Bulgaria (Fig. 1, curves 1–5). For this aim we employed the IR-spectrometry and DNES method relative to the control – deionized water. 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 Ca^{2+} and HCO_3^- ions (Fig. 1, curve 2). DNES-spectra of cactus juice and mineral water have magnitudes of local maximums at -0.1112 ; -0.1187 ; -0.1262 ; -0.1287 and -0.1387 eV. Similar local maximums in the DNES-spectrum between cactus juice and seawater were detected at -0.1362 eV. The spectrum of the control sample of deionized water (Fig. 1, curve 5) was substantially different from the spectra of seawater and mineral water. Another important parameter was measured by the DNES method – the average energy ($\Delta E_{\text{H...O}}$) of hydrogen H...O-bonds among individual molecules H_2O , 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 among individual H₂O molecules with a statistically reliable increase of local maximums in DNES-spectra.

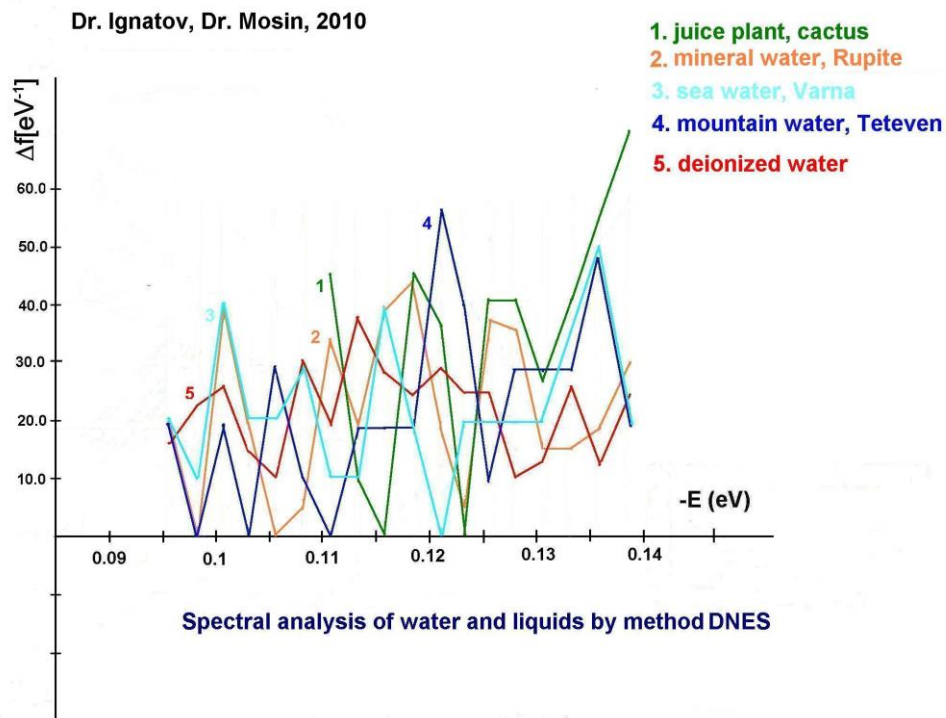


Figure 1. DNES-spectra of water samples of various origin: 1 – cactus juice; 2 – mineral water from Rupite village (Bulgaria); 3 – seawater (Varna, Bulgaria); 4 – mountain water (Teteven, Bulgaria); 5 – deionized water (the control)

As shown from these data, the closest to the IR-spectrum of cactus juice was mineral water from Rupite Village (Bulgaria), which DNES and IR spectrum is shown in Fig. 2 and Fig. 3 (Thermo Nicolet Avatar 360 Fourier-transform IR). IR-spectra of cactus juice and mineral water with HCO₃⁻ (1320–1488 mg/l), Ca²⁺ (29–36 mg/l), pH (6.85–7.19), have local maximums at 8.95; 9.67; 9.81; 10.47 and 11.12 μm (Fourier-IR spectrometer Brucker Vertex). Common local maximums in the IR-spectrum between cactus juice and seawater are detected at 9.10 μm. The local maximums obtained with IR method at 9.81 μm (1019 cm⁻¹) and 8.95 μm (1117 cm⁻¹) (Thermo Nicolet Avatar 360 Fourier-transform IR) are located on the spectral curve of the local maximum at 9.7 μm (1031 cm⁻¹) (Fig. 3). With the DNES method were obtained the following results – 8.95; 9.10; 9.64; 9.83; 10.45 and 11.15 μm, or 897; 957; 1017; 1037; 1099 and 1117 wave numbers.

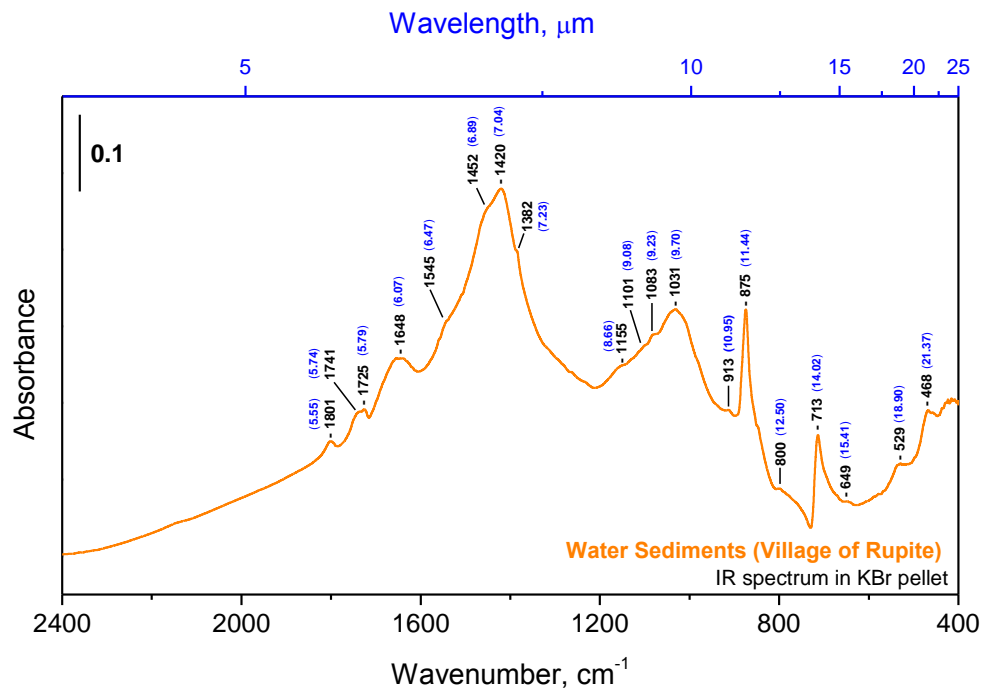


Figure 2. IR-spectrum of water obtained from Rupite Village (Bulgaria)

Table. Characteristics of spectra of water of various origin obtained by DNES-method*

-E, eV			λ , μm	κ , 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

The note:

*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) are observed the biggest local maximums of this function; λ – wave length; κ – wave number.

The results with Mediterranean jellyfish *Cotylorhiza tuberculata* indicated that jellyfish has local maximums in IR-spectra at 8.98 and 10.18 μm (Fig. 3). Before measurements the jellyfish was kept in seawater for several days. On comparison seawater has a local maximum at 8.93 μm in IR-spectra. These

results were obtained with Thermo Nicolet Avatar 360 Fourier-transform IR. With DNES method the local maximums in spectra for jellyfish are at 8.95 and 10.21 μm , and for seawater at 9.10 μm . A differential spectrum was recorded between jellyfish and seawater by using the Thermo Nicolet Avatar 360 Fourier-transform IR method. In IR-spectrum of jellyfish are observed more pronouncedly expressed local maximums, detected by Thermo Nicolet Avatar 360 Fourier-transform IR and DNES method. Measurements 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 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 stromatolites. The explanation for this is the smaller concentration of salts and, therefore, the smaller number of local maximums in the IR-spectrum in relation to seawater.

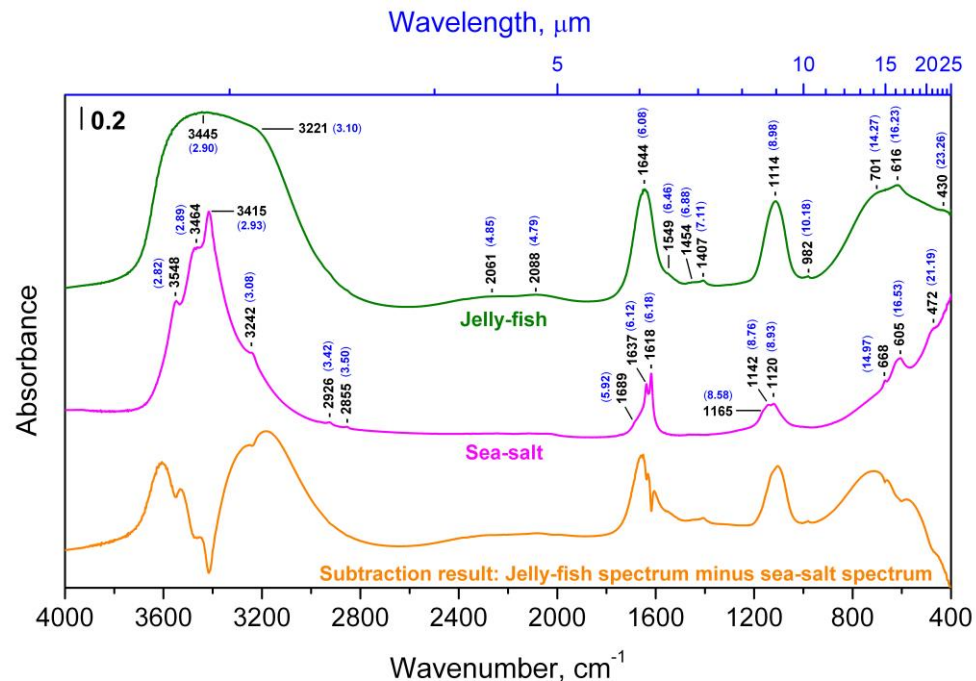
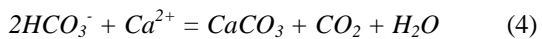
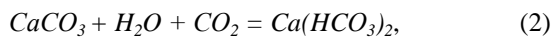
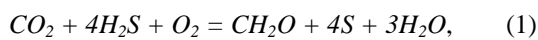


Figure 3. IR-spectrum of seawater obtained from Varna (Bulgaria) and jellyfish *Cotylorhiza tuberculata*, Chalkida (Greece), Aegean Sea

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 +20 °C to +95 °C at each 5 °C according to Student t-criterion – $p < 0.05$. 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 pH value. The most closed to the IR- and

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 local maximums in IR-spectrum of 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 (1) shows how some chemosynthetic bacteria use energy from the oxidation of H_2S and CO_2 to S and formaldehyde (CH_2O). The equation (2) 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 (3)). Equation (4) 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) (Schirber, 2010). 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 (Ponsa et al., 2011). It is known that water in geysers is rich in carbonates, while the temperature is ranged from $+100^\circ\text{C}$ to $+150^\circ\text{C}$. In 2011 a team of Japanese scientists under the leadership of T. Sugawara showed that life originated in warm or, more likely, hot water (Kurihara et al., 2011). From aqueous solution of organic molecules, DNA and synthetic enzymes were created proto cells. For this the initial solution was heated to a temperature close to water's boiling point $+95^\circ\text{C}$. Then its temperature was lowered to $+65^\circ\text{C}$ with formation of proto cells with primitive membrane. This laboratory experiment is an excellent confirmation of the possibility that life originated in hot water.

The above-mentioned data can predict a possible transition from synthesis of small organic molecules under high temperatures 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 $\text{pH} = 9\text{--}11$. The important factor in reaction of condensation of two amino acid molecules into dipeptide is allocation of H_2O molecule when a peptide chain is formed. As reaction of polycondensation of amino acids is accompanied by dehydration, the H_2O removal from 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, 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 H_2O molecule.

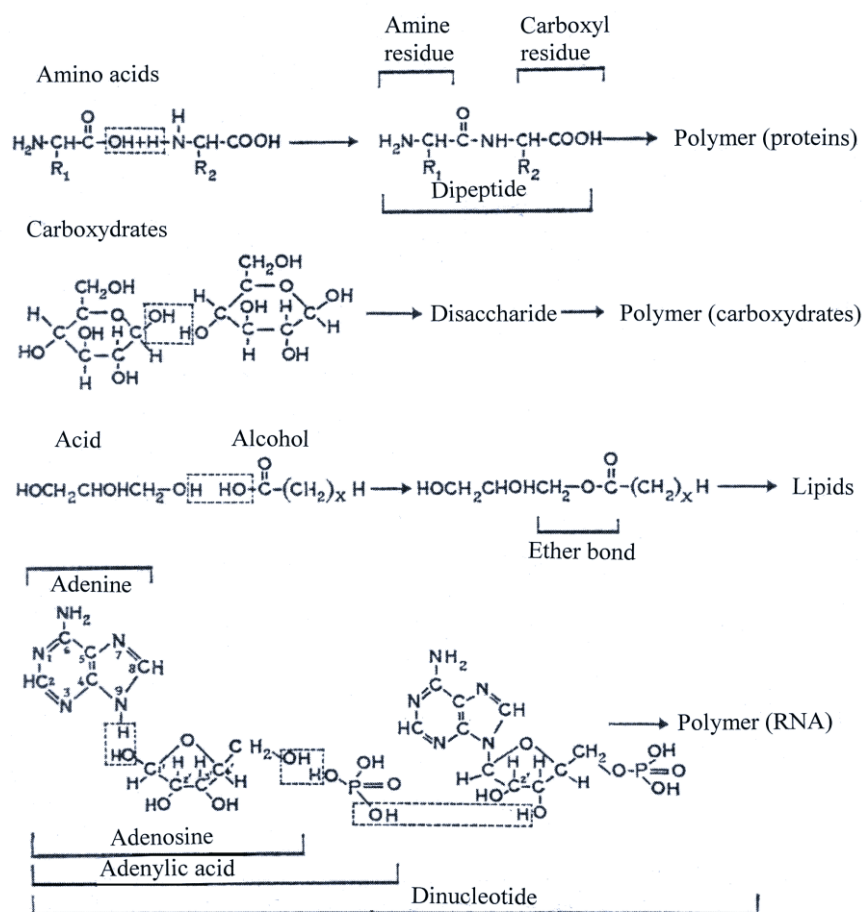
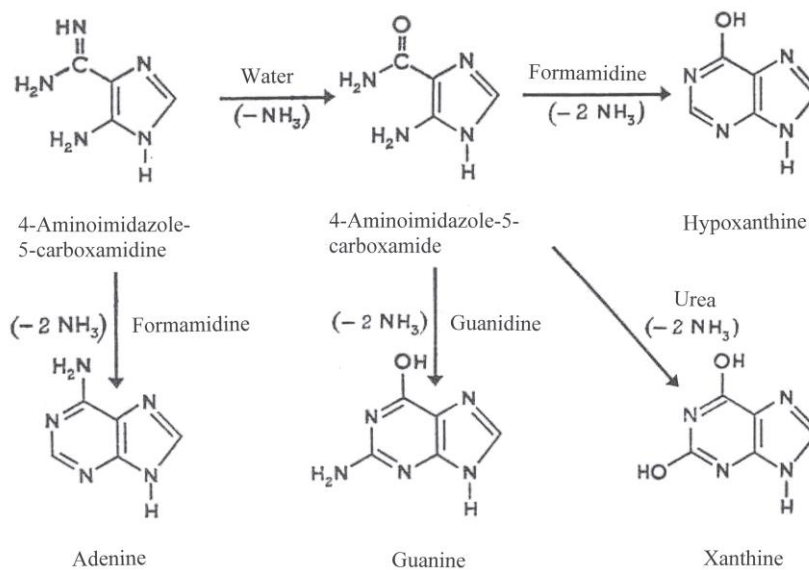


Figure 4. Reactions of condensation and dehydration in alkaline conditions with pH = 9–10 catalyzed by HCN and its derivatives, resulting in synthesis from separate molecules larger organic molecules of polymers. The top three equations: condensation and the subsequent polymerization of amino acids in proteins; carbohydrates – in polycarboxydrates and acids and ethers – into lipids. The bottom equation – condensation of adenine with ribose and H_3PO_4 , leading to formation of dinucleotide

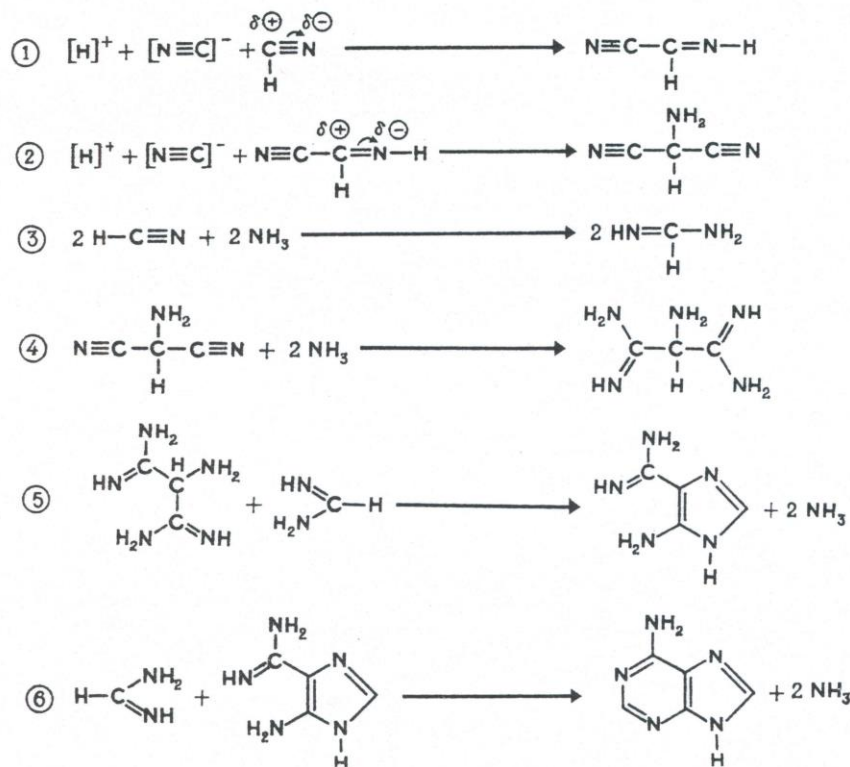
In 1969 the possibility of existence of condensation-dehydration reactions under conditions of primary hydrosphere was proven by M. Calvin (Calvin, 1969). From most chemical substances hydrocyanic acid (HCN) and its derivatives – cyanoamid (CH_2N_2) and dicyanoamid ($\text{HN}(\text{CN})_2$) possess dehydration ability and the ability to catalyze the process of linkage of H_2O from primary hydrosphere (Mathews & Moser, 1968). The presence of HCN in primary hydrosphere was proven by S. Miller's early experiments (Miller, 1953). Chemical reactions with HCN and its derivatives are complex with a chemical point of view; in the presence of HCN, CH_2N_2 and $\text{HN}(\text{CN})_2$ the condensation of separate blocks of amino acids accompanied by dehydration, can proceed at normal temperatures in strongly diluted H_2O -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 (Fig. 4). Furthermore, polycondensation reactions catalyzed by HCN and its derivatives depend on acidity of water solutions in which they proceed (Abelson, 1966). 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 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 heating of a reactionary mixture to +95 °C (Harada & Fox, 1964). In model experiments reaction products were polymerized into peptide chains that is the important stage towards inorganic synthesis of protein. In a reactionary mixture with a HCN–NH₃ solution in water were formed purines and pyrimidines (Fig. 5). In other experiments amino acid mixtures were subjected to influence of temperatures from +60 °C up to +170 °C with 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 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 (Fox & Krampitz, 1964) and to have an effect similar to the action of α-melanocyte-stimulating hormone (Fox & Wang, 1968). The best results on 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.



a)



b)

Figure 5. Prospective mechanisms of thermal (+95 °C) synthesis of purines in aqueous solutions: a) – synthesis of hypoxanthine, adenine, guanine and xanthine from 4-aminoimidazole-5-carboxamide, 4-aminoimidazole-5-carboxamide, water, NH₃, formamidine and urea; b) – synthesis of adenine from NH₃ and HCN (total reaction: 5HCN = adenine)

Under certain conditions in hot mixture of proteinoids in water solutions are formed elementary structures like proteinoid microspheres with diameter 5–10 μm (Nakashima, 1987). Gas electric discharge with color coronal spectral analyses was applied in this type of experiment analogous to S. Miller's experiments (Ignatov & Tsvetkova, 2011). In S. Miller's experiments one of the basic conditions is electric gas discharge. The analogous experiment was conducted by the authors under laboratory conditions. The first living structures were most probably formed in warm and hot mineral water with more bicarbonate and metal ions (Na, Ca, Mg, Zn, K, etc.). 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 coronal electric discharge on water drops placed on the electrode of the device for gas coronal electric discharge formation. Water drops were heated to the boiling point in an electric field of high frequency and voltage and an electric discharge was applied, analogous as in the primordial atmosphere. As a result, an organized structure with a size of ~1.2–1.3 mm was formed in interelectrode space (Fig. 6). It was formed as a result

of the self-organization of elementary structures sized of $\sim 5\text{--}10\ \mu\text{m}$ in the biggest structure with size $1.2\text{--}1.4\ \text{mm}$ and concentrated in a large structure where the basic electric voltage is applied. On its form it resembles a small jellyfish.

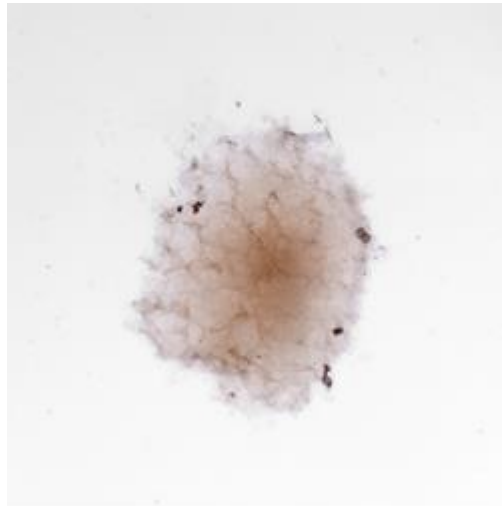


Figure 6. Organized structure in water on an electrode, which is heated to boiling point in an electric field of high frequency and voltage

It should be noted that no structure was organized in a control sample of water placed on the electrode. Before its placement on the electrode, the water was heated to boiling point and then cooled. The structure organization increased with the increase of the duration of the gas electric discharge. Moreover, in experiments was observed formation of small structures and their further “adjoining” to the larger structure. It should be noted that the large structure was preserved with original unchanged size for 2 years in the absence of electric discharge.

This experiment shows that the organization of structures in water under certain external conditions as the temperature takes place. Water in natural conditions was heated by the magma. The structure formed from heated water was evidently a result of self-organization. Living organisms are complex self-organizing systems. They are open 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 (Nikolis & Prigozhin, 1979).

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 polycondensation of amino acids into thermal proteinoids at temperatures $65\text{--}95\ ^\circ\text{C}$. After that in a mix of proteinoids in hot water solutions were formed membrane like structures. In 2011 T. Sugawara (Japan) created membrane like proto cells from aqueous solution of organic molecules, DNA and synthetic enzymes under temperature close to water’s boiling point $+95\ ^\circ\text{C}$ (Sugawara, 2011). These experiments are excellent confirmation of

the possibility that life and living matter originated in hot water.

4. Conclusions

The data obtained testify that origination of life and living matter depends on physical-chemical properties of water and external factors – temperatures, pH, electric discharges and isotopic composition. Hot mineral alkaline water interacting with CaCO_3 is closest to these conditions. Next in line with regard to quality is seawater. For chemical reaction of dehydration-condensation to occur in hot mineral water, water is required to be alkaline with pH range 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.

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