Reduced condition on early Earth and ATP-related mechanism of prebiological evolution.

E.M. Galimov
V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, 119991, Moscow, Kosygin str., 19, GEOKHI

ABSTRACT

I have proposed a model, in which adenosine triphospate (ATP) plays a key role in prebiological evolution. Life is a phenomenon of evolving ordering. It can be shown that a system of conjugated irreversible reactions supplied by energy and dwelling near a steady state, is charged to produce ordering[1]. ATP has properties which are the most appropriate to be involved in such a system. Primary synthesis of ATP demands strong reduced conditions. I show here that such conditions may exist on the early Earth.

Keywords: life origin, concept of ordering, early Earth, ATP, reduced condition, irreversible thermodynamics, entropy, Earth's mantle, redox evolution.

1. THE CONCEPT OF ORDERING

All spontaneously going processes are accompanied with entropy growth. This principle was initially formulated as applied to the theory of heat engines, and is known as the Second Law of Thermodynamics. Disordering is the most universal principle of matter motion.

Life on the contrary, reveals increase of order, both within the life of an individual organism (*ontogenesis*) and on the scale of the entire history of life evolution.

What does mean ordering? As follows from interpretation of entropy in statistical mechanics *the ordering is restriction of freedom*.

$$S = k \ln W,$$

where S – entropy, k – Bolzman constant, W – number of ways by which the system could form (degree of freedom).

The higher W, the higher its entropy, and vice versa, the lower the number of degrees of freedom, the lower the entropy.

Any irreversible process is characterized with positive production of entropy:

$$\frac{\partial S}{\partial t} = \sum X_k J_k \ ,$$

where X_k and J_k are generalized force and flux respectively.

However a particular reaction can proceed with the negative production of entropy, if it is conjugated with the reaction going with positive production of entropy so that the summary entropy production is greater than or equal to zero:

$$X_1J_1 + (-X_2J_2) \geq 0$$
$$\Delta S = \Delta S_1 - \Delta S_2 \geq 0$$

The episodes of ordering controlled with disordering are omnipresent in nature. But this does not account for a trend of increase of ordering. In order the process to persist an attractor must exist. Equilibrium state is the attractor of the disordering process. All systems tend to reach the minimal free energy and the maximal entropy. In this state, equilibrium is attained. If a system is taken out of this state, it tends to return to it. The equilibrium state is an attractor.

Is there an attractor to the ordering process?

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I argue that this is a property of a steady state system of conjugated chemical reactions. A steady state is fundamentally different from an equilibrium state. In a steady state concentrations of the reactants and products are invariant as well as in equilibrium system. But for different cause: reactants are continuously supplied from outside, while products come off the system with the same rate. In equilibrium state a system is characterized by the minimum of free energy, whereas the free energy of a steady-state system is maintained at a level different from the minimum. Sustaining a steady state requires a continuous energy flux from external sources. Steady states are in principle impossible in isolated systems.
A steady state is characterized by minimal production of entropy. This theorem was proved by I. Prigogine. When the system is brought out of its steady state, it tends to return to it. If the stationary system includes the conjugated reactions with positive and negative production of entropy, then attaining of the minimum of entropy production *necessarily requires* carrying out a reaction with decreasing entropy. Thus, there exists a natural mechanism that has its attractor in ordering. Moreover the principle of the minimum entropy production is equivalent to the principle of the maximum decrease of entropy. This suggests that the system seeks the way to produce maximum ordering. In general case ordering includes limitation of freedom of movements, freedom of choice (selectivity), and prescription of behavior. The concept of the ordering in more details is considered elsewhere[1, 2].

2. ATP SIGNIFICANCE

I supposed that the primeval ordering mechanism was represented by a system that included adenosine triphosphate (ATP) hydrolysis.

$$ATP + H_2O \rightarrow ADP + P$$
$$M + N \rightarrow H_2O + MN$$

In chemistry conjugation occurs when a reactant of one of the reactions act as a product in the other one.
The important property of ATP is that ATP hydrolysis is accompanied by the uptake of a water molecule, whereas the majority of reactions of synthesis proceeds with the release of water, for instance, formation of peptides, polymerization of nucleotides, etc. Thus the ATP hydrolysis is generally conjugated with reaction of biosynthesis.
There are some other reasons for distinguishing the prebiological role of ATP.
ATP hydrolysis is accompanied by a considerable release of free energy, about ΔG = -31kJ/mol. The participation of ATP can therefore *supply energy* to the chemical reactions that cannot occur spontaneously.
In modern organisms, ATP participates in all energy-absorbing biochemical reactions. It accumulates various types of external energy in the process of phosphorylation and transforms them into chemical energy during hydrolysis. ATP plays this role both in primitive and in higher organisms. This implies that the mechanism related to the participation of ATP appeared at a *very early stage of evolution*.
It is very intriguing that ATP (except for the polyphosphate group) is a structural unit of RNA. The structure of ATP is included into the structure of many biochemical important compounds, for instance, DNA (in the deoxy form), NADP, FAD, coenzyme A, and others. This suggests that ATP originated *before* the formation of nucleic acids and, consequently, the genetic code. i.e., ATP is a substance formed during the prebiological stage of evolution.

3. ORDERING BASED ON ATP

Small-sized polymers, including amino acid chains (peptides), nucleotide chains, etc. might be products of primary ordering. The formation of a polymer molecule implies a restriction of translational and rotational degrees of freedom for each monomer group. Therefore, the appearance of polymer structure associates with a decrease in entropy. The limitation of choice means the development of a correspondence and a prescription. In particular, catalysis is related to the restriction of choice, because it established a certain (not arbitrary) way of reaction progress.
The operation of catalyst is based on a stringent prescription: only molecules of a certain chemical composition, structure, and chirality's can interact. Selectivity is a property of a catalyst, which is no less important than its property to speed-up the rate of a reaction. Production of catalysts and their participation in reactions is most efficient form of ordering. Currently existing biochemical catalysts – enzymes is a result of a long evolutionary process. However, even

short amino acid chains manifest amazingly high catalytic activity. Other compounds and minerals may act as catalysts as well. There are no other organic compounds, which perform ordering more efficiently than peptides.
But amino acid sequences are not capable of self-replication. Therefore, the ordering process solely based on peptide synthesis would have no evolutionary prospective.
In contrast to peptides, nucleotide chains are known to be self-replicated. It should be noted that they also show some catalytic activity. The discovery of the catalytic properties of RNA molecules fostered the RNA world hypothesis, which postulated the fundamental importance of RNA in a prebiological world. However, the catalytic activity of RNA is much lower than that of proteins. The catalytic properties of RNA are manifested only with respects to a few types of interaction. Moreover, catalytic activity is characteristic of relatively long RNA sequences composed of at least tens or hundreds of nucleotides, whereas ever-short peptide chains accelerate reactions by several orders of magnitude. For instance, a peptide containing only a dozen amino acids accelerates the decarboxylation of oxaloacetate by more than three orders of magnitude. On the other hand, the information of long RNA chains is almost impossible without a controlling protein enzyme, because of the doubling of the sequence due to coupling of complementary nucleotides.
Nucleotide sequences have relatively weak catalytic properties compared with peptides, but their remarkable replication properties are far superior to those of any organic polymer owing to the complementary character of purines and pyrimidines.
Thus, two important properties necessary for evolution: the capability of ordering and self-replication appeared to be separated between two classes of compounds. I believe that during evolution along the pathway of increasing order, nature has found a way to eliminate this collision. The copying of peptides is aided by nucleotides. This process requires that each amino acid must find its reflection as a combination of nucleotides. The correspondence is referred to as the *genetic code*. It allows replication of a sequence of amino acids using the reproduction properties of a nucleotide sequence.
The appearance of the genetic code completed prebiological evolution and initiated the evolution of life proper.
I subdivided the process of the origin and evolution of life into three stages. The first stage includes accumulation of various organic compounds generated in many terrestrial processes or delivered to its surface from outer space. There is still no evolution during this stage. This is a preevolutionary stage resulting in the formation of a chemical environment.
Prebiological evolution proper begins from ATP formation. The main content of prebiological evolution is the ordering of organic structures related to the increasing role of selective catalysis; an increase in the length and number of oligomers, peptides, and nucleotides; appearance of a mediator between the structure of peptides and nucleotides (such as tRNA); and, eventually, formation of the genetic code.
The living organisms started from a cell.

4. PLANETARY DIFFERENTIATION AS A PREREQUISITE FOR ATP SYNTHESIS

Although ATP is rather complex compound its two organic constituents (adenine and ribose) have very simple natural precursors: hydrogen cyanide (HCN) and formaldehyde (HCHO), respectively.
Adenine consists of five HCN molecules, and ribose consists of five HCHO molecules. Hydrogen cyanide and formaldehyde are widespread organic substances in comets; they occur in interstellar space and are readily synthesized in an environment containing the elements hydrogen, carbon, and nitrogen.
Adenine was first synthesized by Oro[3] in electric spark experiments in an atmosphere of methane and ammonium.
Sugars, including ribose, can be synthesized during formaldehyde condensation. This process is known as the formose reaction, which was first studied by Butlerov. ATP was synthesized by Ponnamperuma et al.[4] from a mixture of adenine, ribose, and phosphate, although with a very low yield of 0.05%.
The attractive simplicity of ATP synthesis is not easily realized in nature. There is a considerable literature dealing with nucleotide synthesis. The attention to the synthesis of nucleotides, including adenosine, was related not only to ATP but to a larger extent to the concept of the RNA world, which has been widely discussed in the western literature. According to this concept, ribonucleic acids were the primordial substance that gave rise to the evolution of life. In my opinion, the concept of the RNA world is counterproductive. This concept was formulated about 20 year ago and has not resulted in any substantial progress in understanding the origin of life, although it stimulated a number of experimental investigations on nucleotide synthesis.
The RNA world concept was criticized by Shapiro[5], who pointed out the fundamental difficulty of nucleotide synthesis from simple compounds, HCN and HCHO. The same difficulty concerns ATP synthesis. The fact is that coexisting HCN and HCHO interact with each other, producing cyanohydrin via the reaction:

$$2HCHO + 2HCN \rightarrow 2H_2COH - C \equiv N \xrightarrow{3H_2O} \underset{hydroxy\ acid}{H_2COHCOOH} + \underset{amino\ acid}{H_2CNH_2COOH} + NH_3$$

This reaction (Strecker reaction) produces important organic substances, amino and hydroxy acids. However, it blocks the pathway of adenine and ribose synthesis.

This difficulty can be circumvented by the separate synthesis of adenine and ribose. Under geologic conditions, this implies that the synthesis of nucleic base; (including adenine) and sugars (including ribose) must be carried out in different environments: adenine is synthesized in a reduced atmosphere containing methane and molecular nitrogen, whereas ribose forms in an aquatic environment, in primary water reservoirs containing formaldehyde and phosphorylating agents.

Thus, our model suggests that one of the prerequisite for the origin of life is the differentiated structure of the cosmic body. In other words, life could be generated only on planet-sized bodies capable of retaining the atmosphere and hydrosphere.

In addition it should be noted that ATP undergoes rather rapid hydrolysis in water. Moreover, when ATP occurs in water medium, its capacity of chemical conjugation with synthesis reactions becomes unimportant. Therefore, an anhydrous environment would be most favorable for ATP hydrolysis. The presence of water is, however, important in other respects, in particular, for the mobility of reactants. Therefore alteration of the dry/wet conditions, for instance, a periodically flooded bank, is a favorable environment for the ATP-based processes. Also temperature changes facilities the nucleotide chains replication/decoupling process. These environments are characteristic of a planet rather then asteroids and meteorites.

5. REDUCED ENVIRONMENTS AS A PRECONDITION OF THE ATP SYNTHESIS

Synthesis of adenine needs an atmosphere, containing methane and nitrogen. The primary role of the adenine nucleotide reconciles best with highly reducing conditions, as adenine the only nucleic base containing no one atom of oxygen.

The synthesis of ribose implies the reduced condition as well. Experimental investigations demonstrated that direct formaldehyde polymerization by the formose reaction does not result in the efficient synthesis of ribose. Ribose was obtained from glycolaldehyde phosphate in the presence of formaldehyde and a mineral matrix[6 - 9]. It implies early phosphorylation of glycolaldehyde. Krishnamurthy *et al.*[9] demonstrated that phosphorylation becomes efficient in the presence of amidotriphosphate, which is produced by the reaction of cyclo-triphosphate with ammonium.

The presence of ammonium suggests reduced conditions.

All experimental investigations indicated a key role of phosphates. The availability and mobility of phosphorus in the primitive Earth can be regarded as one of the major prerequisites for the origin of life. Phosphate minerals, for instance apatite, are poorly soluble, and phosphorus is therefore not very mobile in the orthophosphate PO^{-3}_4 form. In a reducing environment, phosphites (salts of phosphorous acid, H_3PO_3) are stable mineral compounds of phosphorus. In the phosphorous acid, one H atom is directly connected to P. This H atom is easily replaced by carbon-bearing radicals with the formation of a C-P linkage. As a result, phosphonic acids are produced. Phosphono-acetaldehyde easily recombines with formaldehyde, which results in the synthesis of ribose 2-4 biphosphate. In contrast to poorly soluble apatite, phosphites are soluble and mobile in water. We recall that phosphites can be stable only in a reducing environment.

Thus having based on our model one should to claim that reducing condition is necessary prerequisite of the origin of life.

6. REDUCED ENVIRONMENT OF THE EARLY EARTH?

In the above considerations, I repeatedly emphasized the importance of reducing environments as a prerequisite for ATP-based origin of life. However, most geologists refute the possibility of the existence of a reducing atmosphere on early Earth. The extant paradigm is that the primordial atmosphere contained carbon in the form of CO_2 rather than CH_4 and nitrogen as N_2 rather than NH_3, i.e., the atmosphere was neutral (oxygen-free) but not reducing.

The idea of the reduced ancient atmosphere was popular in 1950s. But it was subsequently abandoned because of a number of significant arguments. It was shown that CH_4 and NH_3 are not stable because of photodissociation and could not exist in the atmosphere for a long time. In addition, the Earth's mantle is relatively oxidized. The redox potential of the upper mantle corresponds to the quartz-fayalite-magnetite buffer (QFM). A reducing atmosphere could not be in equilibrium with such a mantle. On this basis the experiments performed under highly reduced conditions, such as synthesis of amino acids by Miller and Urey[10], and synthesis of adenine by Oro[3]) have been negated as not appropriate for the actual natural environment.

The discussing concerning the composition of primary atmosphere of planets has reemerged recently. It was promoted by study of Mars. It has been established that liquid water existed on ancient Mars. The presence of liquid water on early Mars at the relatively low luminosity of the early sun was possible only in the presence of gases producing a greenhouse effect. Kasting[11] showed that CO_2 could not provide such an effect because of its condensation. The only possibility is methane, with lower temperature of condensation.

In agreement with this Sagan and Chyba[12] reasoned that the CH_4 destiny in planet atmosphere is probably not as fatal as it was considered before. They suggested a mechanism for methane self-shielding. The photodissociation of methane was accompanied by the formation of a layer of organic aerosol in the upper atmosphere, which shielded methane from further photodissociation.

Also, I have demonstrated[13] that the observed anomalous enrichment of Martian carbonates in ^{13}C can be explained if methane was the major carbon species in the early Martian atmosphere.

Could the Earth contain methane in its primary atmosphere similar to Mars?

The main objection here, as I mentioned, is a relatively oxidized state of the Earth mantle. However the available facts would be consistent if one assumes that the Earth's atmosphere as well as the upper mantle was initially reduced, while the present day mantle condition was acquired as the result of the redox regime evolution.

I have proposed a model linking the redox evolution of the mantle to the slow growth of the core[14]. The thermal effect of this process is responsible for the excess heat released by the Earth compared with the heat flow due to the decay of radioactive elements. On the other hand, the disproportionate of FeO contained in silicate material into metallic iron incorporating into the core and ferric iron remaining in the mantle increases the oxygen content of the mantle.

There are several possible mechanisms explaining this process in more detail. The simplest mechanism was proposed by Ringwood[15] and includes wüstite disproportionation into ε-Fe and a high-pressure magnetite phase. A number of experimental studies have recently been performed on phase transformations in high-pressure iron-bearing minerals. The major mineral of the upper mantle, olivine, transforms to ringwoodite in the transitional zone and decomposes to perovskite and ferropericlase in the lower mantle. It was recently shown[16, 17] that perovskite has a strong affinity to Fe^{3+} under lower mantle conditions:

$$\left(Mg_{1-x}Fe^{2+}_{x}\right)SiO_3 \rightarrow \left(Mg_{1-x}Fe^{2+}_{x-3y}Fe^{3+}_{2y}\right)SiO_3 + yFe^0$$

This may result in the formation of metallic iron and a considerable decrease in oxygen fugacity in the environment.

In the process of global convection, perovskite with excess oxygen is transported by ascending flows into the upper levels of the lower mantle and undergoes the reverse transformation. The release of oxygen produces the observed high oxygen fugacity in the upper mantle:

$$\left(Mg_{1-x}Fe^{2+}_{x-3y}Fe^{3+}_{2y}\right)SiO_3 \rightarrow \left(Mg_{1-x}Fe^{2+}_{x-y}\right)SiO_{3-y} + \frac{y}{2}O_2$$

In the context of dynamics, the process of mantle-core interaction can occur in the boundary layer, which is identified by geophysicists as the D" layer.

Thus the arguments, which were risen against the reduced state of the early Earth, might be disproved.

7. PREREQUISITES OF LIFE GENESIS

The universally accepted prerequisites for the origin of life include: presence of water and energy sources, a favorable temperature range, and the availability of primary forms of organic compounds. They should be supplemented by the two additional ones following from our concept. These are:

- Planetary body enables to retain an atmosphere, and provide cyclic alternation of temperature and dry/wet conditions.
- Strongly reduced atmosphere, which favorable for ATP formation.

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